

T W O T H O U S A N D T H I R T E E N

ADDITIVES REFERENCE GUIDE

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Additives belong to a broad and diffuse category of key components in a coating formulation. They comprise a small percentage of the coating formulation – their use level rarely exceeds 1 or 2%, and the total level of all additives in a formulation seldom exceeds 5% of the total product. Their impact, however, is significant as they contribute to the ease of manufacture, the stability of the coating in the package, ease of application, quality and appearance of the final film.

Additive function is almost always very specific in nature. Some additives are multi-purpose; for example, they may be important to the manufacturing process as well as to the coating's performance. In recent years, more multi-purpose additives have been developed, thus allowing the use of fewer additives in many formulations. Occasionally the use of one additive will require the use of another to counter some undesirable effect of the first.

Some additives are proprietary products with highly specific functions that work well in some systems but cannot be used in others. In

addition, because of the proprietary nature of many additives, their chemical composition is not disclosed. This can make general recommendations difficult as the lack of structural knowledge means that additive substitutions cannot be made on the basis of fundamental structural chemistry.

The focus on green technology, sustainability, nanotechnology, lower cost and safer products has led to the introduction of newer additives and chemistries. The industry demands that green additives perform the same or better than their traditional counterparts and that they combine performance, sustainability and efficiency along with lower cost. With a larger number of additives available for a particular problem, formulators can find themselves in trouble if the wrong additive is initially selected or added to alleviate or correct a problem. Correct additive selection is important to success, and such selection is made through vendor assistance or years of experience.

Additives are generally categorized by function rather than by chemical composition or physical type. Because the actual

chemical composition of many additives is proprietary, a formulator may run into problems with chemical side reactions. It is important to consider the total additive package and to always seek recommendations from the manufacturer. Because of the changing technology within the industry driven by cost, VOC and other legislation, eco-friendly products and sustainability, many of today's additives are multi-functional; some are also incorporated into polymeric backbones. These factors, in addition to nanotechnology, make it much more difficult to categorize additives by function.

Please note that there are a number of new nano-sized additives and biobased additives in the market today; their functions are varied and they tend to overlap the past traditional categories. For this reason we have included a number of these types under the Nanotechnology and Biobased sections.

The following is a brief description of various coating additives, along with some generic examples. The majority of additive types are represented.

ABRASION-RESISTANCE IMPROVERS

See Slip Aid, Nanotechnology, Burnish-Resistant

Abrasion is a phenomenon caused by the mechanical action of rubbing, scraping or erosion. It has two forms, marring or wearing. Mar abrasion is the permanent deformation of a surface, but the deformation does not break the surface. Wear abrasion is removal of a portion of the surface by some kind of mechanical action: wind erosion, sliding back and forth of an object, wear of tires on traffic paint, etc. The surface removal is gradual and progressive in nature.

Abrasion resistance is a combination of basic factors such as elasticity, hardness, strength (both cohesive, tensile and shear strength), toughness, and, especially in the case of wear resistance, thickness. In addition, abrasion resistance is intimately related to scratching and slip. Thus, compounds that enhance these properties will improve abrasion resistance.

The nature of the polymeric resin and the pigments affect abrasion resistance. In the case of pigments, it should be noted that extender pigments are noted for their ability to contribute to a variety of mechanical properties. Examples of compounds that have been used to enhance abrasion resistance include: silica glass spheres, specialty glass spheres such as UVT™ Sunospheres, and similar compounds that improve hardness (see Microspheres). Certain silicones and other oils will decrease surface friction, making it easier for objects to slide over the surface and thus reduce wear abrasion. Increasing crosslink density by use of higher functionality oligomers and/or larger amounts of crosslinking agents has been used to improve abrasion resistance.

Waxes have also been used to improve slip and thereby abrasion. Hard waxes resist abrasion better than soft materials. Both PE and PTFE waxes function by the ball bearing mechanism, while the softer microcrystalline waxes work via the layer (bloom) mechanism.

The use of nano-sized materials in coating formulations can significantly improve scratch resistance. These improvements can be used in clear topcoats, ink over-print varnishes and pigmented finishes. The commercial availability of nanoparticles allows formulators to obtain new properties that were unachievable in the past, not only in scratch resistance but many other physical performance attributes.

For nanoparticles to be of use in transparent coatings, it is critical that aggregates present in the powder be dispersible to their primary particle size in the coating formulation to avoid rapid settling and excessive light scattering. In addition, it is critical that the dispersed primary particles avoid re-aggregation during the coating curing process.

There is available in the marketplace a VOC-free, aqueous dispersion of nanohybrid particles to protect glossy, aqueous, pigmented and unpigmented topcoats from scratching and abrasion. It is recommended for aqueous high-gloss systems and has no effect on transparency.

Thousands of scratch-resistant coating applications are present in our everyday lives. Examples of these applications include coatings for wood flooring, safety glasses, electronic displays, automotive finishes and polycarbonate panels. Improving the mar, scratch and/or abrasion resistance in these transparent coating applications is a major challenge, particularly with regard to not affecting the other performance attributes of the coating.

Inorganic Fillers

Incorporation of inorganic fillers into coatings to improve mechanical properties is well known. Drawbacks associated with this approach can include loss of transparency, reduced coating flexibility, loss of impact resistance, increase in coating viscosity and defect appearances. To overcome these defects, a filler material should impart improved scratch resistance without causing the aforementioned drawbacks. Nanomaterials have the potential to overcome many of these drawbacks because of their inherent small size and particle morphology.

Maintaining transparency in a coating containing inorganic filler particles is a challenge. Four properties dictate the degree of transparency in a composite material: film thickness, filler concentration, filler particle size, and the difference in refractive index between the bulk coating and the filler particle.

Silica particles, colloidal or fumed, and clays are among the most widely studied inorganic fillers for improving the scratch/abrasion resistance of transparent coatings. These fillers are attractive from the standpoint that they do not adversely impact the transparency of coatings due to the fact that the refractive indices of these particles (fumed silica = 1.46; bentonite clay = 1.54) closely match those of most resin-based coatings. The drawback to silica-based fillers is that high concentrations of the particles are generally required to show a significant improvement in the scratch/abrasion resistance of a coating, and these high loadings can lead to various other formulation problems associated with viscosity, thixotropy and film formation.

Alumina

The use of alumina particles in transparent coatings is much more limited even though alumina is significantly harder than silica-based materials and, as a scratch- and abrasion-resistant filler, higher performance at lower loadings is often observed. For alumina particle sizes greater than 100 nm, the high refractive index (1.72) results in significant light scattering and a hazy appearance in most clear coatings. Currently, only high-refractive-index coatings, such as the melamine-formaldehyde resins used in laminate production, can use submicron alumina for scratch resistance and maintain transparency.

To use alumina as a scratch-resistant filler in transparent coatings, the particle size must be sufficiently small to overcome its refractive index mismatch. A Physical Vapor Synthesis (PVS) process has been developed that allows production of nonporous crystalline metal oxides having primary particle sizes less than 100 nm at economically viable rates with essentially no byproducts or waste streams.

Two grades of aluminum oxide can be produced using the PVS process: NanoTek™ and NanoDur™ alumina. Both grades feature a mixture of γ - and δ -crystal phases and are spherical in shape, but the grades differ in terms of primary particle size. NanoTek alumina has a surface area of 35 m²/g corresponding to a mean particle size of 48 nm, whereas NanoDur alumina has a surface area of 45 m²/g with a mean particle size of 37 nm.

There is a proprietary particle dispersion stabilization process that involves specific surface treatments designed to yield nanoparticles that are compatible with a variety of different coating formulations. For example, stable dispersions of metal oxide nanoparticles can be prepared in solvents such as water, alcohols, polar and nonpolar hydrocarbons, plasticizers, and even directly in acrylate monomers with the appropriate surface-treatment process. These surface treatments allow solids levels of up to 60 wt% to be dispersed, and yet maintain a sufficiently low viscosity for ease of blending.

The use of highly concentrated, non-aggregated nanoparticle dispersions allows incorporation of the nanoparticles into a coating formulation without substantial dilution of the formulation with the dispersion liquid. This feature is particularly important in 100%-solids coating formulations wherein the nanoparticle is dispersed in one of the reactive monomers.

Within a given coating class, formulations that result in harder/stiffer coatings tend to show greater improvement with alumina incorporation than formulations that lead to softer/more elastomeric coatings. In addition, transparent coating formulations that exhibit crosslinking upon

curing, such as UV-curable, 2K polyurethane, and melamine-based coatings, show greater improvement in their scratch resistance upon alumina nanoparticle incorporation compared to transparent coatings that do not crosslink but rather coalesce, such as emulsion-based coatings.

For OPV coating formulations, the combination of sub-micron size alumina particles with nano-size wax particles provides a level of wear protection that exceeds that possible using either of the additives alone. The behavior has been observed in different OPV formulations and with different wax compositions. The mechanism that drives the synergistic behavior is still under investigation.

SNC

SNC is an abbreviation for silica nanocomposites that are composed of colloidal silica particles with an organic surface modification. These particles, which improve the scratch and abrasion resistance of a variety of coatings including radiation-curable formulations, are produced by a unique process that results in monodispersed, non-agglomerating spheres with a diameter of about 20 nm. The flexible manufacturing process is also capable of producing a broad range of cationic (epoxide) and free-radical (acrylate) radiation-curable oligomeric composite materials. These products are stable, transparent and have low viscosity, even at a silica loading of 60%.

Nanoscale materials for coatings also include complex silicon oxides and aluminum silicates. Nanoparticles of these materials have been incorporated into automotive coating formulations that have good sag resistance. The cured coatings have excellent chip and scratch resistance, outstanding appearance, superior sandability, and resistance to water spotting and acid etching. Some properties, such as scratch resistance, are maintained after accelerated weathering.

Sol-Gel

It is also possible to improve the scratch- and wear-resistance properties of a coating as well as its photostability/weatherability by the addition of nanoparticles prepared by sol-gel processing. This method has the advantage in that it starts from existing, well-developed formulations to which a sol containing nanoparticles is added. After curing, the modified systems give transparent coatings with high wear and scratch resistance.

Very often, hybrid (organic-inorganic) materials are produced by sol-gel. The most common way to produce nanocomposites is to form, in-situ, an inorganic phase by hydrolysis and condensation of alkoxides or alkoxysilanes. A further curing results in covalent bonding between the organic and inorganic phase.

ABSORBENTS

Absorption is a process wherein a material is taken up and held, or retained, by another material. The material taken up is called the "absorbate" and the material that retains the material from the absorption process is called the "absorbent." Thus, absorbents are materials that are able to take up another material with the formation of a homogeneous mixture. For example, cotton fibers will take up moisture, charcoal will take up a gas, baking soda will take up odors, silica gels will take up moisture; certain pigments, clays or extenders will take up oils and others will take up moisture; and so on. This should be contrasted with adsorption, which is a surface phenomenon wherein adsorbed molecules can have markedly different properties than those of absorbed molecules. Compounds such as zeolites or molecular sieves are adsorbents that take up compounds by the adsorption process (See *Moisture Scavenger*).

ACCELERATORS

See *Hardeners*

These products increase the epoxy-amine reaction rate and subsequently reduce the possibility of undesired blushing or blooming reactions. Controlled use of the amount and type of accelerator ensures minimal impact on the cured binder performance. Although there are numerous products capable of accelerating epoxy-amine reactions, the most commonly used are: tertiary amines [e.g., DMP-30 = 2,4,6-tris-(dimethylaminomethyl)ph-



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anol], phenol derivatives (e.g., nonylphenol), alcohols (e.g., benzyl alcohol) or acids (e.g., salicylic acid). Be aware that adding accelerator will significantly reduce the pot-life of the binder system.

Iron phosphate conversion coatings for general industrial application use accelerators, such as molybdate or vanadate, to provide active sites for iron phosphate deposition.

Alkyd resin technology frequently uses metal driers to promote air oxidation and resin crosslinking. The activity of cobalt or manganese drier metals can be enhanced by the addition of chelating agents, also known as drier accelerators. The chelating agents function by stabilizing the valence state of the metal so that the oxygen up-take rate is maximized. One such chelating agent is 1,10-phenanthroline.

ACID CATALYSTS

See Catalysts

Acid catalysts are used to accelerate chemical reactions. Strong acids such as p-toluene sulfonic acid (PTSA) are frequently used. Also used are catalysts based on dodecylbenzene sulfonic acid (DDBSA) and hexafluorophosphoric acid. In using strong acids as catalysts, acid strength does not necessarily influence the cure rate but it does affect some film properties. The most widely used of the strong acids is PTSA. Weaker acids, such as butylphosphoric, and those based on aromatic phosphates and various carboxylic acids, are also used in some coatings systems. Blocked acid catalysts are also used for many crosslinking reactions.

There are catalysts based on very strong acids, such as hexafluoroantimonate or triflic acid (trifluoromethanesulfonic acid), that can be used in conjunction with cycloaliphatic epoxies, glycidyl ester and glycidyl ether resins. Polymerization of the epoxy resin occurs via a cationic mechanism, thus allowing reaction with hydroxyl, lactone, oxetane or vinyl functional groups. High solids or solventless coatings for high-speed or low-temperature applications can be obtained using this technology. These types of catalysts are formulated for use in solvent-free, high solids and waterborne coatings. Catalysts based on hexafluoroantimonate cannot be used in waterborne systems.

ACID SCAVENGERS

Acid scavengers remove the small amounts of acid that are formed during the lifetime of a coating or ink. For example, when vinyl copolymers are aged small amounts of hydrochloric acid are formed as they age. An acid scavenger reacts with the acid, which removes it from the system so it cannot cause harm to the coating, substrate or abutting objects. Compounds such as cycloaliphatic epoxides and soybean oil epoxide, which readily react with strong acids, are examples of acid scavengers.

ADHESION PROMOTERS

See Coupling Agents

Adhesion promoters improve a coating's ability to withstand mechanical separation from a substrate. That is, they improve adhesive strength. Quite often these compounds contain two different functional ends, one of which will interact with the substrate and the other that will interact with the coating binder. Examples of the various coupling agents are the silanes, which are trihydrolyzable; the titanates, which can be mono-, di-, and tetrahydrolyzable; and the chromiums, which are complex in nature.

For metal surfaces that are to be coated, this is particularly important because metals, as a class, are unstable. The pure metal is always oxidizing to the metal oxide on the surface of the metal substrate. Exposure to moisture, oxygen and salts accelerates the process. Almost all coatings contain microvoids through which oxygen, small molecules like water, and ionic materials can diffuse. If the coating can remain bonded to the metal, then the damage done by these diffuse agents will be nonexistent. In other words, corrosion can be prevented. It is, therefore, very important to do all that is possible to maximize adhesion.

For some materials this involves a mechanical roughening of the substrate surface to increase the surface area for physical absorption. Chemical pretreatments such as zinc/iron phosphate and various other materials have also been used because tightly bound phosphated sur-

faces will retard access to the metal and, therefore, impede corrosion.

Because the industry has moved away from chrome-VI pretreatment to chrome-free systems, the older adhesion promoters may have a reduced level of performance with respect to corrosion resistance and adhesion. There is new technology developed for chrome-free metal substrates that improves adhesion and increases salt spray resistance.

Typically, organofunctional silanes have been used in coatings as adhesion promoters because they provide a polar functional group to contribute to increased bonding to a mineral substrate. They also are hydrolyzable and provide wetting ability and surface activity. The silanes are moisture sensitive and will hydrolyze over time to silanols. This is not a problem in solventborne coating systems but can cause problems for waterborne systems. The silanes react with both the polymer and the substrate to form covalent bonds across the interface. Silane adhesion promoters are used in urethane, epoxy, acrylic and latex systems.

Receptive inorganic surfaces are those that have hydroxyl groups attached to elements such as Si, Al, Ti and Fe. Nonreceptive surfaces, such as boron, and alkaline earth oxides, do not form stable covalent bonds with silanols. A number of different commercial silane coupling agents are used in coatings. Levels that range from 0.05-1.0% are generally effective.

Methacrylic phosphate monomers that improve adhesion to metal, concrete, glass and other inorganic substrates and that can be used in both water- and solventborne formulations are available. Some methacrylic phosphate monomers improve metal adhesion and also significantly improve corrosion resistance. There are also acrylic phosphate functional monomers that improve adhesion to various metal substrates. The acrylic reactive group provides a higher reaction rate in UV- and EB-curable applications.

Other adhesion promoters in the marketplace are titanates [such as isopropyl tris-(N-ethylaminoethylamino) titanate], zircoaluminates, zirconates, aryl/alkyl phosphate esters and proprietary metal organic compounds. The titanates and zirconates suffer from moisture sensitivity as well, so caution is necessary when using them with waterborne systems. Neo-alkoxy products are claimed to not have this problem. Alkyl/aryl phosphate esters, zircoaluminates and the metal organic promoters are stable in waterborne coatings. They are quite different in chemical nature and, therefore, the formulator needs to evaluate them separately.

Epoxy/methoxy functional additives are effective in promoting adhesion of a variety of coating systems to glass, aluminum and steel. Methacrylate/methoxy functional additives improve adhesion of free radical cured resins, such as polyacrylates, to inorganic substrates. Epoxy functional silanes improve adhesion and water resistance of a variety of coating systems to inorganic substrates. Amine/methoxy functional additives improve adhesion and water resistance of coatings and adhesives when bonded to glass or metal substrates.

Radiation-Curable Coatings

Radiation-curable coatings applied over a variety of metal surfaces can pose an adhesive challenge. There are proprietary phosphate ester monomers that are best used on an additive basis to provide enhanced adhesive properties. These acid-functional monomers (AFMs) range in functionality from mono to tri, with differing acid level content. The AFM additives promote adhesion to a variety of metal substrates including aluminum, cold-rolled steel and tin-plated steel as well as promoting adhesion to wood and plastic substrates. AFMs should not be used with amines, as instability may result.

Powder Coatings

The same precautions regarding clean substrates and pretreatments that apply to liquid coatings are advised for powder coatings. Adhesion promoters such as the silanes and titanates may also be used to enhance adhesion. Silanes designed for use in powder coatings have an organo functionality that has an affinity for the powder resin system. The organo-silane must orient itself at the coating-substrate interface. The choice of organo-silane is usually governed by the resin system, and experimental screening is advised to determine which promoter

provides the most improvement. Adhesion promoter types commonly used in powder include mercapto-silanes, amino-silanes, carbonyl/hydroxyl-silanes, and carboxyl-silanes.

Plastic Substrates

Due to high chemical stability, low price, excellent balance of physical properties, possible recycling, etc., the amount of polypropylene (PP) and thermoplastic olefin (TPO) consumed by automotive parts, household electrical appliances and molded general goods businesses is increasing. However, PP and TPO are materials with low surface energy that make painting and adhesion problematic, hence chlorinated polyolefin (CPO) has found wide use as an adhesion promoter. Solventborne CPOs have traditionally been used. Excellent adhesion between TPO substrates and CPO can be obtained as the result of good wetting and higher dispersion interaction, which are affected by the properties of the CPO's chlorine content, crystallinity, melting temperature, molecular weight and its polydispersity.

There are several factors that can affect the performance of a CPO-based adhesion promoter. Application parameters play a significant role in designing a system that will provide optimum adhesion performance. Of particular importance is the temperature at which a coating applied to a PP or TPO part is cured or baked. In addition, substrate and CPO composition can influence overall adhesion performance.

Coating bake temperature is the temperature at which the coating applied to the TPO part is cured. Coating bake temperature can have an effect on the interaction between a CPO-based adhesion promoter and the surface of TPO, which can affect performance. For best results, coating adhesion is enhanced when the coated TPO parts are baked at temperatures over 100 °C, given the same coating type. However, CPO-based adhesion promoters are successfully used in applications, such as automotive refinish applications, where the coating is air-dried or baked at temperatures lower than 100 °C.

The chemical and physical properties of the CPO can also have a significant effect on adhesion performance. Addition of co-resins to CPOs can enhance adhesion, reduce blistering, and improve the appearance of coatings applied over the adhesion promoter layer. CPOs have limited compatibility with most resin types, but unlike conventional coatings this may not be detrimental to performance. CPOs promote adhesion best when they are at the interface of the substrate and the coating applied over the substrate. This means that a formulated adhesion promoter system with a CPO and borderline compatible co-resin may actually allow the CPO to reach the interface more readily. A number of co-resin types can be used with CPO, including acrylic, acrylic-modified alkyds, polyesters and others. The level of CPO used in the formulation will be dependent upon the substrate, coating type and required performance properties.

Research efforts are focused on waterborne coatings applicable to TPO substrates that coalesce well at baking temperatures as low as, or lower than, 80 °C (176 °F) in order to save energy costs and to avoid thermal deformation of TPO substrates at the higher temperatures. Chlorine-free adhesion promoters are also being used and are highly desirable.

ALGAEICIDES

See *Biocides/Fungicides/Anti-Fouling*

Chemical agents used to destroy algae. Algae are chlorophyll-containing plants whose green color is often masked by a brown or red pigment. Representative compounds include glutaraldehyde, methylenebis(thiocyanate), quaternary ammonium compounds and zinc oxide. Methods for algae control generally fall into three categories: total removal, environmental control of the surroundings to curtail algae growth and destruction.



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ANTI-BLOCKING AGENT

Additive used to prevent the undesirable sticking together or adhesion of painted surfaces under moderate pressure, or specified conditions of pressure, temperature and humidity; or during storage, manufacture, or use. Blocking is a measure of the coating's ability to resist adhesion to itself (on another freshly coated surface) or adhesion to other substrates, for example, weather-stripping, doors, hardware etc. A well-known example of blocking is when a freshly painted window frame is too rapidly closed. Sometimes it can be very difficult to open the window again.

Blocking is a key performance parameter for architectural application and for industrial and OEM applications; block resistance is important in the manufacture of roll stock that will be unrolled at a later date. It is also important for reducing the need for storage space for freshly painted parts. ASTM D4949 may be used to measure blocking performance. Factors affecting blocking include the coating surface free energy, topography of the coating, the hardness and the Tg of the polymer.

One approach to improve the block resistance of a coating is to introduce a surface-active agent that will bloom to the top – the air interface – of a film as it dries/cures.

Carbinol-functional silicone polyether copolymers impart mar resistance and anti-blocking properties in addition to leveling and wetting. Methacrylate functional silicone polyether copolymers provide consistent and long-lasting slip, mar resistance and anti-blocking to UV-cured coatings.

Fluorochemical additives can be mixed into coating formulations, often as post-adds, and migrate to the air interface where they can provide effective protection where it is most needed, without affecting recoat adhesion. Common applications include latex semi- and high-gloss architectural paints used on doors and window trim, and applications where painted parts are stacked for shipping.

Waxes decrease blocking so that unwanted transfer or adhesion to a contacted surface is prevented. This can be very important for materials that are coated, dried and stacked for storage and shipping. Waxes can be used in any type of coating that could benefit from mar resistance and/or a slip aid. Both water- and solventborne metal coatings benefit from added lubricity and abrasion resistance. HDPE, paraffin and Carnauba waxes are typically used to counteract blocking. Anti-blocking agents are also very useful for any type of items that are coated, dried and immediately stacked or rolled up for storage or shipment.

It should be noted that anti-blocking additives, since they tend to gather near the top surface of a film, can change the appearance of a film – the gloss level. The type of paint is also a variable.

ANTI-CRATERING AGENT

A chemical additive used to prevent the formation of small, bowl-shaped depressions in a coating film. Very small areas of contamination that have a low surface tension will produce a surface energy gradient that pulls the coating away from the contaminant to form a bowl-shaped depression surrounded by a raised rim. As a result, the coating film is left with a roughly rounded depression – either a crater if the central contaminant is not visible or a “fish eye” if the central area is visible. As the coating pulls away from the contaminant and starts to lose solvent it becomes higher in viscosity and is not able to flow out, with the result being the thicker rim of the crater. Craters are typically 1-3 mm in diameter. Craters are not always caused by a contaminant within the coating or on the substrate. Frequently airborne particles will come in contact with the wet surface of a newly applied coating to cause cratering. Certain coatings tend to be more prone to these surface defects than others. Low-molecular-weight resins that do not dry quickly are prone to this. Coatings with defoamers and wetting agents may also cause surface defects.

Related phenomena caused by surface energy gradients are picture framing, Bénard cell formation, orange peel and edge-pull. In general, such defects are caused by the fact that the coating will flow from a low-surface-energy area to a high (relatively)-surface-energy area. A variety of surfactants will alleviate or remove this problem, but the fluorochemical surfactants are particularly effective in many cases.

ANTI-CRAWLING AGENT

A chemical additive that prevents the wet coating film from receding from small contaminated or otherwise altered areas of the substrate, leaving the area with only a very thin coating and often having the appearance of being uncoated. Changing solvent systems or the addition of a low-energy surfactant (silicones or polyether-modified silicones) may solve the problem.

ANTI-FLOAT AGENT

A chemical added (usually a wetting additive) to single- or multi-color pigmented coatings that prevents the separating or floating apart of one or more pigments from the other. This prevents a streaked or mottled effect in the final film. During drying or storage, one or more of the pigments floats apart from the others and concentrates in streaks or patches on the surface. The effect may happen even if a single pigment is used if the particle sizes of the pigment are varied over a broad range. Silking is a type of float confined to parallel striations in the film; dipping and flow coating are more prone to the effect of silking.

ANTI-FLOODING AGENT

A chemical added to a multi-pigmented coating that prevents the separation and concentration of one pigment at the surface of the film upon drying or in a dispersion.

The terms flooding and floating are often used interchangeably within the industry but they are distinct events. Both events occur in the liquid coating phase. Some have referred to flooding as being a horizontal separation of the pigments as opposed to floating, which is a vertical separation. Some also refer to floating as being a problem on the surface of the film as opposed to flooding, which occurs beneath the surface of the film.

The terms are not standardized and both are the result of an uneven distribution of the pigment that appears in the film as it is drying. Some also use the term floating to describe a mottled effect and the term flooding to describe a surface color that is uniform but darker or lighter in color than it should be.

Compared to many organic-based pigment dispersants in the market, high-molecular-weight silicone gives better anti-floating and anti-flooding results when added at the same weight percent addition level to the formulation.

ANTI-FOAMING AGENT

See Defoamer, Foam Control

An anti-foam additive is used in coatings manufacture to prevent the formation of foam, or it is added to a mixture to destabilize foam and act as a bubble breaker, breaking the foam that has already formed.

The terms ‘defoamer’ and ‘antifoaming’ agents are often used interchangeably. In fact, they are not quite the same. A defoamer is a surface-active agent that stops the foam and breaks the bubble once it has been formed. It is a bubble breaker. An antifoaming agent prevents the formation of foam so it never forms. The term ‘foam-control agent’ is a more appropriate term to use and they function by a variety of mechanisms to prevent or rupture foam.

Quite often defoamers are proprietary blends of various ingredients such as mineral oils, organic solids and surface-active compounds; fatty oils, surfactants and silica derivatives; alcohols, silica derivatives and surface-active compounds; esters, mineral oils and silica derivatives; and the like. Such blends are compounded for special problems such as:

- quick foam “knock-down” coupled with long-lasting foam prevention in latex manufacture and latex coatings;
- controlling foam in stripping operations;
- foam control in food applications where FDA product acceptability is needed;
- foam control in paper coating and dyestuff applications;
- foam elimination in effluent systems;
- prevent air entrainment and/or facilitate air release from coatings during the filtration and filling processes;

- prevention of foam formation during roller application of architectural coatings;
- aid in the breaking of bubbles formed during roller application of latex coatings; and
- prevention of air entrainment in flash tanks and stripping columns.

With such product and specific end-use complexity, it is desirable to contact a supplier for product suggestions, point of application and amounts needed to efficiently eliminate difficulties.

ANTIFOULING AGENTS

See Biocides/Fungicides/Algaecides

These additives protect underwater marine hulls, or other coated structures, from harmful effects of marine life in coastal areas. Antifouling paint is used to protect the bottom of ships against living organisms that attach themselves to the hull. These organisms cause reduced slippage (the ship advances more slowly and consumes more fuel) and can increase the weight of the ship, thereby affecting safety.

Because they keep algae and barnacles from attaching to ship bottoms, tin-based antifouling agents have most often been used – in particular, tributyl tin (TBT). For years in the marine industry, the use of TBT with cuprous oxide was an effective antifouling system that deterred algae, barnacles and other organisms from adhering to the ship's hull. However, TBT is being phased out of use because of safety concerns for a variety of marine life and its long half-life that causes it to accumulate in the environment. There are a number of co-biocides used with cuprous oxide that are replacing the TBT-based systems. These include zinc and copper pyrithione and isothiazolinone (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one)-based products. All of these co-biocide antifoulants have been used successfully in Japan for many years.

Cuprous oxide is a fungicide that deters attachment of marine organisms such as barnacles and mussels and thus is an active ingredient in antifouling paint. It is typically used with other co-biocides to enhance paint performance and improve the coating's resistance against algae and slime attachment. The use of an algicidal co-biocide minimizes the attachment of algae and grasses to the coating surface.

The International Maritime Organization (IMO), in late 2001, approved a ban on the application of antifouling marine paints containing organotin such as TBT, beginning on January 1, 2003. The IMO agreement also required removal or sealing of all TBT-based coatings from vessels by Jan. 1, 2008. The actions affected all vessels engaged in international voyages. Tin-free products have been on the market for more than 10 years, and marine paint companies offer the same performance guarantee as given with the tin-containing coatings. While most ships dry-dock every three years or less, some owners want a dry-dock interval of five years. Several of the new self-polishing systems can now meet that five-year standard ensuring most, if not all, marine markets can be serviced using a tin-free product. Registration requirements in the United States and Europe mean the new tin-free products have already undergone significant testing that show they are environmentally preferable to TBT.

There are barnacle inhibitors based on natural bioproducts – small molecules with menthol-like configurations. In particular, a menthol derivative called menthol propylene glycol carbonate is a GRAS (generally recognized as safe) food ingredient used as a cooling agent in gum and cosmetics. This chemical has repellent characteristics against barnacles as well as other insects.

ECONEA [1H-pyrrole-3-carbonitrile, 4-bromo-2-(4-chlorophenyl)-5-trifluoromethyl] is a metal-free antifouling agent that protects vessels against aquatic growth without a potential negative impact on the marine environment compared to traditional, copper-based antifoulants. It is being applied to U.S. Coast Guard aluminum hull crafts, eliminating the risk of galvanic corrosion that can occur when copper-based paints are applied to aluminum. Research has shown that ECONEA provides effective protection against fouling at substantially lower concentrations in the paint formula than traditional copper-based antifouling agents. Unlike copper compounds, ECONEA degrades rapidly once

released at the surface of the paint – thereby not accumulating in the marine environment.

Currently marine coating research is highly focused on foul release coatings – i.e., those that are biocide free and do not release additives into the environment. These coatings function by using polymers that prevent living organisms from attaching themselves to the surface of the coating.

ANTI-FREEZING AGENT

A chemical that will prevent freezing or damage resulting from the freezing and thawing of a coating's composition. Typical examples are ethylene and propylene glycol.

ANTI-GELLING AGENT

A chemical that prevents the progressive, irreversible increase in consistency of a pigment-vehicle composition usually caused by: an interaction between the vehicle and pigment, reaction between resin and solvent, or polymerization of the vehicle. Some anti-gel agents for air-dry and stoving systems are based on a ketoxime and a phosphorous ester salt. They delay/prevent thickening, which can occur as a result of oxidation or condensation of the binder. They also reduce the reaction of the pigments with the vehicle and prolong the shelf life of a coating.

ANTI-LIVERING AGENT

A chemical that prevents the progressive, irreversible increase in consistency of a pigment-vehicle composition, usually caused by an interaction between the vehicle and pigment, or polymerization of the vehicle. Two typical anti-livering agents are 2-amino-2-methyl-1-propanol and N,N-dimethylethylamine.

Livering is the slow, irreversible change that increases the consistency of a formulated (pigment-vehicle combination) coating. It usually results from a strong interaction between the vehicle and the pigment or other solid, dispersed material. However, it can be caused by a slow polymerization of the vehicle and entrainment of the pigment or filler. Livering often can be seen as a thick skin covering the surface of previously opened and stored cans of paint.

ANTI-MARRING AGENT

A chemical or composition that will enhance the ability of a coating to resist damage caused by light abrasion, impact or pressure. Silicone polyether copolymers impart mar resistance, improve leveling and reduce cratering, pinholing, orange peel and cissing. Carbinol functional silicone polyether copolymers impart mar resistance and anti-blocking properties in addition to leveling and wetting. Methacrylate functional silicone polyether copolymers provide consistent and long-lasting slip, mar resistance and anti-blocking to UV-cured coatings. Waxes are frequently used to improve mar resistance.

There are new mar and slip additives that improve wetting of low-surface-energy and contaminated substrates, resulting in uniform film coverage. They are engineered for solvent, solvent-free and aqueous systems and are well suited for coatings in which surface slip and/or resistance properties, such as block, stain, or scrub resistance, are required. By performing various additive functions and with low use levels (as low as 0.1%) they can be very cost-effective for manufacturers. (*See Slip-Aid and Abrasion-Resistance*)

ANTIMICROBIAL AGENT

See Biocides/Fungicides

The term 'antimicrobials' is generally defined as substances – or mixtures of substances – used to destroy or suppress the growth of harmful microorganisms whether they be bacteria, fungi, or viruses, in, on, or a substrate or article where it is not desired. Historically, the term 'antibiotics' is used in reference to controlling bacterial infections specifically in humans. For substances that control or inhibit yeast and fungi, the term used is 'anti-fungal' whether on animate or inanimate substrates. Similarly, for inhibiting viruses, we refer to anti-viral substances.



Besides these various terms for antimicrobial concepts, in many industries terms like bactericides, fungicides, algacides, virucides, preservatives and biocides are commonly used. For example, in the coatings industry, the term 'biocide' is historically employed to indicate preserving a wet formulation from microbial spoilage which, in most other industries like personal care or household markets, would be defined as 'preservatives'.

In addition to these various terms to indicate chemicals that inhibit or destroy microorganisms, we are also exposed to layman's terminology of 'mildewcide' or 'moldicide' to refer to chemicals controlling unsightly biological defacement on surfaces that are 'black'. Even though it is implied primarily for fungal growth, it can also be caused by a consortium of other microorganisms including lower forms of algae, moss, amoeba, protozoa, etc. For non-microbiologists, these terms may be confusing with each term meaning different things depending on the implied uses and claims by different suppliers. All of these chemicals can be referred to as antimicrobials irrespective of their applications, target organisms and mode of activity under a given condition.

Government regulations on treated articles, including coatings with antimicrobials, and guidelines on claims come under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA), EPA and FDA. Under FIFRA, an antimicrobial product that claims to control microorganisms such as bacteria and fungi requires registration. According to the EPA, an article or a substance that is treated with, or containing, a registered pesticide is defined as a treated article and is limited to protecting the article itself from microbial spoilage or contamination [for example paints supplemented with fungicides or bactericides to protect the paint in storage or after application, or preservative treatments used in wood to protect wood against insects or fungal infestation].

The EPA in 2000 issued a Pesticide Regulation Notice 2000-1 to clarify the Agency's policy with respect to the scope of the treated article exemption. It is a guidance document that focuses on the various types of antimicrobial claims that the EPA considers acceptable or unacceptable.

Antimicrobials used in public or non-public health claim products have to go through a battery of testing using acceptable microbiological methods to show efficacy in the product in use. There are many test methods in microbiology described to demonstrate the antimicrobial nature of a substance and when it is incorporated in an article. There are various screening stages adopted that may include primary, secondary and in-use final testing. A typical primary-screening protocol involves testing for the minimum inhibitory concentration [MIC] of the chemical to be incorporated in an article. Normally the MIC is determined in an in-vitro system like growth media against a set of bacteria, fungi, viruses and/or algae depending on the target microorganism. After getting selected in the primary screen, the substance enters the secondary screening process in an in-vivo system meaning the application matrix in which it is expected to be incorporated. Because not all selected antimicrobial substances are expected to be universally acceptable in varied systems, they next go through the rigor of compatibility, stability and efficacy testing evaluations. Some examples of this rigor in coatings applications include the chemical stability in the formulation, pH compatibility, heat stability, color acceptance, shelf storage longevity, exterior weather sustainability, etc., in addition to testing for its bio-availability to function as an antimicrobial throughout the process.

With so many scenarios for defining an antimicrobial, the challenge becomes how to test and what test methods to use for demonstrating and claiming broadly the 'antimicrobial' property of a treated article such as a coating. There are several ASTM methods available such as: ASTM D5589, ASTM D5590, ASTM D3273 and ASTM D2574. Also used is the Japanese Industrial Standard JIS Z 2801-2000: Antimicrobial Products—Test for Antimicrobial Activity and Efficacy. This method was developed by a consortium of workers comprised of manufacturers of silver-based antimicrobial agents, government-based research organizations and universities, and under organizations such as the Society of Industrial Technology for Antimicrobial Articles (SIAA) to test the antibacterial activity of silver ions impregnated in rigid hydrophobic polymers.

This method is a quantitative measurement method that tests survival of low-dose bacterial inoculum deposited between the tested antimicrobial surface and a thin plastic film that keeps the inocula wet and nourished in a nutrient-rich environment throughout the 24 h incubation at 35 °C. This differs from other traditional methods of testing antimicrobial resistance in coatings surfaces where the surface is not kept deliberately wet or moist with a nutrient medium. Inoculum survival and growth in the other methods depends only on the moisture from either media or humidity created in the incubated unit, so only microorganisms that can survive some level of desiccation on the surfaces in 24 h can be recovered and can be compared to the non-treated surface. In this respect, the JIS Z 2801 method is so severe it is not necessarily a realistic surface contamination model for dry walls and other coated vertical surfaces.

In spite of this limitation, JIS Z 2801 has emerged as one of the industry standards for perhaps the 'worst case scenario' of a surface that retains wetness and permits microbial survival. Following the method as written for hydrophobic coatings surfaces, yields results that may provide useful information, but for hydrophilic and porous substrates and surfaces, a deviation in the inoculum delivery and validation for each different substrate would be required to get useful data. There is no one universal test protocol or one pesticide product that can demonstrate all the antimicrobial properties on all surfaces.

ANTIOXIDANT

A chemical compound that prevents oxygen from reacting with other compounds that are susceptible to oxidation. Antioxidants are additives that are expected to prolong the lifetime of a coating and thus assist in maintaining its original high-performance characteristics as long as possible. Components of a coating, adhesive, ink or sealant are subjected to opportunities for degradation during component manufacture, storage, and transportation as well as during application and final use.

The cause of degradation is almost always by oxygen or UV radiation attack (*see UV Absorbers and Light Stabilizers*). Oxygen attack can be by oxygen or ozone and it may occur under ambient or elevated temperature conditions. At elevated temperatures antioxidants decrease thermal oxidation and formation of peroxide radicals that, in turn, can cause formation of colored chromophores and/or other deleterious changes in coating properties.

Effective antioxidants include the p-phenylenediamine derivatives such as the N,N'-diaryl, the N,N'-alkyl-aryl, and the N,N'-dialkyl compounds, but these compounds have a tendency to discolor or scorch during cure. Also effective and widely used are the hindered phenolic compounds, such as 2,6-di-*t*-butyl-4-methylphenol (BHT), octyl and certain higher alkylphenols, phosphites (trisnonylphenol phosphite, triphenyl phosphite, tris(2,4-di-*t*-butylphenyl) phosphite, bis(2,4-dicumylphenyl) pentaerythritol phosphite), and synergists that are mixtures of antioxidants that act in a synergistic manner. Antioxidants are usually used in a concentration range of 0.1-0.5%, and they are consumed in the stabilization process.

For powder coatings, the purpose of the antioxidant is to minimize thermal degradation of the polymer in the coating. Thermal degradation causes yellowing and a reduction in mechanical and chemical properties. Usually hindered phenols are used as primary antioxidants. Organo-phosphites are sometimes used as secondary antioxidants. An organo-phosphite acts synergistically with a hindered phenol to check the thermal degradation of the polymers. These compounds act as peroxide decomposers and can be incorporated in a 2 or 3 to 1 ratio (hindered phenol to organo-phosphite). Hindered phenol-based antioxidants are usually used at a level of 0.2-0.8% of the binder. Higher levels will cause yellowing. It should be noted that antioxidants do not reduce degradation from UV light exposure.

Various classes of antioxidants have different thermal stabilization mechanisms. The classic high-molecular-weight hindered-phenolic antioxidant is effective as an oxygen-centered radical scavenger, but

can suffer from "pinking" in the presence of combustion gases like NO_x, which can be found in gas oven exhaust. The phosphite antioxidants act as decomposers of hydroperoxides and provide protection during high temperature processing and/or curing cycles. The new lactone antioxidants function as carbon- or oxygen-centered radical scavengers and inhibit auto-oxidation. The development of a high-performance "phenol-free" antioxidant blend exploits synergistic effects between phosphite and lactone properties while illuminating the possibility of pinking. There is a synergistic effect when using different antioxidants blended together and the combination can meet heat and processing stability requirements.

ANTI-RUST AGENTS

See Corrosion Inhibitors/Flash Rust Inhibitors

Anti-rust agents are compounds that, when added to water, alleviate or lessen rust formation. The term also refers to a variety of chemicals used to prevent corrosion on the surface of iron or other ferrous metals resulting in the formation of products consisting largely of hydrous ferric oxides. The same or different agents may be used to prevent flash rusting, early rusting or to provide long-term corrosion resistance. Anti-rust agents are important in preventing rusting in cans or other metal containers of waterborne paints.

ANTI-SAG AGENTS

See Thickeners, Rheology Modifiers

This is a common term for a class of compounds used to increase the viscosity of paints, and control or prevent sagging of a coating film during application and curing. The potential for sagging tends to increase as wet film thickness increases and/or as drying is prolonged. Most of the anti-sag agents impart a thixotropic rheology to the paint.

Treated clays are the main type of thixotropic agent used in alkyd systems. These are Bentonite clays that have been treated so that they build a gel structure by hydrogen bonding in the paint. They are either added into the mill base where the dispersion shear breaks the agglomerates, or added as a pre-gel. These clays are of two types depending on whether or not they need a polar activator. The activators are usually alcohols. The choice of clay is dependent on the system.

In many latex systems, structure is formulated into the coating and settling is not as much of a problem as it can be in solvent systems. For some aqueous systems the choice of colloid is very important. A variety of thickeners are available for waterborne systems. Assistance should be sought from the supplier of these various types of materials.

There is a new sag-control technology for some applications using functionalized particles i.e., BaSO₄ particles that are epoxy- and amino-functionalized. The key to this technology is an increased coating network density via direct chemical bonding, which offers new formulation opportunities. Functionalized BaSO₄ particles can be utilized as cost-efficient anti-sagging additives in selected coating systems.

ANTI-SETTLING AGENT

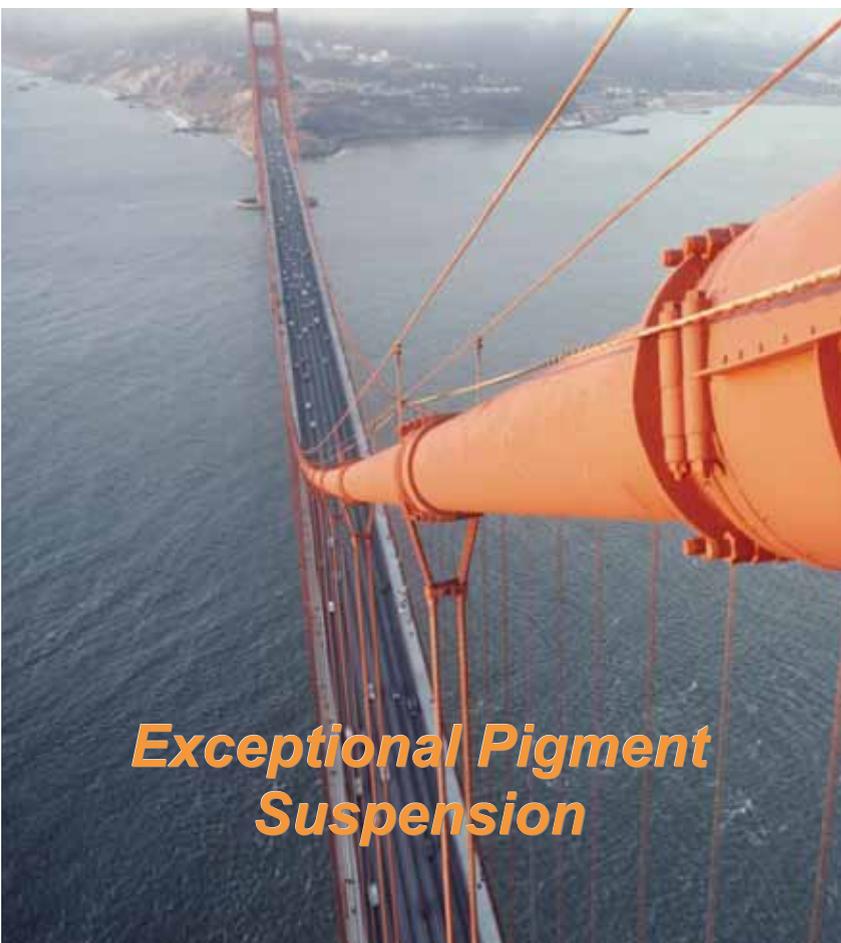
See Rheology Modifiers, Thickeners

An anti-settling agent is a suspension or rheological additive whose function is to prevent or retard pigment settling, and to maintain uniform consistency of the coating during storage and application.

ANTI-SILKING AGENT

See Anti-Flooding

Additive used to prevent a particular type of float that results in parallel hairline striations of different colors running throughout the film of a pigmented coating.



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ADDITIVES REFERENCE GUIDE

ANTI-SKID AGENTS

See *Anti-Slip Agent*

Slip-resistant or anti-skid additives are compounds that function directly opposite of slip additives or lubricants. They make it more difficult to move one surface past another surface. Compounds such as the colloidal silicas are used for this purpose. In the marine coating segment, antislip or antiskid coatings are those that reduce the sliding and slipping of humans and cargo on decks. Silica sand is widely used as a point-of-application stir-in additive in floor, deck and stairway coatings.

ANTI-SKINNING AGENTS

Anti-skinning agents prevent the formation of an insoluble film or skin formation on the surface of a liquid coating during storage or during application. Coatings that cure by an oxidative mechanism are most susceptible to skinning. Replacing air with an inert atmosphere such as nitrogen in the headspace of storage containers is an effective way to prevent skinning during storage.

Skin formation may occur in a dipping tank that is open to the atmosphere. Here the skin may begin forming as surface gel particles that are formed by oxidation. As time passes, the gels coalesce into a continuous film as further oxidation takes place. Additives such as the oximes, particularly 2-butanone oxime, phenolics, solvents, and retention aids are used. Oximes such as butyraldoxime, 2-butanone ketoxime (methylketoxime or MEKO, which is the most widely used compound), and cyclohexanone oxime are compounds that complex with polymerization catalysts and prevent polymerization. Phenolics such as hydroquinone, 2,6-di-*t*-butyl-4-methoxyphenol (BHT), *o*-alkylphenol, and similar compounds act as antioxidants that retard auto-oxidation reactions. These are used at low levels of about 0.05% to as much as 0.2%. Solvents dissolve the components that cause the skinning. Currently undisclosed composition products are on the market from various suppliers. Retention aids prevent applied paint films from drying too rapidly. Waterborne paints usually contain retention aids that slow down the evaporation of water.

ANTI-SLIP AGENT

See *Anti-Skid Agent*

Any material added to a coating that will reduce or eliminate the hazard of slipping on the surface of the dried film. Surface roughness or an increase in coefficient of friction accomplishes this. A coating surface on floors, curbs, streets, porches, decks and so forth may be slippery particularly if damp and, therefore, there is often a need to add an anti-slip agent to the coating to enhance the surface roughness. Polyolefins with high COFs (coefficient of friction) are widely used in both commercial and consumer formulas for floor finishes.

This is not to be confused with the slip or lubricity that many coatings are designed to have particularly in manufacturing, packaging and transporting coated goods.

ANTISTATIC AGENTS

Anti-stats are materials that, when added to the coating or applied to the film, make it less conductive, or less attractive to dust, lint or other airborne particulates.

Conventional antistatic agents used to increase the conductivity of polymeric materials so as to permit dissipation of electrostatic charges can be separated into four general categories.

1. Hydroscopic surfactants such as tertiary fatty amines and their quaternary ammonium salts, monoacyl glycerides, monoalkyl and dialkyl phosphates, alkane sulfonates and sulfonamides work by blooming to the surface and attracting a conductive film of atmospheric moisture. These antistatic surfactants are humidity-dependent and work on the chemical principal of limited polymer solubility, blooming to the polymeric surface to provide sites for water absorption from the atmosphere. Examples are: glycerol monostearate, stearyl phosphate, dodecylbenzene and sulfonamide.

2. Conductive pigments, metal powders and other additives, which dissipate the electronic charge proportionate to their loading in the polymer. Carbon black, graphite fiber, metal powders, barium titanate

powders, potassium titanate whiskers, metal-doped silicas, TiO₂ and fibers provide a low-resistance pathway to dissipate the electrostatic charge and provide permanent antistatic protection.

3. Metallocenes that provide a low-energy transfer of electrons between adjacent aromatic layers. The primary example is bis(methyl)cyclopentadienyl cobalt.

4. A new class of antistatic agents based on combined neoalkoxy titanates and/or zirconates and subsequent tri-neoalkoxy zirconates that can be added in minor amounts during compounding.

Antistatic agents are in hydrophobic coatings such as the silicones to improve the coating's resistance to dirt pick-up. These additives are usually cationic in nature, but in certain instances they are nonionic hydrophilic compounds.

Anti-static additives enhance the electrical conductivity of electrostatic spray paints, improve gloss, reduce the Faraday effect in powder coatings, and retard dust attraction on the finished product. (The Faraday cage effect is observed in the powder coating of parts that have recesses, inside corners, channels or protrusions on the surface of the substrate. The Faraday cage is the area of the part where the external electric field created by the gun does not penetrate.)

These static dissipative materials can be blended internally with powder coatings to enhance the electrostatic spray characteristics of the coating and minimize dust attraction. This increases the transfer efficiency, which improves penetration into corners and recesses. The anti-stats seem to have no adverse affect on the physical characteristics of the final powder coating such as: impact resistance, pencil hardness, gloss, gel time, color, adhesion, cure time, salt spray and condensing humidity. These agents are able to control gassing and minimize pinholing in the coating.

For powder coatings both charge control and antistatic agents are used. Charge-control agents improve the transfer efficiency and the ability of the powder to penetrate the Faraday cage areas. The function of antistat agents is to improve the ability of the coating to conduct extraneous electrical charges to ground. These additives are used to decrease the surface resistivity of the powder and the applied powder coating.

Antistatic additives reduce the powder resistivity so that the powder particles charge more efficiently. This in turn improves the overall efficiency of the coating process. Several types of materials are used to reduce resistivity. Quaternary ammonium salts (cationic) or alkyl sulfonates (anionic) based on fatty acid derivatives are often used.

Some of the cationic antistatic agents are catalysts for epoxy-containing powders and have a tendency to cause yellowing when baking. Barium titanate is also used to promote powder-charging characteristics.

ASSOCIATIVE THICKENERS

See *Thickeners*

Associative thickeners are polymeric compounds that provide consistent and reliable control of coating rheology during manufacture and use. They obtain their efficiency presumably by association between thickener molecules or thickener and latex particles.

BACTERICIDES

See *Biocides/Fungicides/Antimicrobials*

Bactericides are additives that will kill bacteria (single-celled aerobic or anaerobic organisms) that can cause a variety of problems in liquid coatings and coating films. Examples of suitable compounds include: hexahydro-1,3,5-tris(2-hydroxyethyl-s-triazine), sodium pyrrithione, isothiazolinone-based chemicals, 1-(3-chloroallyl)-3,5,7-tri-aza-1-azonia-adamantane chloride, formaldehyde-releasing compounds, and biguanides (polyhexamethylene biguanide [PHMB]).

BARRIER COATING ADDITIVE

See *Seal Coating*

BIOBASED MATERIALS

A biobased product was defined by the United States Secretary of Agriculture in the Farm Security and Rural Investment Act of 2002 as follows, "The

term 'biobased product' means a product determined by the Secretary to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials OR an intermediate feedstock."

GRAS Additives and UV-Curables

There are two reasons to explore using UV radiation to create coatings from foodstuffs. One is increasing public demand for more non-petroleum-based products, thereby putting more focus on biobased materials. The second reason is the scarcity of UV-curable materials acceptable for direct food contact.

A mixture of proteins, available as GRAS (generally regarded as safe) foodstuffs, has been identified for a variety of uses in UV-curable coatings. For example, the protein mixture may be used with a water carrier as a self-photoinitiating film former. Other GRAS additives may be used to resist oil or grease. The mixture may also be used as a pigment extender, which also aids in cure, or as a photoinitiator or co-initiator with more conventional UV-curable components.

For UV-cured systems, in addition to free radical and cationic curing there is a third type of curing using thiol chemistry. With the addition of UV light and optionally another photoinitiator, hydrogens are removed from S-H functionalities. At this point, a sulfur-containing charged species is formed. This species may attack a double bond, a process known as thiol-ene coupling. It may also bond with another sulfur and form an S-S bond. When acting purely as a photoinitiator, we can expect a sulfur-containing charged species to act upon a double bond. When dealing with the formation of a self-photoinitiating film formed by proteins, S-S bonds will form. The S-H functionalities in proteins are found on the amino acid cysteine.

Proteins containing the amino acid cysteine contain S-H functionalities. Albumin is one such protein. While most are familiarly found in animal products, albumin and other proteins may be extracted from vegetable products such as oats. The S-H bonds from cysteine may be oxidized to form S-S bonds. Natural proteins are usually tightly curled and this type of structure may shield S-H bonds from reactions. A curled structure may be relaxed mechanically, thermally or by treatment with a GRAS mild acid such as 2,3 dihydroxysuccinic acid, ethanoic acid, 3-hydroxypentanedioic acid, salts of these acids or mixtures thereof. Albumin, transferrin, ovomucin, lysozyme, or combinations of these proteins in powdered form may be mixed with a mild acid and dissolved in water.

For a flavored coating, an oil such as peppermint oil may be adsorbed on a GRAS starch product and added to the mixture. A GRAS starch product may be used as a sole additive to increase barrier qualities to such substances as grease. Natural gums may also be used as additives, as well as GRAS dyes, emulsifying agents, vegetable fillers and defoamers.

Various powdered and dehydrated foods may be used as fillers for coatings using the protein-forming film. Cruciform vegetables are of particular interest due to both availability and cellulose content. Fillers seem to contribute to abrasion resistance.

Edible dyes can be used to produce colored coatings that might function as inks. The dyes can be dispersed in propylene glycol using lecithin as an emulsifier.

Water-resistant coatings have been developed using the protein mix, a mild acid and natural gums. Natural gums such as guar and xanthan gum are often used as thickeners because many gums have OH functionalities that enable them to form hydro-colloids. Water is held at the surface, allowing such foodstuffs as sauces and gravies to thicken. Another important usage of gums, particularly xanthan gum, has been in the addition to baked goods that do not contain gluten. Yeast-raised baked goods without gluten are very difficult to make without these additions because they are missing the long elastic strings of protein that trap the carbon dioxide produced by fermentation. Gums aid in the development of a suitable gas barrier so that the bread may rise. When used in protein film-forming coatings the gums may act in at least two ways. One is to loosely bond to water to spread

it out at the surface of the coating instead of passing through it. The other is to provide actual barrier qualities.

Edible dots are a very interesting application. Any edible oil such as peppermint may be used. The oil is adsorbed on a GRAS starch product forming a powder. The powder is then mixed with the protein mixture and a mild acid. Water is used as a carrier. The amount of water may be very low, yielding a paste. The dots may be applied to the interior of packaging to add extra flavor, aroma or other properties. Many herbs have been shown to have inhibitory effects on microorganisms. These include everything from allspice and cinnamon to rosemary and sage. Oils from such herbs may likewise be adsorbed and incorporated into coatings. The efficacy of such coatings for the inhibition of microbial growth remains to be tested.

The use of pigments in UV-curable coatings presents a unique challenge. Pigments can absorb the very UV light that is meant to cure the coating. The UV industry gets around this problem with the use of two approaches, which may be employed separately or in combination. The first approach is the use of doped lamps. Elements such as iron or gallium are added to mercury vapor UV lamps. The addition shifts the spectral output in such a way that frequencies are produced that are not absorbed by the pigments. Generally, iron-doped lamps are used for dark pigments such as carbon black, and gallium-doped lamps are used for light colored pigments such as titanium dioxide.

The second approach involves the use of photoinitiators that are activated by frequencies not absorbed by the pigments. For example, 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO) may be used to cure white pigments. Isopropylthioxanthone (ITX) is used for dark pigments. A combination of approaches would combine TPO with a gallium-doped lamp or ITX with an iron-doped lamp.

Unfortunately a number of facilities, especially in the printing industry, do not use doped lamps. In addition, photoinitiators designed to cure pigmented coatings are often more expensive. In the case of ITX, there have also been fears raised of migration into food products, even without direct food contact.

The use of protein mixtures as pigment extenders presents a different approach. Cure is actually promoted by the mechanism of thiol curing instead of being impeded. With the addition of the protein mixture, it is possible to use less pigment and less expensive photoinitiators. Doped lamps may not be required.

Some UV-curable acrylates have been approved under FCN 772. They are tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), trimethylolpropane ethoxylate (TMPEOTA) and epoxy diacrylate. In addition, one photoinitiator, Esacure One, has also been approved. These components may be combined with any reactants previously approved for food contact. The use of a GRAS photoinitiator will increase the number of possible formulations and decrease the number of extractable measurements necessary. Both TMPTA and TMPEOTA could be cured, although slowly, with the protein mix.

The amino acid cysteine, even when not acting as a component of the proteins, may be used as a curing agent. Cysteine is dispersed rather than dissolved in these monomers, producing a milky appearance. Curing is much more readily accomplished with a very thin coating. The coatings have a smooth, almost slick feeling. This is in direct contrast to the free radical curing normally used with acrylates in which curing of very thin films is inhibited by the presence of oxygen. Curing with cysteine alone is done somewhat differently than with cysteine incorporated in a protein. The unprotected cysteine is very sensitive to oxidizing agents, including acids. Therefore, acids are not added as a matter of course. Furthermore, the amount of acidic material in a formula must be minimized to prevent gelling.

The use of GRAS materials can provide an interesting addition to the toolbox of formulators of UV-curable coatings. Many aspects of the use of these materials remain to be explored. Among them is further exploration of the diffusion of air, aromas and odors through self-initiating protein films. The addition of anti-microbial herbal oils to films is also an area to be investigated.



Corrosion Inhibitor

MCI® corrosion inhibitors are based on amine carboxylate chemistry that is USDA-certified to be biobased. It is a sustainable technology derived from renewable natural resources. These inhibitors have demonstrated effectiveness in lab testing as well as field monitoring. MCI admixtures are dosed at low levels to provide corrosion protection with negligible effect on concrete properties. Having an affinity to steel, MCI molecules migrate towards steel reinforcement forming a monomolecular layer that passivates the surface. When MCI comes in contact with steel it forms a protective layer. This layer has been measured [using X-ray Photoelectron Spectroscopy (XPS)] to be between 20 and 100Å thick at the molecular level. A key advantage of the technology is its effectiveness even in cracked concrete.

Matting Agent

Over the last several years, the development of solvent-free formulations has progressed significantly but the omission of solvents results in new challenges. Conventional coatings are relatively easy to matte because the film shrinks upon hardening due to emissions, but solvent-free systems, such as 100% UV-curable systems, are notoriously difficult to matte.

Silica matting agents are very common and efficient in most coating systems. The amount of silica needed in solvent-free systems, especially for deep matte coatings, is significantly higher than in other coatings. Standard silica matting agents often cause a strong increase in viscosity and add additional thixotropy. Thus higher amounts of reactive diluents are needed or specially designed wetting and dispersing agents have to be used in order to reduce the viscosity, to give a Newtonian flow behavior and to provide anti-settlement properties. There are also many organic modified-silica matting agents available that do not influence the viscosity significantly, but these are less efficient in gloss reduction and often exhibit foam stabilization and less transparency.

In general, wax additives do not influence viscosity as much as silica, but they are not efficient enough to achieve low-gloss surfaces. With some amide waxes, negative side effects like foam stabilization and haziness are observed as well. The benefit of using wax additives like modified HDPE are improved film properties, such as mechanical resistance. Often, wax additives are used in combination with silica because of improved film properties like scratch and abrasion resistance. Polymer matting agents are likely to be used because of easy incorporation and little influence on viscosity, however they often don't achieve the desired performance.

Biotechnology opened the door to an entirely new matting additive with an unprecedented combination of properties compared to conventional matting agents, such as waxes and silicas. The new additive is based on a biopolymer, which is obtained by bacterial fermentation from sugars. The biopolymer-based product originates from renewable resources, is fully biodegradable and GMO (genetically modified organism) free.

The matting performance of the new biobased product was tested in three different solvent-free UV systems: a polyester acrylate, a polyurethane acrylate and an epoxy acrylate containing a photoinitiator and DPGDA as reactive diluent. Untreated and treated silica were tested for comparison.

The matting efficiency of the novel micronized biopolymer, commercially launched as CERAFLOUR® 1000, showed excellent matting with no detrimental influence on viscosity. Compared to treated silica, the matting efficiency of the biopolymer was higher or equal in common UV systems. In polyester acrylate and urethane acrylate systems the gloss could be reduced to 10-20% at an angle of 60° with 7.5% of added biopolymer-based additive. This is comparable to non-treated silica and better than treated silica.

The haptic properties of an object describe the sense of feeling and are a popular field in research. It is becoming increasingly important from a product's competitive point of view. The haptic properties can be adjusted by the properties of the coating. Good haptic is a smooth

surface with a soft touch effect. The biobased additive has been consistently judged as the smoothest and most pleasant. It is noteworthy that improved haptic properties don't generate an increase in slip.

In general, applied films containing the biopolymer-based additive show good leveling. In addition, the additive may improve the scratch and abrasion resistance of a coating. Regarding the enhancement of the mechanical film properties, the biopolymer-based additive performs better than silica and polymer matting agents, but is inferior compared to a modified HDPE wax. Combination with modified HDPE wax is recommended to achieve additional improvement of mechanical resistance. With the biopolymer-based additive, burnishing or polishing effects and finger marks are not observed.

This biopolymer-based additive is 100% based on renewable resources and is completely biodegradable under normal conditions, such as landfills, with zero toxic waste, as it is ultimately converted into carbon dioxide and water. The key benefits are excellent matting efficiency, especially in UV systems, combined with high transparency and a warm smooth haptic feel without influence on slip. The additive improves scratch, abrasion and blocking resistance. It can be used in solvent free, solvent- and waterborne systems without detrimental influence on viscosity. Easy incorporation without dust formation and foam stabilization is combined with good storage stability of the coating systems.

CERAFLOUR 1000 biodegradable polymer can be used for aqueous, rad-cure, solvent-free and solventborne systems providing wax-like properties to improve matting efficiency and haptic (soft-touch).

Solvent

Provichem® 2511 Eco is a dimethylsuccinate (DMS) that can be used as a solvent and a raw material for fine chemicals such as pigments and UV stabilizers. Biosuccinium™ is made from renewable resources and has a much better carbon footprint than several other fossil based chemicals - such as adipic acid or the petrochemical version of succinic acid. As a result, Provichem 2511 Eco enables customers to improve the sustainability characteristics of their products.

Biosuccinium-based DMS, finds use in various applications such as pigments, UV stabilizers, solvents, flavors and fragrances. The unique features of DMS-based pigments make them suitable candidates for usage in a large number of products such as inks, coatings, plastics and textiles. Solvents made with DMS have good paint removal properties and they offer a potential sustainable alternative to dibasic ester (DBE) solvents or other fossil-based solvents.

Rheology Modifier

For the adhesives and sealants industry, the use of amides as rheological additives as grown significantly. A new generation of amide (Crayvallac SLT) is a biobased solid material - it is VOC-free and more than 90% of the ingredients are bio-sourced and renewable. What is new about this rheological additive is that it allows manufacturers to use a cold manufacturing process, thereby saving energy costs and time.

BIOCIDES/FUNGICIDES/ANTIMICROBIALS

See *Enzyme*

Because coatings are largely organic in nature, they provide a source of food for microorganisms. Microorganisms are found everywhere and they work around the clock trying to cause viscosity loss, putrefaction, gas formation, emulsion breakdown, and other undesirable physical and chemical changes. These attacking species can cause discoloration, marling, loss of adhesion and finally coating failure.

Microorganisms can contaminate paint in different ways during the manufacturing process. Unsanitary conditions may exist, such as for the raw materials (including thickeners, extenders, pigments, emulsions, surfactants and defoamers), water (process water and recycled water), containers and equipment (tanks, pipes, hoses, etc.).

The ability of some microorganisms to attach to surfaces and form adherent biofilms is also important. Biofilms are functional consortia of microbial cells entrapped within an extensive matrix of extracellular

polymer (glycocalyx) produced by them. Biofilms can be formed in water systems, processing tanks and other areas. Biofilms may be sources of contamination of the product, and may cause corrosion, scaling, the reduction of heat transfer efficiency and other problems in addition to the spoilage. Microbial biofilms are usually resistant to biocide treatments or disinfectants. Depending on the growth conditions (nutrients, minerals, gas composition, temperature, pH, water activity, etc.), microorganisms can reproduce very rapidly in the paint.

Coatings need to be protected from microbe attack, and there are a number of microorganisms that the formulator needs to be conscious of when formulating paints. Sometimes the terminology of available agents is confusing: biocide, mildewcide, fungicide, algicide (also spelled algicide) and so forth. Product literature and the suppliers will certainly assist in this regard. Many of these additives are multi-purpose and can curtail the growth of a number of organisms. In terms of coatings use, there are biocides for in-can preservation and those used to protect the dry film.

Biocides (or microbiocides) are substances that will kill organisms and thus are used to protect coatings from biological attack caused by algae, fungi and other organisms that propagate in moist environments – particularly in warm climates. The “-cide” nomenclature refers to compounds that kill, in this case, microorganisms. A biostat prevents or interferes with the growth of the organism but does not kill it.

The additives are often further defined as follows to describe the particular types or organisms that are killed or affected.

Algicide/Algicide – Chemical agent used to destroy algae.

Bactericide – Compound used at low levels to kill bacteria.

Bacteriostat – Substance that prevents or slows the growth of bacteria.

Biocide/Microbicide – A chemical agent capable of killing organisms responsible for microbiological degradation.

Efficacy – The effect of the microbiocide on the target organism or group of organisms; can be measured as percent killed versus a control containing no biocide. Efficacy can be expressed as MIC, or minimum inhibitory concentration, against a specific organism.

Fungicide – Chemical agent that destroys, retards or prevents the growth of fungi and spores.

Fungistat – Compound that inhibits the growth of a fungus, or prevents the germination of its spores.

Mildewcide – Chemical agent that destroys, retards or prevents the growth of mildew.

Spectrum – Refers to the effect a microbiocide may have on more than one organism such that a broad-spectrum biocide will be effective against more than one group of target organisms.

For coatings we are concerned with bacteria (aerobic and anaerobic), fungi (multicellular [molds], unicellular [yeasts]) and algae (green and blue-green). The addition of an in-can preservative will protect coatings in the wet state during storage and transport. But after a coating has been applied and dried, it becomes susceptible to colonization by fungi and/or algae.

Biocidal agents are available to work both “in-the-can or batch” and also in the dried film. For this reason, many manufacturers include a biocide (anti-microbial) agent in the formulation of the paint so that it can kill both bacteria and yeasts that can be present. If not corrected before they start, microorganisms can lead to the production of gases – this can occur in the container and result in can lids popping and cans distending, offensive odors emanating and loss of film and application properties. Bacterial enzymes and certain fungi attack organic thickeners, and this can lead to viscosity changes in the liquid coating. The pH of the paint can be affected and the paint can undergo discoloration.

Microbial contaminants can be introduced with water (process water, wash water), with raw materials (latex, fillers, pigments, etc.) and by poor plant hygiene. Bacteria are the most common spoilage organisms, but fungi and yeasts are sometimes responsible for product deterioration. Spoilage of waterborne products, which may go unnoticed until the product reaches the consumer, can result in significant economic loss. Good plant hygiene and manufacturing

practices, when combined with the use of an optimized biocide, will minimize the risk of microbial spoilage.

Enzymes are organic catalysts, which means that they are not consumed in any reactions. They are produced by living cells and are protein in chemical nature. Bacteria and their enzymes can degrade the organic components of paint – the polymer and its organic additives. One enzyme molecule can change hundreds of organic molecular structures and degrade them. The most obvious immediate result is a loss of viscosity. This renders the product unstable and unusable. This is more of a problem for architectural coatings, which tend to be warehoused, shipped and then stored on shelves for longer periods than typical industrial coatings, which are usually consumed rapidly.

Manufacturers and formulators need to be conscious of the fact that the dried paint film is subject to microbe attack from mold, mildew and algae – particularly in certain climates where temperature and humidity encourage microbe growth. For dried coating films, algae and fungi can cause discoloration, dirt entrapment, cracking, blistering and loss of adhesion. A loss of adhesion is commonly associated with fungi growth as well as corrosion on certain substrates due to the moisture produced by fungi. Dependent on the climate, many exterior surfaces and roofs may be subject to algae growth, and not all fungicides are necessarily effective against algae. Certain areas of the world have already recognized this as a serious problem and one of concern for the preservation of exterior buildings.

The type of microorganism that can attack the coating depends on many factors including the presence of nutrients, the moisture content and the composition of both the substrate and the coating itself. Moisture is affected by the amount of rainfall, dew, humidity, temperature and time of year. Local environment conditions such as surfaces that are sheltered from wind and shaded areas also have an impact on microbial growth. Nutrient sources include constituents of the coating, partially biodegradable material from other microorganisms or simply dirt. The substrate may affect the pH of the surface and make it suitable for microbe growth. Fungi favor acidic conditions such as those provide by wood and some species of wood are more susceptible to fungi attack than others. Algae favor alkaline conditions such as those provided by masonry.

For use in architectural coatings, it is important that the fungicidal material have a low solubility in water so that it is not readily leached out of the paint film. It should also not cause any weathering effect such as fading, chalking or discoloration. Some antimicrobial agents can cause fading in architectural coatings; therefore, it is always wise to expose the formulation to weathering testing.

There are thousands of kinds of fungi and algae throughout the world. However, only a relatively few disfigure and deteriorate exterior paint films. In general, research on painted panels and structures from around the world indicates that two types of fungi are the dominant causative agents of disfigurement and degradation of modern exterior paint films. These fungi were identified as *Alternaria sp.* and *Aureobasidium (Pullularia) pullulans*. *Aureobasidium pullulans* is the fungus predominantly responsible for the development of mildew in exterior paints. The *Pseudomonas species* attacks paints, joint compounds, roof coatings, exterior insulation and finishing systems and clear finishes in the can.

There are many effective biocides available for use. It is important to understand the operation of these agents and the differences in their activity. Some may be effective against certain bacteria in one concentration and effective against fungi in another concentration. Some biocides may be biocidal in certain concentrations and in other concentrations exhibit biostatic behavior. It is very important for the formulator to work with the supplier of these agents to understand their use and mode of action. Blends of biocides may often be used to enhance coating performance, as one biocide alone cannot always provide the desired results under demanding and varying climate conditions.

Some of the typical chemistries of these agents include: formaldehyde donors; ortho-phenylphenol (OPPs); isothiazolinone derivatives (such as 2-n-octyl-4-isothiazolin-3-one [OIT]); guanides and biguanides



(such as PHMB or polyhexamethylene biguanide); carbamates (such as 3-iodo-2-propynylbutyl carbamate [IPBC]) and dithiocarbamates; copper or sodium or zinc pyrithione; benzimidazoles; n-haloalkylthio compounds; 1-(3-chloroallyl)-3,5,7-tri-aza-1-azonia-adamantane chloride; tetrachloroisophthalonitriles; cis[1-(3-chloroallyl)-3,5,7-tri-aza-1-azonia-adamantane] chloride and 2,2-dibromo-3-nitropropionamide (DBNPA); and quaternary ammonium compounds. These are but a few examples of the many agents available to the formulator.

Some biocides on the market today are two-for-one and eliminate the need for separate in-can preservatives and mildewcides. DCOIT (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one) is an example of one such biocide, which controls bacteria that cause coatings to degrade in the can and prevent mildew growth after the films dry. This particular biocide controls a wide range of microorganisms including fungi, algae and bacteria.

DCOIT-based BIOBAN 200 is an aqueous dispersion that is easily incorporated into formulations, has low leaching characteristics and is U.S. EPA registered for use in coatings. It is formaldehyde-release free, does not contain heavy metal-based active ingredients and does not require ZnO for mildewcidal stability.

The microbiological activity of 2,2-dibromo-3-nitropropionamide (DBNPA) was documented as a seed fungicide in 1947 and later as an antimicrobial agent. DBNPA, when formulated as a 20% solution in water and polyethylene glycol, is completely miscible with water and readily disperses upon introduction into a water-based system. The DBNPA molecule begins functioning as an antimicrobial agent immediately upon introduction into a system; the rate of this activity is not affected by pH, and antimicrobial control is usually achieved before complete degradation occurs. The combination of instantaneous antimicrobial activity and rapid chemical breakdown makes this a cost-effective and environmentally friendly biocide.

It is used as a quick-kill biocide and short-term preservative in water-containing systems that require microbe control; it is ideal for the treatment of wastewater generated during the manufacture of paint. The collection and reuse of all wash water used to rinse paint mixing vats has been emphasized as crucial to achieving environmentally responsible production. This wash water contains a high concentration of paint solids and is usually heavily contaminated with microorganisms; it must be decontaminated prior to its re-introduction into the paint production process. DBNPA is ideal for this type of application.

Mildewcide (fungicide) and algaecide testing has been very confusing for paint companies. A paint formulation's resistance to attack by fungi and algae is the most difficult performance characteristic to determine; testing requires a specialized laboratory with trained personnel to work accurately with fungi and algae.

The use of a single active ingredient may be sufficient to protect a coating against in-can spoilage or dry film defacement, but in many cases it may be advantageous to use a blend of the actives. For example, the combination of certain active ingredients can result in synergy whereby lesser amounts of each active are needed to bring about the same inhibitory effect as the use of either active alone. Thus blends of actives may allow manufacturers to protect a product at reduced levels, providing not only a potential cost benefit but also a product that is more environmentally friendly.

Even more important is for formulators to recognize the fact that **even a minor change in a formulation may have a major effect on the biocide in that formulation**. It is crucial with every change in formulation that the coating be tested for biocide efficacy. Some of the common factors that will decrease biocide efficiency are: pH, temperature of addition to the batch, nonionic surfactants, solubility, the presence of other formulation additives that deactivate the biocide, UV radiation and so forth. The only way to determine the efficacy of a biocide in a coating is through testing.

In testing various biocides in coatings there can be significant differences in performance of paint systems by exposure location. Since there can be such a wide variation in product performance by location, it is

very dangerous to rely on data from one exposure site to assess how a national paint product might perform. **To truly assess the potential commercial performance of paint systems, they should be tested at a variety of locations across the country.** Laboratory tests alone are not sufficient to assess how well a particular film preservative will perform in the field.

For evaluating mildew resistance of interior coatings there is some uncertainty about which test method to follow for a realistic assessment of the coating. Testing coatings in interior environments presents different challenges than for exterior coatings. There are several test methods and each claim to be the best for predicting in-service performance. The most popular are Mil Spec 810F, ASTM D5590, ASTM D3273, ASTM C1338 and ASTM G21 as well as a test method from the Forest Products Laboratory.

Caution is urged in testing because evaluating coatings on non-porous substrates, like vinyl charts that resist wetting by moisture, makes it more difficult for fungi to proliferate on the coating surface. Therefore using these charts may overestimate the coating performance.

Most interior paints are used on typical gypsum wall board with paper facing both sides. They absorb more moisture and retain it under humid conditions and thus are frequently susceptible to mold growth. So to evaluate interior paints, ASTM D5590 with paper as a substrate or a variation of ASTM D3273 with fungal inoculum deposited directly on the surface of a paper-based wall board may provide more realistic results.

Antimicrobial Polymer Emulsions

The traditional biocidal agents often are lost over time due to leaching or degradation of the film. Driven by the European Biocides Directive, many of these traditional biocides have come under greater scrutiny regarding their potential affect on the environment. There is also concern regarding the ability of microorganisms to easily adapt to the additives used and build resistance over time. The result is a growing need for alternative solutions that provide sustainable antimicrobial protection while minimizing many of the potential issues related to the use of conventional additives.

There is antimicrobial technology that offers unique ways to mitigate the effects of microbes on products. Unlike conventional active ingredients, the technology relies on antimicrobial polymers that either have inherent antimicrobial characteristics, or incorporate a conventional antimicrobial additive encapsulated or embedded into a polymer.

Since the active ingredient, or part of the molecule that is primarily responsible for the antimicrobial action, is attached to a polymer or uniformly embedded into the polymer at a nanoscopic level, these materials provide a more sustained and effective antimicrobial action over time.

In addition to the antimicrobial action, these same materials can provide polymer-related attributes such as binding, adhesion, barrier and bonding properties that conventional antimicrobial additives cannot. This multifunctional aspect may be of value where an ingredient is required to perform more than one function and thereby help in delivering a simpler and cost-effective solution. The intention for these new materials is thus not a direct replacement of the active ingredients used today but to provide additional benefits that cannot be provided in terms of durability, uniformity, consistency and greater functionality.

Data shows that this polymeric route to antimicrobial functionality may be well suited for applications in textiles, nonwovens, medical products, hygiene and personal care products, building materials and a variety of formulated products including coatings and adhesives. The requirements of the specific application determine which of the two approaches provides the best combination of antimicrobial and polymer properties.

Inherent Antimicrobial Polymer Approach

The inherent approach to antimicrobial functionality relies on the fact that the active site is part of the polymer and is tightly bound to the polymer backbone. The polymers are waterborne, easy to handle and envi-

ronmentally favorable. Also, unlike conventional antimicrobial additives, these polymers are high-molecular-weight materials and, therefore, less likely to be of concern regarding potential toxicology. These polymers can be designed to provide additional attributes such as static control, permeability, barrier and strengthening properties, and can be tailored to suit a given application need.

These materials would also be of interest in areas where a conventional AI (active ingredient) may not be desirable. Such applications could include hygiene products, medical devices and products or personal care products where the additional multifunctional aspects of this polymeric approach may be of greater value.

Unlike conventional antimicrobial additives that function by disrupting a biochemical pathway, these polymers function by breaching the integrity of the cell wall of the microbe. It is therefore believed that they are less likely to contribute to development of resistance in the targeted microbes. A variety of active sites and polymer backbones can be designed to suit a given application. Since they are waterborne they can easily be deposited on surfaces by well-known processes such as coating, spraying, saturation or wet end deposition.

Active Ingredient Carrier Polymer Approach

The active ingredient (AI) approach involves the incorporation of active ingredients into a polymer whether it is inherently antimicrobial, as in the case above, or if the polymer is inert. The AI is typically incorporated during the polymerization process in such a way that it is uniformly distributed into the polymer at a nanoscopic level.

This embedding of the AI into the polymer matrix provides complete additive coverage of the surface in a more uniform and consistent manner thus increasing the longevity of the antimicrobial effect. In this way it is possible to get increased efficacy and sustainability from an AI while providing the benefits of a polymer in terms of ease of handling and durability.

It is also possible to use this approach to deliver a concentrated dose of the AI into a given formulation or application, coatings for example, where the AI is finely distributed into a polymeric carrier used only to deliver the AI. This is possible only because the method of incorporation allows high levels of the AI to be suspended into a polymer at a nanoscopic level without affecting the clarity of the polymer film.

This approach also makes it possible to enhance the inherently antimicrobial polymer with AI by creating a “tunable” antimicrobial polymer where the activity can be selectively controlled using either the additive or the polymer as the situation demands.

Polymers containing the AI are waterborne and will have the performance properties associated with waterborne technology. Waterborne polymers are useful in applications where an additive is desirable, and would allow formulators to design sustainable solutions without many of the handling and durability issues related to the conventional additive approach. The choice of polymers and AI that can be used to provide a solution is varied and can be tailored to meet specific needs.

The antimicrobial technologies that include inherently antimicrobial polymers as well as polymers that have encapsulated active ingredients provide a comprehensive approach to providing antimicrobial benefits across a wide variety of applications where sustainable antimicrobial functionality is needed, combined with the stated benefits of a polymeric offering. These technologies present real value to customers interested in providing the multifunctional benefits derived from a polymer that has inherent or embedded antimicrobial characteristics.

Polymeric Design Approach

An “antimicrobial paint” developed at MIT can kill influenza viruses that land on surfaces coated with it, potentially offering a new weapon in the battle against a disease that kills nearly 40,000 Americans per year. If applied to doorknobs or other surfaces where germs tend to accumulate, the new substance could help fight the spread of the flu. The coating’s polymers poke holes in the membranes that surround influenza viruses.

The new substance can kill influenza viruses before they infect new hosts. The “antimicrobial paint,” which can be sprayed or brushed onto surfaces, consists of spiky polymers that poke holes in the membranes that surround influenza viruses. Influenza viruses exposed to the polymer coating were essentially wiped out. The researchers observed a more than 10,000-fold drop in the number of viruses on surfaces coated with the substance.

The polymers are also effective against many types of bacteria, including human pathogens *Escherichia coli* and *Staphylococcus aureus*, deadly strains of which are often resistant to antibiotics. For example, *S. aureus* causes serious problems in hospitals, where it can spread among patients and health care workers.

The coating acts in a very different way from the many antibacterial products – such as soaps, sponges, cutting boards, pillows, mattresses and even toys – that are now on the market. Those products kill bacteria but not viruses and depend on a timed release of antibiotics, heavy metal ions or other biocides. Once all of the biocide has been released, the antimicrobial activity disappears.

With this type of polymeric architecture it is highly unlikely that bacteria will develop resistance because it would be difficult for bacteria to evolve a way to stop the polymer spikes from tearing holes in their membranes. Repeated testing thus far suggests that the microbes are not becoming resistant and the polymer coating is 99% effective.

The MIT researchers are working with industrial and military partners such as Boeing and the Natick Army Research Center to develop the coatings for practical use. Once the polymer coating is applied to a surface, it should last about as long as a regular coat of paint.

AM Technology – Mechanical Anti-Microbial Protection

A growing problem in the world is that, for reasons of health and the environment, more biocides are being prohibited, and at the same time, bacteria are becoming more resistant. AM coating technology operates completely differently: it is not chemical protection against microbes but rather nanotechnological/mechanical. By using a double polymerization process, an anti-microbial binding agent is fabricated. AM Coatings technology is part of the high-quality polymer: the acrylic resin. AM Coatings technology grafted on the polymer is made with common and widely available raw materials, all are REACH-compliant. It is non-leaching, there is no negative environmental impact and no loss of effectiveness. Its effectiveness is evenly distributed in time and long lasting against bacteria, fungi, algae and other microorganisms.

The binding agent has a very special property, creating a “nanotechnological barbwire” surface, during the curing process. When a microbe (or any micro-organism) comes in contact with this surface, its cell wall is punctured like a balloon, and the microbe dies. Apart from being completely safe for man and environment, this mechanical action has another big advantage: microbes will not become resistant to this kind of control; a phenomenon that appears to be a growing problem, for instance with the notorious MRSA infection in hospitals. Because it works mechanically, it is therefore impossible to build up resistance against the AM technology. AM technology is patented and has been proven, based on American ASTM E2149 and Japanese JIS Z 2801 standard test methods.

This technology is not harmful to humans or animals; it can be applied everywhere and without special precautions. No special labeling or costly and time-consuming registration and admission procedures are required. Waterborne paints based on this technology possess enhanced low-odor and non-bleeding properties, and are just as green and sustainable as common, unmodified paints not containing additional antimicrobial components.

Silver Ions

Silver-based antimicrobials are compounds that contain silver whose beneficial properties make it useful as an antimicrobial agent. Such silver-containing compounds are stable in the presence of light and ultraviolet radiation, are thermally stable, offer broad spectral activity



against target organisms, and usually have a low order of toxicity, which can be determined from manufacturers' literature.

The effectiveness of silver products is based on the slow and continuous leaching of superfine silver ions that interact with the metabolism of microorganisms. Silver ions can inhibit enzyme activity, especially those containing sulfur. In doing so, they have a major influence on the energy metabolism of these microorganisms. Products containing silver demonstrate a broad level of antimicrobial effectiveness, however, significantly less activity is observed for attack of fungus when compared to bacteria. Examples of these antimicrobials are products where silver is embedded into base materials, such as special zeolites or glass. Furthermore, combinations of Ag and Zn used in zeolites may lead to synergistic effects.

AgION™

A silver-bearing zeolite antimicrobial compound, known as AgION, has been incorporated into polymer-based coatings to control the growth of harmful bacteria, mold and mildew. These coatings may be applied to stainless or carbon steel products for use in appliance, food processing and HVAC applications. The active ingredients in the coating are the silver ions that are held within an aluminosilicate zeolite carrier particle. The silver ions exchange with other ions (counter ions) that may be present in nutrients or moisture and in this manner are transported to areas that support microbial growth. The antimicrobial properties of the silver ion have been recognized for a long time.

Silver Plus Benzisothiazoline

The combination of silver or silver with benzisothiazoline gives a new and very effective preservative system. By using this combination, the amount of sensitizing benzisothiazoline can be significantly reduced and, if an excess of benzisothiazoline is used, the well-known photosensitivity of silver compounds is reduced. This combination is a highly effective and safe new preservative system for coatings.

SmartSilver™

Coatings enhanced with SmartSilver antimicrobial silver nanotechnology are effectively protected against a wide range of molds, fungi and bacteria, making it a highly efficient industrial antimicrobial. It can be incorporated into aqueous and polar organic solventborne coatings, powder coatings and injection-molded plastics. SmartSilver additives do not impact the mechanical or flame-resistant properties of coatings, and are stable against UV light and high temperatures. The dispersible powders are highly concentrated, silver-containing antimicrobial additives made with proprietary stabilizers, and deliverable as powders or pre-dissolved dispersions. Typical use levels range from 0.1-1.0% based on application and process conditions. The dispersed additives release silver ions when in contact with moisture, inhibiting the growth of microbes.

Ca(OH)₂

Ca(OH)₂-based surface coatings, now available in a variety of pigmented colors, act to prevent infections – in particular influenza, sinus infections, pneumonia, allergic rhinitis, asthma and some indications are it is beneficial for anthrax as well. These one-application, antimicrobial-antibiotic surface coatings are effective against all classes of microbes including bacteria, viruses, fungus and algae. The coating combines calcium hydroxide as its active biocide with a special Bi-Neutralizing Agent (BNA), a biopharmaceutical whose mode of action keeps the coating continuously working year after year.

Calcium hydroxide inhibits the growth of common microorganisms on the coating's surface through its high alkalinity (at levels normally incompatible with the life of microorganisms). Normally, hydrated lime is highly susceptible to atmospheric attack – carbon dioxide in the air quickly converts calcium hydroxide to calcium carbonate, reducing its alkalinity and rendering it ineffective. With BNA, calcium hydroxide is safely stabilized by this patented technology

into a semi-permeable calcium hydroxide-encapsulated matrix system. This specially engineered matrix system protects hydrated lime from atmospheric degradation, preserving its antimicrobial-biocidal potency long after the coating is applied.

What is unique is its benign nature to humans and its lethal nature to microbes. The active ingredient is coming from a naturally occurring mineral and has been used for centuries as a safe and effective way to kill pathogens.

The end-use product is waterborne, fast drying, virtually odorless and remarkably contains no VOCs. It offers a widespread solution to the problems caused by the presence of the common microorganisms. Using an antimicrobial agent registered by the U.S. EPA, this multi-patented technology works by creating a surface coating that resists the growth of microbes on its surface for over six years.

Controlled-Release IPBC

The growth of microorganisms on dry film not only affects the appearance of the coating (discoloration), but may also compromise performance (biodegradation). Fungi can penetrate coatings, resulting in cracking, blistering and loss of adhesion, leading to decay or corrosion of the underlying substrate. Algae colonies, which seem to grow more rapidly on porous substrates such as stucco, cement and brick, have the ability to occlude water. The freezing and thawing of this entrapped water may induce cracking or increase the permeation properties of the coating, leading to failure. Water may also encourage colonization by other microorganisms that, in turn, may cause biodeterioration.

In order to be most effective, the biocide needs to be present at the coating interface, but this makes it susceptible to water leaching. Controlling the release of the biocide through encapsulation ensures that a minimum concentration of biocide is always maintained at the surface interface, thereby extending the life of the coating. Additionally, controlled release reduces the amount of biocide that is released to the environment over a period of time.

Controlled release of IPBC through encapsulation renders the biocide more resistant to leaching. Encapsulated IPBC [IPBC CR (40% IPBC dispersion also known as Fungitrol® 940CR)] is released more slowly than non-encapsulated. The inorganic carrier provides the molecule additional protection against environmental degradation from UV/heat exposure. Outdoor exposure tests of paints containing encapsulated IPBC show enhanced dry-film protection.

The amount of IPBC released depends on the intrinsic properties and composition of the paint. The controlled release mechanisms maintain a minimum biocide concentration in the coating interface over an extended period of time, preventing fungal growth. This results in a longer coating shelf life given the same initial biocide concentration. Alternatively, lower biocide levels could be used to obtain a similar shelf life.

Photocatalytic Technology

Ultrafine TiO₂ technology has been developed and marketed as Cristal-ACTIV™. It is a non-pigmenting and odorless photocatalyst that can be added to coatings, and has been shown to be effective against MRSA and *Staph. aureus* as well as some fungi and molds.

Zinc

Anhydrous zinc nitrate, or a hydrated form of zinc nitrate such as zinc hexahydrate, has been added to water-based paint in an amount to provide antimicrobial, particularly antifungal, properties. The paint composition retains its antimicrobial and/or antifungal properties when dried. The antimicrobial, and/or antifungal agent present in the paint composition is dissolved in the paint and dispersed so that when the paint is applied to a surface, the antimicrobial agent is dispersed throughout the paint layer. The additive is non-carcinogenic, low cost, non damaging to the environment, and does not have an adverse effect on pigmentation. The paint composition suppresses the proliferation of microbes such as bacteria and fungi, and compromises their physiological functions.

Efficacy Determination Methods

There are many standard methods for determining the efficacy of a biocide for either in-can or dry film use. One should search the literature and/or use the following ASTM methods: ASTM D2574-06, D3273-00, D3456-86.

BLOCK-RESISTANT ADDITIVE

See *Anti-Blocking Agent*

Chemical agent that prevents the undesirable sticking together or adhesion of painted surfaces under normal or specified conditions of pressure, temperature and humidity.

BODYING AGENT

See *Thickeners*

BRIGHTENERS (OPTICAL)

The brighteners are usually fluorescent dyes or pigments that absorb UV radiation and re-emit it as violet-blue light that gives yellowish-white coatings a brighter, whiter appearance. They are used to increase the luminance factor and to remove the yellow undertone of white or off-white materials. Small amounts of blue dyes are also used to achieve the same result.

The optical brighteners or fluorescent whitening agents (FWA) are colorless to weakly colored organic compounds. In solution or applied to a substrate they impart bluish-white effects, have good light fastness and excellent heat resistance and chemical stability.

BURNISH-RESISTANT ADDITIVE

See *Abrasion Resistance*

Agent that improves the resistance of a coating to increases in gloss or sheen due to rubbing or polishing.

Both feldspar and calcium carbonate minerals are used in paint formulations to improve abrasion, scrub and burnish resistance. Feldspar is the term given to a group of minerals distinguished by the presence of aluminum (Al) and the silica ion (SiO_4) in their chemistry. This group includes aluminum silicates of soda (sodium oxide), potassium (potassium oxide) or lime (calcium oxide). Feldspar is the single most abundant mineral group on earth. These materials vary widely in chemistry, depending on local formation conditions. Some feldspars are silica free – e.g., nepheline syenites. Calcium carbonate may be aragonite, calcite, vaterite, chalk, limestone, marble or travertine. In the United States, commercial material is mostly calcite and is either limestone (sedimentary) or marble (metamorphic).

Minerals with higher hardness are thought to bring improved abrasion and burnish resistance to most paint formulations, although they are more difficult to disperse and lead to faster wear on processing (dispenser blades) and application equipment (pumps and spray tips).

Mineral additives with a Refractive Index close to that of the resin (most latex resins are ~1.5) tend to give lower haze in clears, but they also have lower opacity and tint strength. Research seems to indicate that marble-based calcium carbonate can be used to replace feldspars to reduce cost while maintaining – and even improving, in some cases – physical performance.

Lightweight spherical additives called hollow glass microspheres can be used for coatings formulations. These hollow glass microspheres offer scrub and burnish properties, in addition to viscosity control, thermal insulation and sound-dampening characteristics, and improved performance properties. Spherical particles composed of styrene and acrylic polymers, as well as ceramic microspheres, are also used for improving mar resistance.

High-molecular-weight micronized polyethylene or micronized polypropylene are used in architectural formulations for increased burnish resistance. These waxes effectively replace silicas in both waterborne and solvent systems without settling.

Polishing or burnishing a satin or flat clear coating occurs when silica is used in the formula to flatten the finish look. The problem with silica

is that it orientates to the surface of the coating, and when the coating is rubbed, washed or marred, the top layer of silica is quickly worn away. With the use of nanoparticles, once again a synergetic effect is created between the silica and nano, giving a uniform distribution to the silica. This gives the coating scratch resistance.

CATALYSTS

See *Driers*

Catalysts are additives that will increase the rate of a chemical reaction but are not consumed or changed in the reaction process. Catalysts have widely varying compositions that depend on the nature of the reaction being catalyzed.

Many of the crosslinking reactions used to form durable films are accelerated by the use of catalysts. For example, melamine-crosslinked systems, polyurethanes and epoxies make use of catalysts. Some systems use acids as catalysts: phosphoric, carboxylic or sulfonic acids [such as p-toluene sulfonic acid (PTSA) and dodecyl benzene sulfonic acid (DDBSA)] can be used. Others make use of typical Lewis acid metal catalysts or Lewis tertiary amine base catalysts.

Acid catalysts (and blocked acid catalysts) are used to accelerate the reaction between the crosslinking resin and the primary resin. Good crosslinking is desirable so that the final cured film will show improved properties. By increasing the molecular weight of the crosslinked product, improvements are gained in chemical, humidity and detergent resistance, corrosion resistance, film flexibility and film hardness.

Typical acid catalysts used in coatings are: dinonylnaphthalene disulfonic acid (DNNSA), dinonylnaphthalene sulfonic acid (DNNSA), dodecylbenzene sulfonic acid (DDBSA), p-toluene sulfonic acid (PTSA), and alkyl acid phosphate (AAP). The relative catalyst strength is: PTSA > DNNSA > DDBSA > DNNSA > phosphates. In general, the sulfonic and blocked sulfonic acids are strong acids, whereas the carboxylic and phosphates are considered weak acids.

The formulator has to balance the properties of the catalyst with that of the crosslinking agent, the cure temperature and time, the pH of the system, and the desired final properties of the coating. This is not trivial and the raw-material suppliers have guidelines that can be followed.

Blocked sulfonic acid catalysts, derived from aromatic sulfonic acids, have been developed that promote the crosslinking of hydroxyl-functional polymers with amino-formaldehyde crosslinking agents such as hexamethoxymethyl melamine, especially in coil coatings. These catalysts are particularly effective in coil primer formulations containing calcium ion exchange anti-corrosive pigments. In addition, the unique deblocking profile of these catalysts provides the so-called snap cure at the desired peak metal temperature and within the specified time.

In coil primers, this class of blocked sulfonic acids provide outstanding cure, viscosity stability upon oven aging, and corrosion/salt spray resistance. In addition to resistance to basic pigment deactivation, these catalysts reduce solvent popping defects and provide excellent adhesion/intercoat adhesion while allowing extended storage of formulated coatings. Products from this class of catalysts also are effective in top-coats where their cure response allows release of volatiles before cure, thereby preventing popping, while providing storage stability.

Dibutyltin dilaurate (DBTDL) and dibutyltin diacetate (DBTDA) are well-established catalysts for the isocyanate-hydroxyl reaction in the formation of urethane coatings. DBTDL is efficient but, as with any catalyst, problems such as reactivity and hydrolysis of ester groups may occur. Diazabicyclo[2.2.2]octane (DABCO) is a commonly used tertiary amine catalyst. The tertiary amines are effective for use with aromatic isocyanates.

There are, however, some unique non-tin catalysts based on bismuth, aluminum and zirconium that are useful for these same reactions. The non-tin catalysts are environmentally more acceptable and offer advantages such as: faster cure rate, improved pot life, improved catalysis in cationic electrocoating and reduced hydrolysis of polyester resins. Catalyst deactivation can occur because of water, resins with high acid numbers, anions and pigments that are carrying water into the formulation.



Oxidation Catalysts

Oxidation reactions are of great interest at both the laboratory and industrial scale. There are numerous applications using the conversion of primary alcohols into aldehydes.

Two types of reactions could fit in with this scheme. First, there are stoichiometric reactions involving the use of strong oxidizing agents such as: the complex chromium (VI) oxide/pyridine (Collins or Sarret reagent); pyridinium chlorochromate (Corey reagent); oxalyl chloride/DMSO (Swern reagent); dimethylsulphide/N-chlorosuccinimide (Corey-Kim reagent); Dess-Martin periodinane; SO_3 /pyridine; $KMnO_4$; MnO_2 ; RuO_4 , etc. Secondly, there are catalytic dehydrogenation reactions with catalysts such as copper chromite, Raney nickel, palladium acetate, etc. All these reactions do not fit in perfectly with the responsible care approach, which is now a priority in all chemical reactions. In effect, they present a number of drawbacks such as a high amount of metal waste, poor selectivity, safety issues in some cases, or harsh conditions.

A new family of green catalysts has appeared in the last few years. TEMPO, or 2,2,6,6-tetramethyl-1-piperidinyloxy radical, is a representative member of this family, and its efficiency in oxidation reactions is well documented. The oxidation of alcohols into aldehydes, ketones and carboxylic acids uses a catalytic amount of the nitroxyl radical and a stoichiometric amount of an oxidant such as sodium hypochlorite, m-chloroperbenzoic acid, sodium bromite, sodium chlorite, trichloroisocyanuric acid, bis(acetoxy)iodobenzene, n-chlorosuccinimide, or oxygen in combination with CuCl or $RuCl_2(PPh_3)_3$. The nitroxyl radical is converted into an active species, which is the corresponding oxoammonium ion, and is then able to oxidize various substrates.

Among these substrates, alcohols are converted into aldehydes, ketones or acids; diols into lactones; sulfides into sulfoxides; benzylic ethers into esters; or α -hydroxy-lactame into anhydrides. Nevertheless, the TEMPO or hydroxyl-TEMPO structures present several drawbacks such as poor thermal stability, strong volatility with a tendency to sublimation, high solubility in water with ensuing difficulties in treating the aqueous wastes, non-negligible toxicity, and a complex synthesis route involving several reaction steps.

Another green nitroxyl catalyst, called Oxynitrox S100, is on the market and was designed for oxidation reactions. High activities and selectivities are achieved for different types of alcohols and its use can be extended to polyols or carbohydrates. It is classified as a green catalyst as it does not contain any metal. Additionally, it can efficiently replace classic metal catalysts such as copper chromite, chromium derivatives, catalysts based on ruthenium, molybdenum, silver, cerium, etc. It belongs to the family of nitroxyl radicals. It features an oligomeric structure that contains several TEMPO moieties.

Its high molecular weight (between 2000 and 3000 g/mol) makes it particularly suitable for possible recycling without losing any oxidation efficiency. It is generally used in homogeneous conditions, and the high molecular weight allows easy recovery of the end products by simple distillation.

The conditions that are generally followed for the use of Oxynitrox S100 correspond to a biphasic medium. The general procedure uses sodium hypochlorite as oxidant, Oxynitrox S100 as catalyst, dichloromethane, ethyl acetate or toluene as solvent, and sodium bromide as co-oxidant. This co-catalyst leads to the in situ formation of NaOBr, which is a more efficient oxidant than NaOCl. The degree of oxidation of the final product can be controlled by the amount of sodium hypochlorite: when using 1 to 1.3 NaOCl equivalents, or when using two NaOCl equivalents, the primary alcohol is respectively converted into the corresponding aldehyde or acid.

Powder Coatings

Caution is advised when using a catalyst in a powder coating formulation. The point in using the catalyst is to increase cure speed during the bake. Excessive catalysis can cause a pre-reaction to occur in the extruder, which in turn causes the formation of 'gel bits' or localized

crosslinking. These gel particles cause defects in the finished film. Significant crosslinking in the extruder can also damage the equipment.

Catalysts are used at low levels based on the binder – usually around 0.1 – 2.0%. Many of the polyester manufacturers offer resins that contain catalysts and they provide information regarding the bake temperature. Catalysts are also provided as masterbatches to improve distribution into the powder mixture. Typical examples of catalysts for powder coatings are: Lewis base, ammonium salts, dibutyl tin dilaurate, dibutyl tin oxide, stannous octoates, sulfonic acid/amine, peroxides, methyl tolyl sulfonamide, dimethyl stearyl amine, onium, and cyclic amidine. Again the catalyst is specific to the binder type.

A non-yellowing catalyst for uretdione crosslinked powder coatings has been developed that promotes the reaction of polyols and uretdione crosslinkers in powder coatings. This catalyst, K-KAT XK-602 uretdione, is designed to improve on the two most common issues associated with using uretdione technology – high temperature curing and yellowing in the presence of common catalysts.

Cure temperatures can be lowered by 30 °C, to 170 °C, at very low use levels and by even more to 150 °C at higher catalyst levels. Physical properties of cured films in both clearcoats and pigmented systems have shown excellent chemical resistance, high gloss and good appearance. In addition, pigmented films have demonstrated little or no yellowing compared to uncatalyzed films under standard and overbake conditions.

By introducing an epoxy acid scavenger into the uretdione powder coatings, cure temperatures can be lowered even further, to 140 °C, at very low use levels. The acid scavenger prevents the carboxylic acid group on the hydroxyl functional polyester from inhibiting the catalyst activity.

The product is a white, free-flowing powder that can be easily incorporated into uretdione-crosslinked powder coatings; it is also an effective catalyst for use in caprolactam-blocked polyisocyanate powder coatings. The storage stability of the powder is excellent, and gloss and appearance of cured films is excellent. There are no adverse effects on corrosion, humidity and UV resistance by using this catalyst.

Photolatent Catalysts

Latent base catalysts are an attractive means of improving control over the curing process of adhesives. At the same time they allow cure speed to be maintained and ensure excellent properties of the cured item. Thermally blocked amine catalysts are known, but require a fairly high de-blocking temperature to maintain sufficient stability of the uncured material, for example during storage and transport. The use of UV radiation to trigger the release of a base or acid catalyst is a worthwhile way of achieving optimum control over the application and the curing process.

Numerous base-catalyzed crosslinking reactions require amines with well-balanced basicity and nucleophilicity properties. The amidine structure provides an attractive alternative approach to photolatent structures: since the exceptionally high basicity of these compounds is attributed to the conjugative interaction of the two nitrogen atoms via the carbon-nitrogen double bond. Elimination of this double bond results in structures with isolated secondary and tertiary amine groups possessing a correspondingly lower basicity. Such amines can be used as latent precursors for the much stronger amidine base, provided the double bond can be created by a photo-initiated oxidation reaction using a suitable photo-removable group (PRG). An advantage here is that the photolatent amines thus obtained are neutral organic compounds.

The development of new photolatent base catalysts that release amidine-type catalysts creates new opportunities for radiation curing of conventional adhesive systems, allowing light-triggered, on-demand curing of formulations catalyzed by strong DBN-type bases. Photolatent curing systems therefore allow better handling and increase the versatility of adhesive systems. Photolatent catalysts extend the pot-life of reactive systems, as they are simply activated with a UV lamp before application.

Different application methods are suitable, depending on the respective crosslinking chemistry as well as adhesive application and the bonding process. Components that react even in the absence of a catalyst have

to be used as two-component formulations, but significantly improved balance between long pot-life and fast curing provides considerable advantages for the end user in the form of easier handling, fewer losses and higher throughput. Consequently, the released catalyst accelerates the curing reaction of the adhesive, increasing production efficiency.

Resin systems that do not react in the absence of a base catalyst can be handled as one-part systems, with an extended shelf life of up to several months in the dark and then fast cure on demand after irradiation. Sensitizers have proven useful in optimizing light sensitivity to the irradiation conditions.

Overall, photolent catalyst curing can lead to better product performance of the end product due to better adhesion and cohesion characteristics. However, careful selection of a photolent base that produces an appropriate catalyst is crucial for efficient curing. Ongoing research and application work on photolent bases aims at further expanding the scope of this new technology platform, which complements existing UV-curing processes and opens up new avenues for radiation curing.

Water Soluble for 2K PU Systems

Two-component waterborne polyurethane (2K WB PU) systems can have difficulty with drying speed, particularly under high humidity conditions. This is especially evident when using typical polyester polyols for the hydroxyl (OH) component of the system. Dry time slowing is not as severe for acrylic polyols under high humidity conditions, but other properties such as flexibility, durability or chemical resistance may be compromised.

The performance of common polyurethane catalysts such as dibutyl tin dilaurate (DBTDL) in waterborne systems is diminished mainly due to incompatibility and hydrolytic instability in the aqueous matrix. Enhanced hydrolytic stability and water solubility are two important features for an effective waterborne polyurethane catalyst. In addition to these features, a suitable waterborne polyurethane coating catalyst should provide the desired reactivity and property development for a wide range of formulation characteristics (chemistry, functionality, additives, percent solids, etc.). Ideally, an effective waterborne polyurethane catalyst should also promote consistent application and performance attributes under a variety of environmental conditions, including temperature and relative humidity.

There is a water-soluble catalyst (Reaxis™ C333) that has excellent hydrolytic stability and provides enhanced properties in 2K WB PU formulations under a variety of environmental conditions compared to typical polyurethane catalysts. It provides fast dry times and very good physical properties for 2K WB PU formulations under a variety of temperature and humidity conditions thus offering a wider application latitude.

The catalyst is unique in that it is soluble in both aqueous and organic media, thereby providing wide formulation latitude and allowing for uniform distribution in the liquid coating, leading to uniform cure response throughout the film. Physical properties and drying times of 2K WB PU formulations containing this catalyst are maintained after aging. Also, the pot life and shelf stability of these formulations are excellent.

CHARGE-CONTROL AGENTS

See *Anti-Static Agents*

CHELATING AGENTS

Chelating agents are compounds that are used to interact with metal impurities and render them harmless in coatings. Their purpose is usually to maintain or improve color by tying up the compounds that can lead to discoloration. Ethylenediamine (EDA), diethylenetriamine (DETA) and aminoethylethanolamine (AEEA) ethyleneamines are appropriate for use as chelating agents. Polycarboxylic acids and their salts derived from ethyleneamines are favored for their use in a variety of applications where specific metal ions interfere with processing, or need to be buffered, concentrated, separated or transported. They operate by forming stoichiometric complexes, called chelates, with most di- or polyvalent metals. The most important commercial

family of chelating agents is ethylenediamine tetraacetic acid (EDTA) and its various sodium salts, made from EDA.

There are geographic areas where water quality makes the use of chelating agents a necessity in order to successfully manufacture waterborne paint by high-speed dispersion methods.

Organic chelating agents have been tested for their effectiveness as corrosion inhibitors. The physical adsorption and chemical bonding properties of chelating agents to aluminum and copper metallic sites on alloy surfaces has been investigated. Multidentate chelating agents that bind strongly to copper have been successful in preventing galvanic corrosion.

CLEANABILITY ADDITIVES

See *Surface Modifier*

Cleanability is the easy surface cleaning property of a coating. Compounds that improve this property include many of the silicone additives that improve the removal of dust and other soiling material. New cleanability additives include hydroxyl-functional silicone-modified acrylates that crosslink through the hydroxyl functionality and remain located at the surface. During film formation, the additives function as surface flow, wetting and anticratering agents. After crosslinking, they provide permanent cleanability, and improve slip and mar. They also can provide anti-graffiti surfaces.

There are fluorocarbon compounds that will alter the surface energy of a film to make it resistant to aqueous or nonaqueous soiling mediums in both liquid and solid forms. This, of course, links the cleanability properties to the efficacy of the soil repellent and stain-resistant additives.

COAGULANTS

Coagulants are additives that are useful for wastewater and water clarification. Quite often coagulants are inorganic compounds that are used at low levels of about 1-20 ppm to yield low turbidity influent and effluent waters and wastewater. In the case of wastewater, up to about 100 ppm are used. Some medium-molecular-weight, highly-charged cationic polymers are used as coagulants. These polymers have also been used to de-emulsify oily wastewater, and to aid drainage and fiber retention in paper forming operations.

COALESCENTS (COALESCING AGENTS)

Coalescing aids have a high boiling point which, when added to a coating, contributes to film formation by way of temporary plasticization (softening) of the vehicle. These aids facilitate the transition from liquid to solid state during the latex drying or film formation process. Coalescing agents have been traditionally used to obtain good film formation. Levels of coalescent affect drying time and ultimate film properties. Important properties of a coalescing agent include: hydrolytic stability, water solubility, evaporation rate, freezing point, odor, color and safety and regulatory concerns.

Architectural latex paints are made from a variety of different polymers that are selected based on performance requirements and cost. The monomers used in these polymers determine the glass transition temperature (T_g), which characterizes the hardness of the final polymer at a given temperature. A polymer that is below its T_g is "glassy" because the molecules have no mobility; a polymer that is above its T_g is "rubbery" and the molecules have free motion. The T_g and polymer type influence the amount and type of solvent required to coalesce the polymer. Substrate, application, dry time, compatibility, VOC regulations and efficiency all play a role in determining the type of solvent or combination of solvents to be used.

A conventional coalescent (acting like a plasticizer) temporarily lowers the T_g, providing mobility to the polymer chains. The softened polymer can then flow and fuse with other polymer chains in the system, creating a protective, decorative film. To be effective, the majority of the water has to evaporate prior to the coalescent regardless of temperature and humidity to ensure that a homogeneous film develops. They actually do evaporate together but the evaporation rate of the coalescent is much slower. A conventional coalescent will evaporate out of the film



after a period of time and the film will regain its initial Tg and hardness. Various coalescents can be used individually or in combination to help formulators optimize performance in architectural coatings, while meeting VOC regulations.

Typical coalescing aids are compounds such as aromatic hydrocarbons, esters, ester alcohols, glycols, glycol ethers and glycol ether esters. As would be expected, the nature of the polymer – its solubility and affinity for various compounds – will affect the particular coalescing agent chosen.

Ethylene glycol monobutyl ether (sold under trade names such as EB and butyl CELLOSOLVE™) seems to have been the preferred coalescent agent in many industrial coatings for years. This is not by accident. While it is a fast-evaporating solvent, it appears to also have more of a swelling effect on emulsion particles that some of the other fast-evaporating aids. It is very efficient in lowering the MFFT of emulsions.

Other typical examples of coalescing solvents are: propylene glycol n-butyl ether, diethylene glycol monobutyl ether (butyl CARBITOL™), ethylene glycol monohexyl ether, dipropylene glycol methyl ether, dipropylene glycol t-butyl ether, dipropylene glycol n-butyl ether, ester alcohol or 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate [(TMB) Texanol™], 2-ethylhexyl benzoate (2-EHB), propylene glycol monophenyl ether, diethylene glycol dibenzoate (DEGDB), di-n-butyl phthalate, butyl benzyl phthalate, K-Flex 850S, a blend of diethylene glycol dibenzoate and dipropylene glycol dibenzoate, K-Flex 975, a tridibenzoate proprietary blend, X-250, a dibenzoate blend, and X-613 monobenzoate. The various trade names can cause confusion at times.

Butyl CARBITOL is a low-volatility coalescent and should be used to ensure proper film formation when air drying or using long flash-off times. Low-volatility coalescents are necessary when air drying in high-humidity conditions. Water-insoluble coalescents, such as hexyl Cellosolve, butyl Propasol™, etc., are hydrophobic solvents and can cause seeding if not premixed with water miscible solvents.

Specific high-purity esters of fatty acids and their blends can also be used to provide low-odor, VOC-free, renewable coalescents to enhance the performance of latexes used in low-VOC paints.

Coalescents based on renewable sources combine various long-chain acids with either a short-chain alcohol like methanol (the most economical option) or higher-chain alcohols and glycols or even glycol esters. Glycerol as an alcohol is not suitable for this use, as glycerol esters can have a negative impact on the adhesion of the paint film. Very short-chained acids like C-8 are also not suitable as they contain VOCs. Longer-chain esters with a higher molecular weight form softer films and act as plasticizers. New “green” coalescents that are high in efficiency, low in toxicity and improve early hardness development are a step in the right direction for making better paint, especially outdoor paint.

A high-purity version of propylene glycol mono-oleate based on renewable oleic acid was introduced to meet stringent VOC requirements in the global consumer coatings market. A second-generation propylene glycol monoester with C-18 fatty acid mixtures is available that has better color and offers an improved value. A third product, based on renewable technology, is a high-purity version of linear short chain fatty esters, which is VOC-free based on the European definition but is over 90% VOC by Federal EPA method 24. This product has been found to be over 30% more efficient than trimethyl pentanediol monoisobutyrate ester (TMB) in many popular types of latexes and offers improved hardness development and dirt pick-up resistance. These renewable-based coalescents are naturally derived, low-odor agents. They can be used in all types of decorative paints and result in improved performance and application properties, while helping to achieve compliance with new VOC regulations.

New developments in polymer technology have introduced latex emulsions for solvent-free architectural coatings. Architectural paints using this new technology do not require the use of coalescing agents, plasticizers or cosolvents to achieve good film-formation properties. Test results have shown that formulated solvent-free paints maintain

the properties of low-temperature appearance, durability, film formation and open time normally expected from quality conventional latex paints. Also, a significant advantage is the low-odor characteristics of these paints, both during and after application. Formulating approaches to solvent-free architectural coatings are now focused on the selection of raw materials that would not contribute any solvents or VOCs to the system. These ingredients include pigment dispersants and surfactants, rheology modifiers, preservatives and substrate wetting agents.

In addition to being the key to latex film formation, coalescing agents also have great influence on paint properties relating to the finished film. The amount and type of coalescent will influence scrub and block resistance, freeze-thaw stability, wetting and defoaming, color development, rheological characteristics, and exterior durability.

The impact of government regulations on coalescing agents has been severe. In the past decade in the United States several regulatory bodies (SCAQMD, OTC, CARB, EPA) have limited the use of VOCs. This has not only limited the use of traditional coalescents but has prompted the study of the long range emission of VOCs from painted surfaces.

For latex paints the primary VOC-containing raw materials were the coalescing agents and the freeze-thaw stabilizers. This has of course prompted increased use of low-VOC coalescents, and research is ongoing in this field. There has been development of new coalescing agents that are partially or completely free of VOCs. The efficacy of these materials in all varieties of formulations with different polymers is still being investigated.

Reduction of VOC using VOC-exempt solvents is not always simple, and formulating with them can be a challenge. These solvents usually bring higher cost and some have very low flash points, which leads to increased shipping cost. Careful formulation evaluation needs to be conducted.

Coalescents for Graphic Arts

The graphic arts industry faces many of the same additive challenges as those experienced in coatings, ink and adhesives applications. Namely, it continues to seek coalescents and plasticizers that not only meet high performance standards, but also the more stringent environmental, health and safety regulations that characterize the industry today.

In the graphic arts industry, coalescents assist in film formation in waterborne overprint varnish, also known as OPV. To date, the coalescents used in the graphic arts industry have primarily been the more volatile types. While they function well, VOC content is an issue. Phthalates, such as di-n-butyl phthalate (DBP) or butyl benzyl phthalate (BBP), have also been used. Although they are both relatively low in VOCs, their use has been recently restricted as a result of health and safety concerns, therefore a need exists for low-VOC, non-phthalate plasticizers and coalescents.

New-generation emulsions used in OPVs seem to be following the same trends that have been documented in other coatings industries. Specifically, the systems are softer and may not necessarily require any coalescent or plasticizer to form a film under their conditions of use. The older-generation systems, on the other hand, which do not necessarily facilitate the formation of film at room temperature, do provide excellent performance for different applications. A plasticizer/coalescent must be used in these harder systems to assist with film formation. One obvious solution would be the use of a low-VOC plasticizer/coalescent for the harder systems.

In 2011, a low-VOC plasticizer/coalescent platform was introduced specifically for use in architectural paint. This plasticizer platform is a blend of three dibenzoate plasticizers. The data indicated that one of the products, K-Flex® 975P, was particularly suited to the role of a plasticizer/coalescent in architectural coatings. Several new dibenzoates and a new grade of monobenzoate are suited for graphic arts applications, in key parameters such as viscosity response, MFFT suppression, dry time, water resistance, gloss and hardness. K-Flex 975P, K-Flex 850S and X-250 dibenzoate blends are better suited than high-VOC ethers in OPVs. The new monobenzoate X-613 is also an excellent lower-VOC plasticizer/coalescent.

COLLOID STABILIZERS

These additives stabilize very finely divided particles that have a size of about 0.01-1 micron (μm). Compounds such as animal glue, casein, cellulose ethers, guar gum, gum Arabic, poly(vinyl alcohol) and similar compounds are used as colloid stabilizers.

CORROSION INHIBITORS

See *Anti-Rust*

Corrosion inhibitors are compounds that improve a coating's ability to protect aluminum, brass, copper and steel. The term refers to a variety of materials used to prevent the oxidation of metals, including surface treatments, undercoats, and additives or elements alloyed to the surface of the metal. Corrosion poses a major potential problem for metal surfaces that are typically protected through the use of zinc-rich coatings, the use of anti-corrosive pigments and the application of a barrier coat.

Flash rust inhibitors are often used to prevent in-can corrosion during the storage of waterborne coatings. Inhibitors also may prevent the corrosion of ferrous metals during the drying time of waterborne coatings. Sodium nitrite typically has been used in the past. Other types of materials include the following: organic zinc complexes, salts of dodecylthiophthalenesulfonic acid, ammonium benzoate, 2-aminomethoxypropanol and amine neutralized thiosuccinic acid.

Long-term corrosion inhibitors have low water solubility and are often used in combination with anti-corrosion pigments although they may be used alone. Some examples of these materials include: metal salts of aminocarboxylates, salts of dodecylthiophthalenesulfonic acids, zinc salts of cyanuric acid, zirconium or amine complexes of toluylpropionic acid, and tridecylamine salts of thiosuccinic acid.

There are also organic, heavy-metal-free corrosion inhibitors to help industry meet regulatory trends toward restricting the use of lead, zinc

and chromate. These corrosion inhibitors can improve wetting and adhesion over traditional corrosion inhibitors, and can be used to formulate high-gloss coatings, as well as corrosion-resistant clear coatings.

NACORR® XR-417 is a rust and corrosion inhibitor based on a metal complex specifically designed to improve the resistance properties of direct-to-metal coatings. Synergistic with select anti-corrosive pigments, XR-417 is particularly effective in waterborne coatings due to its excellent dispersability. Also NACORR 1389, based on an aromatic sulfonic acid/carboxylate complex, is effective in most types of waterborne and solvent-based air-dry and thermoset coatings.

MCI® corrosion inhibitors are based on amine carboxylate chemistry that is USDA-certified to be biobased. It is a sustainable technology derived from renewable natural resources. These inhibitors have demonstrated effectiveness in lab testing as well as field monitoring. MCI admixtures are dosed at low levels to provide corrosion protection with negligible effect on concrete properties. Having an affinity to steel, MCI molecules migrate towards steel reinforcement, forming a monomolecular layer that passivates the surface. When MCI comes in contact with steel it forms a protective layer. This layer has been measured [using X-ray Photoelectron Spectroscopy (XPS)] to be between 20 and 100Å thick at the molecular level. A key advantage of the technology is its effectiveness even in cracked concrete.

Corrosion-Inhibitive Pigment

A pigment that, when made into or added to a paint, has the property of minimizing corrosion of the substrate to which the paint is applied.

In terms of corrosion inhibitors, some of the most effective and widely used anticorrosive pigments such as red lead (PbO_2), lead silicochromate [$4(\text{PbCrO}_4 \cdot \text{PbO}) + 3(\text{SiO}_2 \cdot 4\text{PbO})$], zinc chromate (ZnCrO_4), zinc tetraoxochromate [$\text{ZnCrO}_4 \cdot 4\text{Zn}(\text{OH})_2$] and strontium chromate (SrCrO_4),

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ADDITIVES REFERENCE GUIDE

have been and continue to be under heavy scrutiny due to the hazards posed to humans and the environment. Lead compounds are deemed toxic, zinc and strontium chromate are classified as carcinogenic and most recently, according to EU Directive 004/73/CE, zinc phosphate has been determined to be a danger to the aquatic media.

In general, the latest global trend is to design coatings that comply with the environmental regulations that now exist. These eco-friendly or green coating systems contain only non-toxic, non-reportable raw materials to ensure no hazard to humans or the environment. The industry has found it very difficult to obtain the same level of performance with the eco-friendly systems as compared to the non-compliant systems.

Coatings that meet the eco-friendly definition are high- or 100%-solids systems, powder coatings, UV or EB curing coatings, low/zero VOC, no heavy metal content, zinc-free or systems that contain no reportable compounds or ingredients in order to meet green label compliant status. Therefore, eco-friendly corrosion inhibitors should not contain heavy metals or non-reportable compounds, and be zinc-free in order to meet the green label compliant standard.

Ever since the use of chromates was restricted, the industry has been forced to use a variety of different non-toxic corrosion inhibitors specifically designed for a given substrate or resin type in an attempt to match the efficiency and versatility that chrome-based inhibitors offered. But now coatings formulators are demanding today's non-toxic inhibitors offer as much universal application in a wide range of binders and protective coatings as their toxic counterparts.

Zinc phosphate ($Zn_3(PO_4)_2 \cdot xH_2O$) was the first and most widely used non-toxic inhibitor for replacing lead and chrome-based inhibitors. Historically, standard zinc phosphate has demonstrated acceptable performance in real outdoor exposure, but less efficiency compared to chromates in marine environments and in accelerated weathering tests such as salt spray and cyclic corrosion (i.e., cohesion). However its user-friendly, low cost, universal application, and good package stability in a variety of general-purpose industrial and protective coating applications, made zinc phosphate the most popular choice early on for replacing chrome and lead-based inhibitors.

Today, in order to meet the eco-friendly labelling demands, zinc phosphate and modified zinc-containing inhibitors can no longer be used. This has caused yet another dilemma for the inhibitor suppliers as the current offering of non-zinc inhibitors on the market have generally shown inferior or anti-corrosion performance in accelerated corrosion tests, especially on steel substrates, as compared to most zinc-based inhibitors. Also, current zinc-free inhibitors are very limited in their application scope, performing well in some coating systems and poorly in others.

Today in the marketplace there are available mixed metal calcium-strontium phosphate complexes deposited on silicate cores that provide good overall performance. Also an organo-modified version of this same type of complex produces additional advantages in the areas of film formation, adhesion promotion and substrate wetting.

The basic formula for these products is: $[Sr \cdot P_2O_5 \cdot SiO_2 \cdot xH_2O]$, which represents a mixed metal phosphate complex on a silicate core. These complexes provide excellent direct anodic inhibition from the combination of the calcium and strontium cations but also provide good cathodic inhibition due to the basicity/alkalinity of the silica core. Its basic nature reduces the amount of oxygen needed to passivate the formation of rust.

The organic surface treatment shows improved mechanical properties in terms of better wetting in organic systems without decreasing its performance in waterborne systems, reduced pigment/binder interface, which makes the flow of water and electrolytes through the organic coating difficult and at the same time protects the pigment making it more inert when reactive resins or those with high acid values are used.

Silica Aerogel

Silica aerogel is used as a paint additive to achieve lower thermal conductivities; silica aerogel-enabled coatings, also called Highly Thermally Insulative Coatings (HiTICs) are also being used for condensation and

corrosion prevention. Condensation, and the corrosion it causes, is a major issue in many industrial and architectural structures. Condensation occurs when the temperature of a surface drops below the dew point of the surrounding air, causing moisture in the air to condense on that surface. When this takes place, condensate pooling can cause safety concerns. Affected equipment is likely to experience conditions that can cause corrosion, and the possibility of biological growth (mold), resulting in health and asset protection issues.

Traditional insulation can be used to try to reduce the risk of condensation by increasing the surface temperature above the dew point of the surrounding air, but this method is often met with limited success. Since many insulation systems are porous, condensation still occurs on the surface of the substrate or within the insulation layer, resulting in a higher risk of corrosion under insulation (CUI). In addition to the risk of corrosion, the presence of condensed water in the insulation material dramatically limits its thermal effectiveness, thereby increasing energy consumption. Alternatively, surface heaters can be used to warm the substrate above the dew point, but these tend to be energy intensive and are not always practical.

Aerogel-enabled insulative coatings present engineers and designers with a new solution to this old problem. These HiTICs are advantageous because of their extremely low thermal conductivity (a measure of a material's ability to transfer heat), as well as their high film build (the thickness that can be applied in each coat). These combined material properties allow for superior insulation performance with minimal coats, resulting in lower installation cost.

Since the benefit HiTICs provide is based on raising the surface temperature of the substrate, the same impact seen in architectural is also transferable to industrial. For large storage tanks or process piping, the same principle holds true, making aerogel-based coatings an excellent solution for applications where condensation formation and the resulting CUI are a concern.

Nano Extenders

Nanomaterials have a relatively large surface area and it is believed that replacing larger-size extenders with nanosize extenders could provide improved coating properties and corrosion resistance. Incorporating nanoclay into polyurethane coatings significantly improves dry adhesion as well as high-pressure hot water spray test properties. The nanoclay also improves humidity resistance, VDA cyclic corrosion over mild steel and acetic acid corrosion over aluminum.

Two types of nanoclays, montmorillonite nanoflakes and halloysite nanotubes, at various concentrations have been used in epoxy powder coatings. Both mechanical and corrosion protection properties were improved by using the nanoclays. Halloysite nanotubes are formed by surface weathering of aluminosilicate minerals and are composed of aluminum, silicon, hydrogen and oxygen. They are ultra-tiny hollow tubes with diameters typically smaller than 100 nanometers (100 billionths of a meter), and lengths ranging from about 500 nanometers to over 1.2 microns (millionths of a meter). Selecting the proper diameter and length controls and provides the various functional properties attained using Halloysite nanotubes. Halloysite nanotubes can be coated with metallic and other substances to achieve a wide variety of electrical, chemical, and physical properties or they may be filled with active ingredients for use in many industries, especially when controlled release is desirable.

COUPLING AGENT

Coupling agents are compounds that promote adhesion between dissimilar compounds. These compounds are often used for the surface modification of fillers, wherein they attach themselves to the filler by means of a hydrolysis reaction and then leave a functional group available for reaction with the coating, ink or adhesive. The main general classes of coupling agents are comprised of the silanes and titanates.

Most of the organosilanes have one organic substituent and three hydrolyzable substituents. For surface treatment applications, the alk-

oxy groups of the trialkoxysilanes are hydrolyzed to form silanol-containing species. The final result of reacting an organosilane with a substrate ranges from altering the wetting or adhesion characteristics of the substrate, utilizing the substrate to catalyze chemical transformations at the heterogeneous interface, ordering the interfacial region, and modifying its partition characteristics. It includes the ability to effect a covalent bond between organic and inorganic materials.

Titanates, zirconates and aluminates are used as coupling agents. Titanates act as organometallic chemical bridges between two dissimilar phases such as an inorganic pigment and a polymer binder – or as an adhesion promoter for a coating on a metal substrate. They provide an alternate to silane coupling agents and couple to non-silane reactive substrates such as CaCO₃, carbon black and phthalocyanine blue.

Titanates have six functions.

1. Coupling to form atomic monolayers on inorganics rendering them hydrophobic and organophilic, thus allowing complete dispersion and deagglomeration of pigments and extenders with minimum shear and work energy. They promote adhesion, significantly lower system viscosity and shift the critical pigment volume concentration (CPVC).
2. Catalysis to lower bake times and temperatures; to induce increased strain strength to the polymer binder to increase mandrel flexibility and reverse impact strength; to compatibilize dissimilar organics; and to synthesize polyesters.
3. Heteroatom to phosphatize and prevent corrosion or to intumesce and add flame retardance.
4. Alkyl/aryl functionality to create polarity for adhesion and compatibilization.
5. Thermoset functionality to densify the degree of crosslink and hardness.
6. Molecular structuring to create stable organometallics.

Designer waxes are also excellent coupling agents and since they are produced by metallocene catalysis it is possible to tailor their properties to individual applications. They are important additives in wood-plastic composites (WPCs). WPCs are a new type of natural fiber composite with up to 90% wood fiber or wood flour content. The plastic matrix is usually polypropylene or polyethylene, although polyvinylchloride is also used. Since wood and plastic differ, especially in their polarity, suitable coupling agents such as polyolefin grafted with maleic anhydride must be added. They significantly improve the mechanical parameters of tensile stress and bending load in WPCs. The polar functional groups of the coupling agent react with the OH groups of the wood and form a genuine chemical bond. The non-polar areas of the coupling agent have strong affinity to the non-polar polyolefin chains.

Solvents that cause two immiscible liquids to homogeneously mix are also referred to as coupling agents.

CRAZE-RESISTANCE ADDITIVE

A chemical that will prevent the formation of fine random cracks or fissures on or under a surface of plaster, cement, mortar, concrete, ceramic coating, or paint film caused by shrinkage.

CROSSLINKING AGENT

Crosslinking agents are compounds that convert a thermoplastic into a thermoset. They are multifunctional chemical compounds that react with functionality on the macromolecular chains and thereby form a thermoset or three-dimensional polymeric material. The crosslinking agents are of di- or higher functionality, and they become an integral part of the final thermoset material except for materials lost in a condensation crosslinking process, for example. These agents can range from low-molecular-weight to polymeric materials. Examples of crosslinking

Dodecanedioic Acid (DDDA)

Raw Material for:

High Grade Lubricants

Corrosion Inhibitors

Powder Coatings

Nylon 1212

Nylon 612

Adhesives

Produced using microbial fermentation technology by
Shandong Hilead Biotechnology Co., Ltd.

For more information, please contact US agent:

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agents are melamines, such as hexamethoxymelamine, guanamines and other aminoplasts, isocyanates, epoxides, amines, and so forth.

Epoxy-functional silane crosslinking agents for waterborne coatings are also available that will crosslink under heat or at room temperature on alkaline substrates if used in combination with recommended catalysts. These are designed primarily for carboxyl- or amino-functional acrylic latexes or polyurethane dispersions. The mechanism of crosslinking involves the epoxysilane's dual chemical functionality. The epoxy portion of the molecule is reactive with the matrix resin and the alkoxysilane portion crosslinks after hydrolysis by condensation forming siloxane bonds. The alkoxysilane also can react with surfaces to improve wet adhesion of the coating, or with fillers to improve pigment binding.

Crosslinking causes changes in physical and chemical properties. That is, it causes changes in hardness, tensile strength, modulus, elongation, solubility, swelling and other properties. For example, crosslinking renders a soluble or thermoplastic polymer into a thermoset polymer that is three-dimensional in nature and insoluble. However, the crosslinked polymer system may be swellable to different degrees in liquids that may have been solvents for the uncrosslinked polymer. The greater the degree of crosslinking or the number of bonds formed between chains, the lower will be the degree of swelling in any particular solvent.

UV Powder Coatings

The latest development in powder coatings is the combination of powder coating technology and UV technology. This technology is making strong inroads especially for temperature-sensitive substrates. The most suitable approach for a coating formulation is the use of a major binder and a crosslinker. The crosslinker may control the network density for the coating, while the binder determines properties of the coating such as discoloration, outdoor stability, mechanical properties, etc. Furthermore this approach will lead to a more homogenous concept in powder coating applications as a category bringing similitude to thermosetting coatings where crosslinkers such as TGIC and β -hydroxyl amides are used. A crosslinker should present properties quite specific for the application intended: molecular weight, high functionality, and physical properties compatible to the application.

The existing UV-curing powder coating systems generally build on two binders. There is an option to the existing systems that consists of using unsaturated amorphous or amorphous-crystalline polyesters comprising maleic/fumaric moieties as reactive double bonds in combination with crystalline crosslinkers containing unsaturated reactive groups.

Adhesives

Polyurethane adhesive dispersions usually are processed with isocyanate crosslinkers. There is a new technology for heat-activated dispersion adhesives that is based on a new polycarbodiimide crosslinker Desmodur® XP 2802. The crosslinking reaction takes place immediately after drying in the adhesive layer at room temperature and a high rate. After the formulation is applied to a film or other substrate, the adhesive layer is dried. During drying, the polymer and crosslinker droplets gradually come closer, until they finally flow into one another and form a uniform adhesive film.

Film formation triggers the start of the crosslinking reaction. If the adhesive layer cools prior to the bonding process, the polymer crystallizes in just a few minutes, forming a non-sticky polymer film. To bond two films or other substrates with it, it must be activated within one hour. This is achieved by briefly applying heat, which melts the crystalline segments in the polymer chain. After the substrates are pressed together, the adhesive quickly hardens at room temperature by means of both crystallization of the polymer's crystalline segments and the crosslinking reaction between the polymer and the polycarbodiimide crosslinker. This technology particularly offers advantages for applications in which web-like substrates must be bonded together and quickly achieve high strength at the joint. It is especially applicable for roll-to-roll bonding processes.

CURING AGENT

See Hardeners/Accelerators

Additive that promotes the curing of a film. Anything that promotes, enhances or ensures mechanical or optical property development of a coating (usually liquid) by means of chemical and/or physical change such as through evaporation, polymerization or other means. The curing agent can be anything such as thermal energy, radiation energy, a catalyst, various substances or other means to enhance such property development. Some curing agents are termed "hardeners." Crosslinking agents are also curing agents.

Recent advances in new amine-functional curing agents have improved performance of waterborne two-package epoxy coating systems. These new amine adducts offer performance advancements along with the ability to meet near-zero VOC levels. Those that are designed for cementitious applications in industrial and do-it-yourself markets demonstrate water-reducible epoxy coatings with superior handling, application properties, improved resistance to chemicals and staining and visible end of pot life.

The performance properties that can ultimately be obtained from an epoxy resin system depend primarily on the nature of the curing agent. For many applications where epoxy systems are expected to cure at normal ambient temperature, amine-based curatives are primarily used. Primary and secondary aliphatic, aromatic and cycloaliphatic polyamines, and their derivatives, will react with and cure epoxy resins. Amine-cured epoxy systems are used for general industrial and some architectural (indoor) applications as well as floor coatings and monolithic floor toppings. Each type of polyamine lends different performance properties, assuming the same epoxy resin is used.

Epoxy curing agents based on cycloaliphatic diamines are typically used for coating applications that require low color, good color stability, long open time and good resistance to amine blush (or carbamation). Other desirable properties include high hardness values, good mechanical properties and resistance to chemicals such as alkalis and dilute acid solutions. An undesirable phenomenon that can occur with an epoxy coating cured using a cycloaliphatic diamine-based curing agent is amine blush. Amine blush can occur under a variety of cure conditions, but becomes more likely as the ambient temperature decreases and/or as the relative humidity increases. It should be noted that aliphatic diamines tend to have a higher blushing tendency than cycloaliphatics. Aromatic diamines have the least tendency toward blushing, however they are usually dark in color and many are toxic.

Curing agents containing cycloaliphatic diamines are commonly used in a variety of applications for which epoxy systems are well-suited. Examples include those used as coatings, primers or sealers on a variety of substrates, such as concrete and metals used on floors, walls, tanks, pipes, etc. Cycloaliphatic diamines are also desirable for monolithic, or seamless, epoxy floorings such as self-leveling, broadcast and mortars. As one could expect, different cycloaliphatic diamines offer different advantages and limitations. There are a number of cycloaliphatic diamines that can be used as curing agents for epoxy resins, but relative few are commonly used in the coatings industry. These include 1,2-diaminocyclohexane (DACH), bis(p-aminocyclohexyl)methane (PACM) and 1,3-bis(aminomethyl)cyclohexane (1,3-BAC), but the most commonly used is isophorone diamine (IPD). These diamines are used as building blocks to create a finished curing agent.

The diamines can be modified in various ways to overcome many of their limitations in order to approach the desired level of performance for the intended application. There are many applications that require the high chemical resistance and good mechanical properties of epoxy systems as well as good aesthetic properties such as consistent color development, minimal color change over time and high gloss. Resisting a gradual change in color over time is not a strength of epoxy systems due to their chemical nature; however cycloaliphatic diamine-based curing agents are best-suited for the job. The coating should also withstand aggressive cleaning solutions and cleaning with steam or hot water. These IPD-based curing agents represented the state-of-the-art until recently.



The development of a unique technology – Aradur® 2978 epoxy curing agent – improves upon the performance offered by IPD-based curing agents. It does not contain bisphenol-A, phthalates or solvents.

Comparatively, Aradur 2978 out-performs conventional IPD-based curing agents in many aspects. A key benefit is its longer pot life (or working time) and equivalent thin-film curing speed – a unique combination in two-component ambient-curing epoxies. This ideal combination greatly extends the time available to apply the coating, as the rate of viscosity increase is substantially slower. It offers similar thin-film curing speed and hardness development compared to IPD-based curing agents. It is also ideal for applications that require a low color with a high degree of color stability.

Another class of epoxy curing agents – phenalkamides, derived from cashew nutshell liquid – has been developed for concrete epoxy primers and topcoats. They offer the benefits of both polyamides and phenalkamines by providing formulators with a great alternative to existing epoxy topcoat systems due to improved color retention and balanced properties that address decorative as well as protective requirements.

Polyamide and polyamidoamine curing agents are also used for some applications. Polymercaptans, because of their rapid and low temperature cure, are usually used in fast epoxy systems for adhesives.

DEAERATORS

Deaerators prevent microfoam and pinhole formation in a coating. They are very important in high-viscosity and high-solid systems, and absolutely vital for airless applications. Silicones (polydimethyl siloxanes), mineral oil, organic polymers (polyethers, polyacrylates), modified polysiloxanes (such as polyether-modified polysiloxane with hydrophobic solids) and fluorinated silicones are examples of materials that will function as deaerators.

In waterborne systems, foam occurs as both macro- or microfoam and is manifested as pinholes and air bubbles in the dried film. Macrofoam is readily seen as large bubbles often held together in a honeycomb-like structural formation. Microfoam is often recognized as fine spherical shaped bubbles.

For solventborne systems, microfoam is often a problem and pinholes form from small air bubbles, which create channels as they move through the drying film. During the drying process the viscosity of the coating increases and the channels remain open and fixed in the dried film. Pinholes severely reduce protection properties of a coating, and they may allow salts and moisture to penetrate the coating and deleteriously affect the substrate.

Microfoam is caused by air entrapment during manufacture and/or application, during the mixing of two-component systems, or from byproducts formed from chemical reactions. Deaerators work by coalescing small bubbles into larger bubbles that can rise to the surface considerably faster than microbubbles.

DEFLOCCULANT

See Dispersant or Dispersing Agent

A material that prevents pigments in suspension from forming flocs.

DEFOAMER

See Deaerators for discussion on microfoam

Additive used to reduce or eliminate foam in a coating or coating constituent. The terms 'defoamer' and 'antifoaming' agent are often used interchangeably. In fact, they are not quite the same. A defoamer is a surface-active agent that stops the foam and breaks the bubble once it has been formed. It is a bubble breaker. An antifoaming agent prevents the formation of foam so it never forms.

The term "foam-control agent" is a more appropriate term to use. In an aqueous formulation, it is almost impossible (at acceptable use levels) to totally eliminate all foam. The correct foam control agent will help to prevent foam formation, but more importantly, it will allow the dried film to be free of foam and any resultant film defects that might result from an air void in a film.

There is a difference between macrofoam and microfoam. Macrofoam is located mostly on the coating surface and is surrounded by a duplex film with two liquid/air interfaces (double layer), whereas microfoam occurs inside of a coating film (air entrapment) and is characterized by a single liquid/air interface. These two types of foam also differentiate defoamers from deaerators. Defoamers are mostly effective against macrofoam, whereas deaerators suppress microfoam. In practice, the terms are frequently confused and used interchangeably. Many of the commercial products are optimized to prevent macro- as well as microfoam.

Both kinds of foam impair the surface optics of the coating and cause surface irregularities, as well as reduce gloss and transparency. Microfoam also adversely affects the coating's protective properties because the effective film thickness is reduced and pinholes can form from the micro bubbles.

The function of defoamers is based on disturbance of the double layer of the macrofoam lamella. Substances with very low surface tension are used as they are not wetted by the foam bubble. Foam-stabilizing substances move away from the defoamer droplet, which finally causes collapse of the bubble. Surfactants are often used with defoamers to improve the spreading of the defoamer droplet on the bubble surface.

Foam may be introduced at various stages of manufacture and use of the coating. The raw materials used to make a coating, such as surfactants, dispersants, etc., enable foam to form. Entrapped air, or foam, is introduced into the manufacture of most paints as part of the process. Manufacturing care must be taken to avoid entrapping air during production by choosing the correct stirring equipment and stirring conditions. Letting the product stand for as long as possible is also helpful in preventing air entrapment.

High levels of foam may occur during the milling stage, and defoamers are often used as a component in a grinding paste. Due to the activity of some surfactants at the air/water interface, foam is often created and stabilized in both the pre-mixing and milling chambers of dispersing equipment. Foam slows down the process of dispersion and adversely affects the moisture resistance of the coating. Using silicone anti-foam agents may present an additional potential for surface defects.

Foaming occurs during application to some degree, depending on the method of application. For example, curtain coating carries entrapped air continuously around in the system. Entrapped air also occurs with airless spray systems. Airless spray does not use compressed air. Paint is pumped at increased fluid pressures through a small opening at the tip of the spray gun to achieve atomization. When the pressurized paint enters the low-pressure region in front of the gun, the sudden drop in pressure causes the paint to become an aerosol. Airless spraying has several distinct advantages over conventional air-spray methods. It is more efficient than the air spray because airless spray is less turbulent and, therefore, less paint is lost in bounce back. The droplets that are formed are usually larger than conventional spray guns and produce a heavier paint coat in a single pass. The system is also more portable, production rates are nearly double and transfer efficiency is usually greater. Other advantages include the ability to use high-viscosity coatings and to have good penetration in recessed areas of work pieces. One major disadvantage of airless spray is that pinhole formation from air entrapment is possible. Air-assisted airless spray is similar to airless application except that a small amount of atomizing air is used to further improve coating atomization. Spray application in relatively low humidity conditions or in high-temperature conditions can increase the tendency for foam entrapment.

Latex paints are stabilized with surfactants that easily generate foam under agitation. Elimination of this foam is essential for the manufacturing process, for storage and for good application properties. Foam reduction can also be somewhat controlled by optimizing the settings on a spray gun and by adjusting the viscosity/solids level in the formulation.

Foam is a dispersion of a relatively large volume of gas in a small volume of liquid. Gases are soluble in liquid media to different extents and are influenced by temperature. As the paint film starts to dry, the dissolved gases try to escape in the form of bubbles. A bubble, as a



sphere, requires the least amount of surface energy. Large bubbles rise faster than small ones and collect on the surface. They are often covered by a surface film of surfactant or other additive in the coatings system. On the surface, the bubbles pack side by side as densely as possible. In some systems, densely packed microfoam can form on the surface and remain there even after the film has cured. This is possible for high-build systems like some plastisols.

In the process of bubble escape, tiny pores may be formed in the film. In lower solids films that dry quickly, the viscosity of the coating is increasing quickly with drying. As this is happening, the smaller micro bubbles are still rising to the surface but quite slowly; in the process these bubbles can form small channels. If the rising bubble penetrates the surface, lack of flow allows for the formation of pinholes – a surface defect. Sometimes these microbubbles cannot penetrate the surface, but they will push a very thin, viscous layer of coating to the front surface. This layer will remain on the surface after drying or curing and becomes a spherical blister.

Good defoamers not only need to be good bubble breakers, but they need to be able to keep the action sustained and maintain good defoaming over time in both oven and room temperature aging studies. Good defoamers need to be insoluble in the foaming system. If the product is too soluble it will only increase foaming. Defoamers need to have excellent dispersibility throughout the systems. Spreadability is the ability of the product to spread evenly and uniformly on the surface, coating the bubble particles and eliminating them. They work by lowering the surface tension around the bubble and cause them to coalesce to larger bubbles and eventually to break.

Most foam-control agents for aqueous systems consist of carrier, actives (hydrophobic materials) and other additives that enhance spreading, compatibility, product stability, etc. Some examples of carriers include mineral oils, vegetable oils, glycols, glycol ethers, alcohols, silicone oils and water. Three types of actives are most common: hydrophobic silica, hydrophobic silicone and organic materials that are hydrophobic/lipophilic. Many foam-control agents are blends of the above actives. The other additives vary from surfactants, co-solvents, thickeners, etc.

The actual foam-control agent that functions the best is based on its spreading rate, compatibility, persistency and cost/performance. Many of the above factors oppose each other in a formula. For example, the most compatible is usually the least persistent; the least compatible often spreads the best; etc.

Many defoamers are colloidal suspensions of particles that act as seeds to allow bubbles to collect and burst. These types of additives can be simple alcohols, oils or complex silicone oils on fine particle silicas. Defoamers should spread instantaneously on the bubble surfaces and into the underlying layers, and cause immediate rupture of the bubble.

Silicone defoamers are usually based on a polysiloxane-type structure. For example, there are acrylate-functional polydimethylsiloxanes, polyether-modified polydimethylsiloxane, etc. To select the proper antifoam, the formulator needs to be aware of the nature of the foaming agent, the foaming tendency, the solubility and concentration, pH, temperature and viscosity of the system. Each of these factors has a direct influence on the antifoaming agent of choice. Some examples of other compounds that function as defoamers are waxes, fatty acids, aluminum stearate; amyl, capryl, decyl, nonyl, and octyl alcohols; caster, corn, mineral, pine, silicone, and turkey red oil; palmitic and stearic acid diethylene glycol monolaurate, sulfonic acid salts, tributyl citrate, and tributyl phosphate.

Some foam-control agents have an effect on gloss; but not all do, so the formulator must carefully evaluate this effect. Color acceptance of emulsion paints is also important, and some defoamers can have a negative influence on color development that needs to be evaluated.

Foam-control agents are very formula/system dependent and the best way of selecting them is to test them. This is usually done quickly in the lab by adding various defoamers to a known volume of paint sample, shaking for a set time, and then measuring the height of the foam that is generated. The method actually works quite well.

Foam-control agents should be used with some degree of caution to minimize cratering. It is important for wood sealers and topcoats that the defoamers used do not cause surface defects or create haziness in the final finish. Incorrect use of antifoaming agents can cause craters, fish eyes, floating, flooding, crawling, etc.

New, liquid, mineral-oil-free defoamers based on renewable raw materials have been introduced into the market. These new defoamers are ideally suited for use in the manufacture of synthetic latex, waterborne matte to satin finish architectural coatings, plasters, and aqueous adhesives. They display remarkable performance characteristics retaining defoaming capabilities even after prolonged paint storage. Some of these new materials may be used as an alternative to replace tributylphosphate (TBP).

Another approach has been to replace mineral oil with natural oils like soybean, rape seed, sunflower and rice bran oils.

There are also unique molecular defoamers based on Gemini surfactant technology.

There are no universal defoamers, although certain types function better with certain emulsions, certain plant processing requirements, etc. Most suppliers are willing to provide technical support to make the selection process easier.

DEGASSING AGENTS

Specific chemicals that allow for the release of volatiles in a molten powder film. Volatiles can be interstitial air, blocking agents, and low-molecular-weight polymeric fractions.

Benzoin is typically the choice for degassing powder coatings. In the absence of benzoin, the air bubbles start to shrink very slowly as a result of a diffusion-controlled process. Quite remarkably, in the presence of benzoin, the bubble shrinkage process is accelerated to such an extent that most air bubbles disappear before any significant increase in the viscosity occurs due to the curing of the coating. This suggests that benzoin functions by accelerating the rate of bubble shrinkage. Yellowing side effects of benzoin on powder coatings may be associated with the formation of benzyl, the common oxidation product of benzoin.

Ceraflour® 963 is a specially modified wax that is particularly recommended for powder coating applications on critical, i.e., porous substrates. It is an excellent degassing additive and ensures a smooth and uniform surface without any defects.

DENATURANT

An unpleasant or toxic substance that is deliberately added to make a product unfit for human consumption.

DETACKIFICATION AGENTS

Paints used in automotive finishing operations are a tacky material and tend to adhere to the surfaces of spray booths, particularly in the sump and drain areas. To maintain the design intent of the paint spray booth the paint overspray must be constantly removed from the sump to prevent clogging of the sump drain and recirculating system. In order to assist in the removal of the oversprayed paint from the air and to provide efficient operation of the down-draft, water-washed paint spray booths utilize paint detackifying chemical agents. The detackification products are commonly introduced into the water that is recirculated in the paint spray booth system.

Paint spray booths are typically 100-300 feet in length and usually contain many robotic and manual spray zones. The temperature and humidity are rigorously controlled in these systems. As vehicles are painted in these booths, a certain amount of paint does not contact the article being painted and forms a fine mist of paint in the air space surrounding the article. This paint must be removed from the air. To accomplish this, the contaminated air is pulled through the paint spray booth by exhaust fans. A curtain of circulating water is maintained across the path of the air in such a way that the air must pass through the water curtain to reach the exhaust fans. As the air passes through the water curtain, the paint mist is "scrubbed" from the air and carried to a sump

basin (sludge pit) usually located below the paint spray booth. In this area, the paint particles are separated from the water so that the water may be recycled and the paint particles disposed of as paint sludge.

The paint detackifiers, or “denaturants” commonly added to these systems are either melamine-formaldehyde-based or based upon acrylic acid chemistry. The innovative nature of the chitosan detackifier (BC4200NP technology) lies in the fact that it is derived from chitin, the waste product of food production, namely shell fish harvesting. The solid chitin derived from these operations is treated with sodium hydroxide at an elevated temperature to produce chitosan, also called poly(glucosamine), that represents a deacetylated chitin. The chitosan produced in this way yields a glucosamine polysaccharide structurally similar to cellulose. The degree of deacetylation can be controlled by temperature and reaction time. The chitosan produced, also in a solid state, is not readily soluble in water, but can be rendered more water soluble by the addition of various acids such as acetic, sulfuric, hydrochloric, citric, sulfamic and mixtures thereof.

On a pound for pound basis, the BC4200NP technology is either cost neutral or less expensive than the current paint detackifiers in the market place. Further, field studies indicate that the BC4200NP technology may reduce the overall cost of such programs by lowering detackifier usage and by decreasing the use of ancillary chemicals, i.e., liquid caustic and biocides.

The melamine-formaldehyde detackifiers that BC4200NP is replacing are derived from non-renewable natural gas supplies and contain residual amounts of free formaldehyde as a necessary consequence of the resin production operation. The acrylic acid-based detackifiers are derived from non-renewable crude oil feed stocks and their price is therefore subject to the global oil market. Further, since the chitosan-based is less acidic than the traditional products, less sodium hydroxide is necessary in an operating system to control pH resulting in less overall chemical usage. Additional field studies have also indicated that less detackifier is necessary to treat a given amount of paint and this also makes the BC4200NP more attractive from an application cost perspective.

The environmental advantages of this technology are summarized as follows: no residual free formaldehyde: raw material is not derived from natural gas and/or crude oil and therefore does not utilize non-renewable resources; it is obtained from the waste products of food production (crab, lobster and shrimp shells); low acidity level; chitosan, the main component, has anti-microbial properties.

DESICCANTS

Desiccants are materials that have a high affinity for water absorption and are used as drying agents. The most commonly used desiccants are silica gel or calcium oxide.

DETERGENT

A detergent is a surfactant that is used to clean soiled surfaces. They may be anionic, nonionic or cationic.

DILUENT

See Reactive Diluent

DISPERSANT/(DISPERSING AGENT)

See Surfactants

A dispersant is an additive that increases the stability of a suspension of powders (pigments) in a liquid medium. The pigment-dispersing step is the most difficult and time/energy consuming part of the paint manufacturing process. This is because of the difference in surface tension between the liquids (polymers and solvents) and the solids (pigments and extenders).

Pigments and extenders are often received as agglomerates and then are subjected to a grinding process that incorporates the pigment into the vehicle during paint manufacture. During the grinding the agglomerates are dissociated into a dispersion of particles. In the process, dispersants (surfactants) are used that mainly prevent reassociation of the pigment

and extender particles. The dispersants are adsorbed onto the particles and hinder close approach of particles by charge repulsion effects (ionic dispersants) or by steric effects (nonionic dispersants). Wetting and dispersing agents are used to stabilize pigment dispersions. They often use steric hindrance to avoid flocculation of the pigment particles.

Minimizing pigment-pigment interaction by shielding the particles due to steric hindrance can only be achieved if the polymeric side chains of the additive provide high solvency, thereby stretching and protruding into the liquid system. In contrast, non-sufficient compatibility will result in coiled side chains, reduced pigment particle spacing and flocculation. Stabilized pigment particles is one pre-requisite for achieving long-term stability, low mill-base viscosities, high gloss and high transparency, along with optimal color strength in the applied coating.

The pigment-adsorbing groups in dispersing additives are chosen to interact effectively with as many pigment classes as possible, e.g., inorganic pigments, organic pigments and carbon blacks. Due to the fact that as the particle size of the pigments gets smaller and their surface area simultaneously becomes greater, the design of a suitable dispersing additive must be tuned in such a way that the molecular weight is high enough to provide effective particle shielding to avoid flocculation. Additionally, the number of pigment anchoring groups needed must be optimized to generate a durable and long-lasting adsorption layer at the pigment surface.

Since a dispersant is used to help the suspension of fine particles of a solid in a liquid phase, it must be able to totally wet the solid particle and also be able to interact with the dispersing medium. Dispersants act by being adsorbed on the surface of the pigment particles with the other end of the molecule exposed and usually charged. Since like charges repel, the individually coated pigment particles repel each other and stay uniformly dispersed. Because the individual pigments are all so chemically different – some are attracted to water and some are not – the dispersants have to be chemically different. When changing pigmentation in a formula, the dispersant needs to be checked quite carefully to see if it is stable in the formulation. Good dispersion provides the end user with better hiding and color stability.

Pigment dispersants are necessary to improve the wetting of the pigment and enhance its suspension. The choice of dispersant depends on the nature of the pigment and if the coating is a waterborne or solventborne system. Dispersants are available for organic and inorganic pigment systems and for both solvent- and waterborne systems. The proper choice of dispersant can be useful for obtaining higher gloss, hiding power and lower viscosity. There are dispersants on the market that can be used with all commercial titanium dioxides as well as inorganic pigments (including transparent iron oxides, effect pigments, matting agents, and fillers).

Usually pigments are dispersed in a mill base. A mill base is a concentrated mixture of pigments, a small amount of the binder and solvent and a wetting and dispersing additive. In the wetting stage, the liquid in the mill displaces air from the pigment surfaces. Shear force, applied by a mill, is necessary to break down pigment agglomerates. As pigment particles become adequately dispersed, dispersants that are now on the surface of the pigment particles prevent reagglomeration of the pigment.

Because of their hydrophobic nature, organic pigments are difficult to disperse in aqueous media. Surface-active compounds that are amphoteric in nature are usually effective for both organic and inorganic pigments that are particularly hydrophobic.

In aqueous systems, dispersants must disperse the pigment and form an affiliation between the pigment and the dispersing medium that is water. There are several types of dispersants commonly used in latex paints, for example, phosphates (such as potassium tripolyphosphate) and several sodium phosphates (sodium hexametaphosphate, sodium polyphosphate, sodium phosphate (tribasic)). The potassium salt is preferred because it is less soluble. Ionic types such as the sodium salts of water-soluble polymers are also very common.

There are ionic water-loving (hydrophilic) and oil-loving (lipophilic) types available on the market. The hydrophobic part of the molecule is attracted



to the pigment particle, and surrounds the particle with an ionic layer. Pigment separation by mutual repulsion takes place. These cannot be relied on for in-can stability and need to be used then with nonionic surfactants.

Ionic and anionic surfactants are also essential for good dispersion, and contribute to the latex paint system by helping to optimize hiding power, flow, and leveling. The amount of dispersant used is very small and is directly related to the total surface area of the pigment used. Again, too much or too little of these agents can affect in-can stability and other properties of the paint.

There are new nonionic deflocculation dispersing and wetting additives for waterborne coating systems that have been designed specifically to provide superior performance in wetting, dispersing and deflocculation of pigment particles and to comply with environmental regulations. These are zero-VOC and alkylphenol-free to allow reformulation of existing platforms to comply with new requirements.

Pigments are usually easier to disperse in solventborne resin systems; however, higher solids systems will sometimes show pigment flocculation problems. This can be the result of the lower-molecular-weight polymers or oligomers having less of a buffering effect on the pigments and thereby permitting closer pigment-to-pigment contact. Amphoteric dispersants have been developed that are effective for preventing flocculation of carbon black and other organic and inorganic pigments in higher-solids systems. These dispersants have also been able to keep viscosity from increasing in some coatings where the polymer's solubility is causing rheology problems.

The most widely used wetting agents in the past were primarily alcohol and alkylphenol ethoxylates used alone or blended with anionic surfactants. Alkylphenol ethoxylates (APEOs) include octylphenol (OPEs) and nonylphenol (NPEs) ethoxylates. These were preferred as wetting agents because they were cost effective and provided a number of structural, compositional and performance attributes. APEOs have become less acceptable due to the effects of degradation products on aquatic life forms and their potential effect of fertility of organisms. Consequently many manufacturers and raw material suppliers are gradually phasing out APEO compounds despite the absence of any legislative guideline prohibiting their use. However, by exploiting narrow-range ethoxylation and newer alcohol feedstocks, the properties of non-APEO surfactants are able to match those of the APEOs.

Some typical dispersing agents for organic and inorganic pigments are salts of monosulfonic acid such as: calcium or zinc sulfonate. Acetylenic diols are also sometimes added. Another class of dispersing agents is known as the aromatic ethoxylates. This type of molecule contains a relatively large anchor group that is a polycyclic aromatic structure. No amine or acidic groups are present, so the compound is pH neutral. Aromatic ethoxylates allow high pigment loading and do not tend to foam. Water resistance and gloss retention are both good.

Another widely used class of dispersants is based on soya lecithin. These have been used for many years as pigment wetting agents, grinding aids and dispersion stabilizers in oleoresinous formulas. This class of agent is also available in water-soluble or water-dispersible forms. These are used in much the same applications in latex formulations. The water-compatible versions are also very useful in formulating universal colorants and as agents in both water and solvent formulas to improve universal colorant compatibility and color development.

Polymeric dispersants (hyperdispersants) are a new class of dispersants that have significantly higher molecular weight than conventional dispersants. These dispersants provide improved pigment stability and increase tinctorial properties through their ability to wet and stabilize pigments. The result is cost improvement through faster dispersion, which results in increased throughput, lower pigment loading requirements due to enhanced color strength, and good rheological properties as well as low foaming characteristics. Performance is enhanced due to resulting high gloss, good flow and leveling (surface properties), and improved transparency.

Polymeric dispersants contain polymeric chains for steric stability in solution and they must be able to be strongly absorbed onto the particle

surface. Many functional polymers and/or copolymers are capable of functioning in this fashion. Examples are polyurethane or polyacrylate with tertiary amine functionality, or polyester.

High-molecular-weight dispersants are linear or branched chain polyurethane or polyacrylates that have molecular weights between 5,000 and 30,000 g/mol. These dispersants have pendant anchoring groups, which adsorb onto the surface of the organic pigment particle by hydrogen bonding, dipole-dipole interactions or Van der Waals forces. The remainder of the polymeric dispersant is large enough to cause steric stabilization. The level of dispersant is important because performance depends on the optimum amount of saturation by the dispersant of the pigment surface. Polyurethanes function well for viscosity depression in the mill base, which can lead to higher pigment loading. The polyacrylates are more compatible in nonpolar and highly polar systems.

Controlled polymerization techniques such as GTP (group transfer polymerization) and controlled radical polymerization (CRP) techniques such as ATRP (atom transfer radical polymerization), NMP (nitroxyl-mediated polymerization), and RAFT (reversible addition-fragmentation chain transfer) provide opportunities to customize polymers in a way that is not possible with conventional random copolymerization methods. Each of these techniques has its own characteristics that define to a certain extent the properties of the resulting polymeric additives. These techniques are applied for the synthesis of custom-made structured polymers. Compared to free radical polymerization (FRP) they all allow much better control over polymer structure and molecular weight distribution and they all have their specific characteristics.

Due to the fact that the chain growth mechanisms are different in GTP and CRP, it is clear that the resulting polymers will have different properties and these differences also can show up in their performance as wetting and dispersing additives. Controlled polymerization techniques are not only a tool to synthesize block copolymers, they also make other polymer architectures accessible. Gradient copolymers are one of the polymer architectures that possess a continuous transition of the properties of the respective monomers along the whole polymer chain; these polymers have very unique properties for pigment wetting and stabilization.

In random copolymers the pigment anchoring areas and binder-compatible areas are randomly distributed and generally too small for a strong stabilization effect. In block copolymers (as well as in graft copolymers) the two different areas are large enough for good stabilization of the particles in a pigment dispersion. But the strict separation of the properties in the polymeric structure can cause other drawbacks. Such polymeric structures may have a strong tendency toward foam stabilization. Micelle formation, mainly due to the incompatibility of the anchoring groups with the liquid medium, is also observed and pigment wetting with the additive can become difficult.

The gradient copolymer performs better because there is a gradually increasing concentration of anchor groups along the polymer chain. This obviously helps to increase compatibility, reduces micelle formation but still allows excellent steric stabilization of the pigment particles. These structural differences have a strong impact on the performance of the polymeric additives as wetting and dispersing additives.

Polymeric wetting and dispersing additives are useful for all types of pigments, whereas low-molecular-weight structures with only one or few anchor groups are mainly used for inorganic pigments.

By accurately tailoring the backbone polymer, using various (meth)acrylate and other unsaturated monomers, the position of pigment-anchoring units and other reactive groups for attaching side chains along the backbone can be influenced so that the side chain density and the homogeneity of the side chain distribution are controlled (comb copolymers). The molecular weight and the polarity of the side chains strongly impact the compatibility and product viscosity of the additive. A positive effect is increased uniformity of the polymer chains. The amount of undesired polymeric side products that contain no side chains or no pigment affinic groups is reduced. As a consequence of the

more precise structure, such comb copolymers are excellent wetting and dispersing additives for numerous applications.

There is a new solvent-free liquid comb copolymer consisting of side chains with a well-balanced ratio of tuned hydrophilic and hydrophobic moieties to provide universal compatibility with water, organic solvents and resin chemistries. Additionally, special ionic pigment anchoring groups are attached to the polymeric backbone to specifically interact with ultrafine carbon black, as well as transparent and semi-transparent organic pigments. It has been shown that excellent pigment stabilization and universal compatibility in solventborne, solvent-free and waterborne systems can be obtained with a single additive, precisely tailored in terms of polymeric backbone, side chain polarity and pigment affinity. The tailor-made comb copolymer provides, in comparison to respected benchmark coating additives, lower mill-base viscosities and better coloristic properties in dried films.

There is another new class of reactive surfactants, both nonionic and anionic, for use in both conventional aqueous emulsion polymers and in UV-curable coatings that contains two polymerizable moieties. These new reactive surfactants can be employed either as emulsifiers or as pigment dispersants. The reactive surfactants are block copolymers of two or more moles of allyl glycidyl ether (AGE) and ethylene oxide terminated on the AGE end with a hydrophobic moiety. The addition of a second equivalent of AGE significantly reduces the amount of non-reactive surfactant in the product so that increases in coating repellency may be achieved. These new reactive surfactants may contain various hydrophobes such as styrenated phenol ethers, alkyl ethers such as tridecyl alcohol, or alkylphenol ethers. Varying the level of ethoxylation and adjusting the size of the hydrophobe results in being able to tune the structure for optimal performance for each application. These nonionic copolymers may be further derivatized to convert them to anionic surfactants. Examples of these include sulfonates, phosphate esters and carboxylates.

Because a good dispersant must have pigment-affinic groups, those that are amine-based will react with epoxy systems or any reactive systems. There are emission-free, hyperbranched wetting and dispersing additives for solvent-free epoxy systems that are encapsulated by polyester side chains. This prevents reaction with the epoxy, and storage stability is maintained.

Silicone and silane pigment-treatment additives can cause pigments to disperse evenly throughout coatings formulations. The materials can also help reduce pigment floating from application through cure, producing consistent color. They are effective in low concentrations, minimizing recoatability concerns.

In an ink formulation the pigment must be dispersed and stabilized to achieve good color strength, gloss, transparency and transfer efficiency. Stable, concentrated dispersions with small particles and narrow particle size distribution potentially can lead to higher gloss and color strength per unit mass of pigment. The push towards waterborne formulations and increasing pigment loading underlines the need for good dispersion and stabilization properties.

The use of polyether amines (PEAs) as dispersants for carbon black has been investigated. PEAs contain primary amino groups attached to the terminus of a polyether backbone. The polyether backbone is based either on propylene oxide (PO), ethylene oxide (EO), or mixed EO/PO. Adsorption, contact angle, and color density measurements indicate that a polyether amine having a high ethylene oxide content and high molecular weight provides the best performance. Surface tension and interfacial tension values decrease with decreasing ethylene oxide. Molecular weight has little impact on surface tension and interfacial tension. Low HLB dispersants (below 5) exhibit poor dispersion stability.

Pigment settling is not always prevented by using wetting and dispersing additives, but there is a noted distinction between 'hard' and 'soft' settling. Soft settling may result from weak flocculation of properly wetted pigments and stirring can easily redispense the pigment. Hard settling occurs due to improper adsorption of dispersant. The result is reagglomeration of the pigment that can only be corrected with high-shear mixing.

DRIERS

See Catalysts

A drier is a compound that catalyzes or accelerates the drying (curing, hardening) of oil, paint, printing ink or varnish, or the crosslinking of polymers or drying oils. Driers are usually metallic – metal carboxylates (sometimes called metal soaps or salts).

Driers are not the same as curing agents, which chemically react with functional groups in the polymer. Driers are catalytic in nature and do not chemically react with the polymeric material. Driers promote or accelerate the drying, curing or hardening of oxidizable coatings vehicles. The most common driers that have been used in paints are metallic salts of monocarboxylic acids, usually C8-C10 branched acids, such as naphthenic acid, and neodecanoic acid as an example. The choice of acid does not seem to have an effect on the drying. The choice of acid primarily affects solubility, stability and efficacy. The acid makes the metal soluble in the resin system. Insoluble salts, such as acetates or chlorides, do not function as driers. Drier levels are always expressed as percent metal on resin solids. Use levels are generally in the ranges of 0.01-0.6%. The metal in all cases is the cation and has the capability of more than one oxidation state.

The drying of oil-based paints occurs through a process that is characterized by oxygen absorption, followed by the formation of peroxide, and subsequent peroxide decomposition. The presence of driers in the paint accelerates the oxygen absorption and the resultant drying of the film.

Traditional alkyds absorb oxygen into their double bonds and break those bonds to form free radicals that can undergo polymerization to give a dry film. Driers accelerate this process, improving the rate of absorption and utilization of the oxygen. Alkyds would dry to a soft film without driers over several days. Driers provide tack-free times of a few hours and hard dry overnight. A metal carboxylate drier catalyzes or promotes the crosslinking of resin polymers or drying oils.

Driers are classified as:

1. Oxidation (catalytic, top driers or surface driers). Examples are: cobalt, manganese, vanadium, cerium and iron.
2. Polymerization (crosslinking drier). Examples are: zirconium, lanthanum, neodymium, aluminum, bismuth, strontium, and barium.
3. Auxiliary (promoters) driers or catalysts. These are typically: calcium, potassium, lithium, and zinc. The first three increase the rate of top dry and zinc usually inhibits the top dry.

Some classifications refer to the oxidation type driers as active or primary driers. Polymerization driers are also referred to as secondary (auxiliary) or through driers and the auxiliary driers noted above are sometimes referred to as wetting driers.

The right choice of drier combination allows an almost quantitative reaction of resin carbon-carbon double bonds and fast, uniform and stable wet coating drying. Any single metal is not sufficient to catalyze fast and uniform through drying which is why mixtures are used.

The oxidative driers promote the absorption of oxygen by the film as well as catalyzing the formation and decomposition of peroxides. These driers promote the surface dry of a coating. The top driers catalyze the decomposition of the peroxides formed by the reaction of the oxygen in the air with the resin or drying oil. This leads to the formation of direct polymer-to-polymer crosslinks (top drying) and also the formation of hydroxyl groups and carbonyl groups on the resin polymer and the drying oil. The hydroxyl groups are then available for through drying or crosslinking by the through driers, which form oxygen-metal-oxygen bridges or crosslinks between polymers.

The proper balance of driers in an oxidation-curing system is essential to stability, rate of cure and development of film properties.

Cobalt is the most active drier and a strong oxidizer. It top dries the film very rapidly. Care must be taken because excess cobalt causes wrinkling and color changes in light-colored paints. Excess cobalt has also caused gelation in some varnishes.

Manganese is also an active drier and is a potent oxidizer as well. It promotes polymerization to a greater degree than cobalt. It is often used alone in certain baking finishes. In air-dry systems it is used along with



auxiliary driers. Manganese has a dark color, which can limit its use.

Iron seems to promote rapid drying by polymerization and hence is used widely in baking finishes where the dark color is permissible.

For air-dry finishes, it is useful in eliminating film tack of some paints.

Rare Earth driers perform better than zirconium under marginal conditions such as high humidity or low temperatures.

Lithium improves the efficiency of other driers and is the preferred esterification catalyst in alkyd manufacture.

Zinc is an auxiliary drier and, in conjunction with cobalt, produces a harder film. It retards the surface drying in order to prevent wrinkling and allows freer access to oxygen, thus permitting hardening through the entire film. Zinc naphthenate is a good wetting agent and often improves gloss.

Calcium is used as an auxiliary drier, usually in conjunction with zirconium. It frequently performs better than any other auxiliary drier in baking finishes. Calcium driers are often added to the grind portion of the paint as auxiliary dispersants.

Zirconiums are used mostly with calcium as a replacement for lead. These show improved gloss, color, and gloss and color retention compared to lead, but do not perform as well as lead under adverse conditions such as low temperature and high humidity.

Aluminum offers outstanding polymerization and yellowing resistance without viscosity instability. Neodymium is a replacement for calcium and zirconium in VOC-compliant resins. It is cost effective and has proven performance. Neodymium and lanthanum are recommended for low-temperature/high-humidity applications. Vanadium is excellent for heavy film build (4+ mils) but has shown some discoloration in white coatings.

Waterborne coatings present a different sort of problem when using driers. The presence of surface-active agents, in addition to ammonia and amines and various resins, make proper selection important – particularly so that seeding does not occur. For waterborne systems some potential problems are as follows: incompatibility between the resin and the drier; potential for seeding; potential for resin discoloration. There are many good water-reducible driers including the rare earths: lanthanum, cerium and neodymium. Vanadium octoate is also available in a water-emulsifiable form.

Driers in high-solids systems also present the following possible problems: resin viscosity build, resin yellowing and slow dry times.

The best sources for starting-point drier combinations are the resin manufacturers who have already found combinations that develop desirable properties.

The change from natural acids like naphthenic acids to synthetic acids like octoates or neodecanoates provided more uniform products to the industry.

Water-Based Alkyd Systems

Recently, there has been renewed interest in alkyd technology as environmental concerns have shifted and resin manufacturers strive to use bio-renewable resources. Alkyd resin manufacturers have found low-VOC options using higher-solids resins and water-based or water-reducible resins. When using these new technologies it is important to keep the same drying characteristics of the conventional paint.

Often water-based alkyd resins are used as a mixture with acrylic dispersions in interior paints and enamels for wood and mineral surfaces. Hybrid alkyd/acrylic dispersions as the sole binder are also used. Generally in water-based alkyd/acrylic systems the acrylic part of the binder dries by a physical process (water evaporation and particle coalescence leading to film formation), and the alkyd part of the binder dries via the oxidative polymerization process catalyzed by driers. Initially, driers typical for solventborne systems were used in waterborne formulations. Because of side reactions with water, amines and other dispersion paint ingredients, driers that are more stable and still reactive were needed. Carboxylates and naphthenic salts in the presence of water undergo hydrolysis, and as a result the availability of metal cations in the organic phase decreases dramatically during paint storage, yielding an increased coating dry time or lack of drying.

To overcome this issue, drier complexes with amines and alcohols were introduced. Standard driers for solventborne systems may be applied in water-based systems after premixing with nonionic surfactants. Metals used in the drying process are prone to hydrolysis; their reactivity towards water increases as follows: $Ba^{2+} < Ca^{2+} < Mn^{2+} < Zn^{2+} < Co^{2+} < Zr^{4+}$. Because of side reactions (e.g., hydrolysis) the efficiency of driers in water-based systems is lower, and compared to solvent-based formulations usually a 100% excess of standard drier is needed. A special class of water-dispersible driers for waterborne alkyds has been developed to overcome this drawback. Such additives may be easily incorporated during the let down process.

A new cobalt-free catalyst that helps to achieve the necessary cure time as well as improve properties associated with water-based, high solids alkyds and alkyd-modified resins is available. Borch® OXY Coat is a new oxidizing catalyst that works as well as or better than cobalt but with none of its disadvantages. It is based on a unique, patented highly active iron complex.

It is supplied as a 1% solution of the complex in propane-1,2-diol. This makes it suitable for use in both solvent- and water-based systems. For those who wish to calculate the metal level as a percent of resin solids, it should be noted that the product contains 1% of the complex that corresponds to 0.09% of iron metal. This iron-based new catalyst demonstrates enhanced properties compared to cobalt, and there is no discoloration. This catalyst can be used in all coatings that dry by oxidation, e.g., alkyds, vegetable oils, epoxy esters, polybutadiene, etc.

DRIER STABILIZERS

Compounds that prevent drier absorption or dissipation resulting in the loss of catalytic power of driers.

DYES (FOR USE IN STAINS)

Dyes are soluble colorants, which do not scatter light, but which absorb certain wavelengths and transmit others. Dyes are generally soluble in a solvent, or they may exist in such a finely dispersed state that they do not scatter light and behave as if they were in solution. Pigments are basically insoluble in the medium they are in.

Dyes are frequently used in the printing and coatings industry where a high level of transparency is required. Dyes have also found their way into automotive finishes because of advanced polymer technology – again because of their transparency and color properties. In general, dyes fall into one of three categories: metal-complex dyes, basic dyes and fat-soluble dyes.

For wood applications, dyes may offer deeper penetration of the wood surfaces and less grain hiding. However, they also fade more quickly than pigmented stains and require more effort to prepare the wood. Water-based dyes tend to raise the grain on many woods because the water penetrates the wood and raises the tiny fibers. Wood should be wetted first, then sanded down, before applying water-based dyes.

Nongrain-raising (NGR) dyes need to be used in a nongrain-raising solvent. They dry faster than water-based counterparts, so application must be faster to avoid lap marks.

Liquid, high-concentration anionic dyes with good light fastness properties can be diluted in water or water/alcohol/glycol mixtures and optimized for interior use in water-based and water-containing wood stains.

Neozapon® dyes are metal-complex dyes, available in powder and, in some cases, high-concentration liquid form (Neozapon L). They are highly soluble in polar solvents, but almost completely insoluble in water. Due to their limited weather fastness, these dyes are recommended for interior use.

There is also a fade-a-way polyurethane dye additive which adds temporary color to clear coats. The polyurethane dye additive takes the guesswork out of applying a clear topcoat by providing temporary color contrast between the topcoat and base coat, aiding in uniform application of the clear coat. After approximately 72 hours, the colorant dissipates leaving a beautiful, clear topcoat.

ELECTROCONDUCTIVE ADDITIVES

Compounds that alter the conductivity or resistivity of a system. Silicon carbide is used in the manufacture of coatings to formulate conductive coatings. It is used in paints that conduct electrical charges away from large motors. Sizes are F400, F800. Silicon carbide is also used for wear-resistant coatings, such as for tanks, tubes, etc. It is usually mixed with an epoxy or resin matrix. It is also put on cutting tools with a proprietary method of application.

A few percent of properly dispersed high-conductivity carbon nanotubes (CNTs) can provide significant conductivity. This, in turn, enables relatively transparent conductive films.

CNTs are basically cylinders of graphene. They are becoming increasingly available in both single-wall (SWNTs) and multi-wall (MWNTs) forms and provide an option for forming conductive transparent films. A small amount of MWNTs introduces conductivity into the polymer film. Because so little of the additive is needed, transparency can be 98% or higher.

One key problem with the use of nanoparticles in coatings is the problem of dispersion. For carbon nanotubes the current method is to load a high amount of dispersants and subject the mix to high shear. Ultrasound is commonly used to provide the shear. However, dispersants can interfere with formulation stability and conductivity. Recently, some vendors have announced dispersant-free CNT suspensions. These may help the commercial implementation of MWNTs and SWNTs significantly.

CNTs are not the only polymeric tools used to achieve transparent conductive coatings or to participate in anticorrosion functionality. Novel materials also include inherently conductive polymers (IHPs): poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate) - PEDOT-PSS - and polyanilines PAAs. Both of these tend to be used in waterborne ink formulations.

EMULSIFIER

See Surfactants

Emulsifiers fall into the category of surface-active materials, or surfactants. In general they are used to produce stable mixtures of two partially immiscible liquids. Emulsifiers allow us to make water-in-oil (W/O) emulsions and oil-in-water (O/W) emulsions. They promote the ease of mixing or dispersibility by lowering the surface tension of the liquid, much as a wetting agent lowers the surface tension of the liquid for application to a solid substrate.

ENZYME-BASED ADDITIVES

Enzyme-based additives can be mixed with coatings to create novel biologically and chemically active coatings, including those that self-decontaminate and detoxify organophosphorus compounds such as nerve gases and pesticides. A new understanding of enzyme biochemical capabilities is leading to the development of innovative, biocatalytic "smart coatings".

Many organophosphorus (OP) compounds are potent cholinesterase inhibitors, accounting for their widespread use as insecticides and chemical warfare agents. Common organophosphorus agents include the chemical warfare agents tabun (GA), soman (GD), sarin (GB), cyclosarin, VX and its isomeric analog Russian VX (R-VX). Historically, most approaches to chemical agent decontamination are post-exposure, focusing on the treatment of surfaces after exposure has occurred and been subsequently detected.

Novel enzyme additives are being commercialized that not only remain stable in paint but, remarkably, remain active for extended periods of time. One self-decontaminating coating additive, OPD_{TOX}[™], is biocatalytic in nature, and represents a paradigm shift for chemical agent decontamination. OPD_{TOX} can serve either as a stand-alone decontamination method or as a complementary approach to existing decontamination techniques and products. When incorporated into a coating, the additive creates a reactive surface that will initiate the process of decontamination immediately upon exposure to organophosphorus pesticides and neurotoxins.

Applied in advance of exposure, painted surfaces containing OPD_{TOX} can continue to degrade organophosphorus compounds after repeated

exposures and remain active following washing. The scientific basis of the product lies in the ability of bacterially derived enzymes to efficiently degrade organophosphorus compounds. The results are novel coatings that self-decontaminate following exposure to organophosphorus compounds, which includes many important environmental and security targets such as the nerve agents VX, GD, GB, thickened nerve agents, and pesticides such as malathion [o,o-dimethyl-S-(1,2-dicarb-ethoxyethyl)dithiophosphate], parathion [o,o-diethyl-o-(4-nitrophenyl) phosphorothioate] and coumaphos [o-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl)o,o-diethyl phosphorothioate].

The enzyme of choice for OP decontamination is organophosphorus hydrolase. Of the six major groups of enzymes approximately 80% of industrial enzymes are hydrolases. Hydrolases are enzymes that catalyze the hydrolytic cleavage of C-O, C-N, and C-C bonds. A class of hydrolase known as organophosphorus hydrolase (OPH) can also cleave the P-O, P-F, and P-S bonds of the organophosphorus compounds.

Of the currently stockpiled nerve agents, VX is the most toxic, as well as the most persistent in the environment after release. In addition to the initial inhalation route of exposure common to such agents, persistent agents such as VX and thickened soman pose threats through dermal absorption.

Enzymatic hydrolysis of OPs occurs when the compound is cleaved at the phosphoryl center's chemical bond resulting in predictable byproducts that are acidic in nature but benign from a neurotoxicity perspective. By comparison, chemical hydrolysis can be much less specific and in the case of VX may produce byproducts that are extremely toxic. Although a number of enzymes have been identified that are capable of detoxifying OP compounds, OPH has the broadest substrate specificity. The substrate range of OPH includes numerous insecticides (paraoxon, parathion, coumaphos) and the neurotoxic chemical warfare agents and their analogs. Catalytic specificities for this family of compounds have been shown to range from rates that are diffusion limited (i.e., paraoxon, P-O bond, $k_{cat}=10^4 \text{ sec}^{-1}$) to rates that are six to eight orders of magnitude lower (i.e., acephate, P-N bond). The enzyme is composed of two identical monomers associated to form a remarkably stable dimeric enzyme with a thermal T_m of approximately 75 °C and a conformational stability approaching 40 kcal/mol. Thus, two of the characteristics essential for the successful application of an enzyme as a biocatalyst, stability and broad substrate specificity, are met in this enzyme system.

As the methods available for enzyme improvement have developed over the past 20 years, it has become increasingly possible to rationally redesign enzymes in order to make them more effective catalysts. In the future, it can be expected that it will be possible to build specific enzyme catalysts for the transformation of a given target substrate. As both rational and random methods of enzyme improvement evolve, enzymes are being developed to play an expanding role in the coatings industry.

Enzymes offer substantial advantages over chemical catalysts in a traditional industrial environment. They are biodegradable, work under mild conditions, often can provide benign alternatives to existing processes, and are not associated with the production of hazardous by-products or secondary waste. By tailoring enzymes for specific purposes, one can develop additives and mixtures of additives that have been bioengineered to exhibit increased activity and/or specificity for one or more chemical warfare agents. While there are a large number of potential military applications for self-decontaminating surfaces, including vehicle interiors (aircraft, ground support, marine), barracks and housing, this self-decontaminating technology has numerous non-military commercial applications as well, including surfaces in hospital clean rooms, community safe rooms, schools, government facilities, industrial sites, mobile decontamination facilities, and public transportation systems.

The development of cost effective, self-cleaning surfaces will mitigate contact hazards for first responders, decrease the time needed for recclamation of contaminated spaces, and minimize environmental impacts commonly experienced with caustic solutions and foams.



ESSENTIAL OILS

Essential oils, consisting mainly of highly volatile terpenes, are derived from crushed plant material – leaves, flowers, fruit, peels, seeds, roots, bark or wood. The precious oils are extracted from these materials by physical processes. A commonly used method is steam distillation, in which steam entrains the volatile oils. The “agrumen” essential oils contained in the peel of citrus fruit are extracted by cold pressing.

Unlike fatty oils, such as olive or sunflower oil, which consist mainly of non-volatile fatty acid esters, essential oils evaporate quickly, usually without leaving grease spots on paper or textiles. Their volatility is the reason for their other name of “ethereal” oils, originally meaning “celestial” or “transient.”

Only one percent of all known plant species produce essential oils. Many of these plant fragrances attract pollinating insects and so help to propagate the species. Others protect against pests. Some essential oils act as deterrents to particular creatures. For example, moths steer clear of lavender blossom.

Many individual substances isolated from ethereal oils have a deterrent effect. For example, the methyl anthranilate found in orange blossom oil repels birds. Mosquitoes and horseflies avoid the smell of eugenol and geraniol. Eugenol is the main component of clove bud oil and cinnamon leaf oil. Geraniol is present in high concentrations in palmarosa and citronella oil, and is one of the most widely used fragrances of all. That’s why these two fragrances are used in mosquito repellents. For several years, research institutes, particularly in tropical regions, have been looking for ways of using ethereal oils to protect against insects like mosquitoes or termites and certainly as a way of alternatively controlling or embanking malaria and yellow fever.

Some ethereal oils and their components have an effective antimicrobial action and some can inhibit the reproduction of bacteria and molds. Though natural products, they ultimately derive their effect from chemicals they contain, such as phenols and aldehydes.

Several scientific studies have shown that the oil derived from red thyme is highly effective against both bacteria and molds. The oil mainly derives its action from thymol, its main constituent. Thymol is around 30 times as effective as the disinfectant phenol that was formerly commonly used in hospitals (also known as carbolic acid or hydroxybenzene). The strong antifungal effect of clove bud oil or cinnamon leaf oil has been clearly demonstrated in a number of studies, while cinnamon bark oil is notable for its strong antibacterial effect. But, even with the strongest-acting oils, the effect never lasts long – they evaporate too quickly. However, as compensation, the oils and their components have another advantage: so far as is known, microorganisms do not develop resistance to essential oils.

The fascination that ethereal oils hold for many people is the result of the psychological effect of natural fragrances. Like all fragrances, ethereal oils can affect people’s moods and trigger emotions. The reason is the close link between the olfactory sense and the limbic system. This part of the brain – very old in evolutionary terms – controls emotions, affects and urges. The brain remembers which odors have occurred in which situations. Encountering a particular odor again rekindles the memory of the former situation.

Ethereal oils could give plasters, paints and other coatings hitherto inconceivable properties, which would be invoked simply by exposure to moisture. However, there are two obstacles to using such oils in the construction industry. First, many essential oils are very chemically sensitive. Several of their ingredients are oxidized by exposure to air and light; others are chemically changed by heat or the effects of acids or alkalis. This renders oils ineffective; in extreme cases they are even transformed into harmful substances. Some components would not even withstand the shearing action of mixing them into the plaster-mortar paste or a liquid wall paint. Essential oils are also very volatile and would evaporate from the applied coating or surfacing within just a few days.

There is a way to protect the sensitive fragrances by molecular inclusion, mainly in β -cyclodextrin. The ring-shaped molecules of this sugar can receive a fragrance molecule in their cavities. In the cyclodextrin molecules,

the glucose building blocks are arranged so that they have a lipophilic cavity (i.e., one with an affinity for fat) in their interior. This cavity can receive another lipophilic molecule as “guest,” provided that it has the correct size and shape. The cohesion between the two molecules is relatively weak (van der Waals forces), so that the guest molecule can be liberated again under suitable conditions. The weak van der Waals forces in such inclusion compounds leave the two counterpart molecules unchanged.

This ability to enclose other substances reversibly makes cyclodextrins invaluable in many products and industries, such as household and personal care, pharmaceutical and cosmetic preparations, textiles and foods.

Each cyclodextrin molecule acts like a small strongbox, securely protecting a fragrance molecule against the chemical effect of its surroundings and the key to opening the tiny strongbox is water. When water acts on the inclusion compound, the fragrance is liberated in its original form.

Thus, a cyclodextrin inclusion compound offers a convenient vehicle for employing fragrances in construction applications – like flooring or plasters – that are not exposed to direct rain. Here, atmospheric moisture determines how much fragrance is released to the ambient air. The more humid the air, the more is liberated. The sensitive fragrance does not evaporate away, and it cannot be chemically changed. The protection and release mechanism is so effective that a coating still liberates almost as much fragrance after several years’ use as it did initially.

Several construction material manufacturers are currently testing binders containing fragrance-complexes under various climatic conditions to exploit their applications potential and gather early practical experience. A main focus is on applications in public areas, such as subway and light rail systems, airports, underground garages and public restrooms. The particular fragrance released will depend on the application.

For use in public restrooms, the manufacturers choose a fragrance that most effectively combats mildew growth on the walls. The wall covering or paint would then emit the most active substance under just those conditions that usually promote mold growth. A good candidate for such applications is the β -cyclodextrin/thymol complex.

Construction material manufacturers, too, are very interested in the repellent effect. In tropical Asia, tests are being carried out on paints that emit a mosquito-repellent odor. Early results are highly promising.

Another potential application lies in the bird-deterrent effect of methyl anthranilate. A coating material containing this fragrance in the form of a cyclodextrin inclusion compound could keep pigeons away from walls and masonry ledges, protecting them against bird droppings.

All the signs point to traditional construction binders soon having new functions – all of them based on renewable plant extracts.

EXTENDERS

See *Microspheres*

Extenders (extender pigments) are materials that are added to coatings and have many functions. We provide a definition of extenders here, although we do not consider them as additives per se; typically extender use level in a formulation is considerably greater than that of additives, which is normally less than five percent. The main extenders are carbonates, oxides, silicates and sulfates.

Current formulation practice more appropriately uses these minerals as functional fillers. They are chosen to optimize coating stability, rheology and application properties, and to enhance dry film properties. Very fine-particle-size silicates, particularly certain kaolins and ultrafine talcs, are used as pigment extenders in a more literal sense. The pigment that is extended is TiO_2 . These extenders effectively separate the individual TiO_2 particles and provide the optimum pigment spacing for maximum opacifying effect. Pigment extenders are used in this way to reduce the amount of relatively expensive TiO_2 required for a given level of opacification and whiteness.

Extenders are available in a range of particle sizes and in a variety of shapes including spheroid, needles, fibers and plates. Particle size, size distribution and shape influence many of the physical properties of coatings. They can have positive and negative effects on properties such as scrub resistance, exterior exposure resistance, gloss and sheen.

Nepheline Syenite

Nepheline syenite is a silica-deficient functional filler and additive used globally in a variety of coating, adhesive and ink applications. It is composed of three minerals: soda and potash feldspar, and the mineral nepheline. Although it is deficient in crystalline silica, nepheline syenite otherwise provides physical performance properties that duplicate ground silica fillers. Since nepheline syenite functional fillers are naturally derived, and deficient in free-silica and heavy or transition metals, they are typically less burdened by regulatory requirements such as REACH, RoHS and TSCA.

Nepheline syenite is considered a moderate gloss reducer based on its low oil absorption and combination of angular, rectangular and nodular shapes. Mohs hardness on the 1 to 10 scale is about 6. The particles themselves are moderately hard or rigid and possess high compressive strength, providing scratch and abrasion resistance in the polymer matrix. The low oil absorption contributes to the ease of dispersion and low viscosity build. Chemically, commercial nepheline syenite is anhydrous and consists of sodium potassium aluminosilicates. The surface chemistry of nepheline syenite is ideal for 100% solids and low-VOC systems. Owing a net negative surface charge or a natural "detergency" in aqueous systems, nepheline syenite accelerates dispersion times with little or no polymeric dispersant requirements, although dispersants aid in suspension and shelf life.

Nepheline syenite is a versatile and unique functional filler, offering properties that are useful in a wide variety of clear and opaque coating applications. Newer ultrafine nepheline syenite sizes have refractive index and physical properties that are particularly well suited for use as a performance additive in radiation-curable coatings, inks and adhesives.

Ultrafine nepheline syenite has exceptionally high light transmittance in organic binder systems commonly used for radiation curing in the critical UVA and UVB wavelengths. Thus, unlike other mineral fillers and pigments, ultrafine nepheline syenite is not expected to "interfere" with the UV-curing process. Experiments with regulated curing energy on both pendulum hardness development and double bond conversion rate suggest that it is possible to improve cure efficiency, allowing faster line speeds and/or reduced energy consumption, when ultrafine nepheline syenite is added to the system.

Solid Alumino-Silicate Glass Spheres

Solid alumino-silicate microspheres (<1 to 300 micron) and solid paramagnetic microspheres can also be used as functional fillers in coatings. They are naturally spherical and beneficiation removes surface salts to enhance product performance. The hardness of the glass microspheres (Mohs 5-6) ensures low oil absorption thereby reducing the amount of resin needed in a given formulation. One advantage they have is their density, which is considerably lower than other extenders typically used in coatings.

Spherical magnetite can be used as a highly loaded polymer to form a shield for sensitive electronic equipment. These spherical particles can also be coated to change their surface chemistry for use in various coatings, elastomers, thermoplastics, thermosets and plastics.

Hollow Spheres and Opacity

Hollow Sphere synthetic Pigments (HSPs) are standard value-added components in coatings formulations and have worldwide acceptance. A hollow sphere is prepared through an emulsion polymerization process. In the wet stage, the inner hole is filled with water. On drying, this encapsulated water will diffuse through the polymeric outer shell, and then be replaced by air. Because of the difference in refractive index of the shell ($n \sim 1.5$) and that of the air ($n=1$), light scattering becomes effective and the dry HSP appears like a white, opaque powder.

The polymeric shell consists of a very hard polymer, capable of withstanding the compressive forces that develop during the drying process of a coating film. The HSP has no film forming capability, and the same rules as for common pigments and extenders apply for the calculation of the PVC.

In a coating, the main contributor to opacity is TiO_2 , which, due to a high refractive index and optimized particle size, has very efficient light scattering. Its efficiency, however, is affected by the presence of large-particle-size extenders in the formulation (crowding effect). It is also, on a dry volume basis, one of the most expensive ingredients in the formulation.

The 'pigment crowding' effect normally takes place at high pigment concentrations, but is also perceptible at lower levels when coarse extenders are used in the formulation. When increasing the PVC either with extenders or HSP, the pigment particles are forced to pack inside the voids between the coarse extender particles. The inter-particle distance is no longer optimized, thus their hiding efficiency is reduced.

The second contributor to opacity is air. Above CPVC, paint films become more porous and their porosity increases, thus their opacity (dry hiding effect). But, on the other hand, the higher the film porosity, the worse the resistance properties. The hollow sphere synthetic pigment concept directly addresses the above problems by:

1. Introducing encapsulated air voids into the paint film, contributes directly to hiding without increasing the film porosity (no degradation of the resistance properties). This effect is valid below and above CPVC.
2. Optimizing the spacing between the TiO_2 particles improves the scattering efficiency of the titanium dioxide.

Applications for Opacifying Polymers

In architectural coatings, opacifying polymers are well known and widely used for their ability to scatter light and, at the same time, space titanium dioxide without affecting the overall performance. In paper coatings, HSPs not only bring opacity but also excellent gloss and improved printability. Current technology permits the use of hollow sphere synthetic pigments in various industrial applications like graphic arts or metal maintenance coatings and traffic paints. In these areas the use of titanium dioxide is significant, and reformulation with a synthetic opacifier not only brings cost savings but also improved performance like better early block resistance in metal coatings, better dirt pickup resistance and exterior durability in traffic paints, and a better abrasion resistance and stability in opaque inks application.

In other industrial segments due to severe application conditions (i.e., high curing temperatures) the existing products have some limitations. Their shell is not strong enough to resist high temperature and has a tendency to collapse, which leads to a loss of efficiency.

FIBERS (MINERAL-BASED)

Fibers may be added to paint formulations to enhance coating properties and reduce cost. For years, fibers have been used as a key component in intumescent paint formulations. Other applications include architectural, industrial and special purpose coatings. Fibers create a micro network within the coating film that creates strong, durable and highly effective coating films. Small amounts of fiber can be very effective in reducing the amount of binder needed. Because of the regulatory emphasis on low-VOC coatings, fibers help to restore mechanical properties that are sometimes lost in switching to waterborne or low-VOC coatings.

Some fibers are mineral-based and spun from high-purity volcanic rock. Because of their high-alumina, low-silica chemical composition they are classified as non-carcinogenic. These types of fibers can have surface treatments such as cationic surfactants, sulphursilanes, aminosilanes and rubber.

Fiber-added coating applications include intumescent paints. Fibers are a good raw material for intumescent coatings because they have high thermal and dimensional stability. Many fibers are dimensionally stable up to temperatures of 750 °C (~1380 °F), and some maintain their shape above 1000 °C.

In traffic-marking paints the fibers hold the reflective glass beads longer, thereby prolonging the reflective life of the coating. They are also beneficial in roof coatings where they reinforce the film and provide chip and impact resistance, and UV degradation resistance. When used in floor coatings they provide non-slip properties. In marine coatings fibers provide excellent strength and flexibility.



The addition of fibers increases viscosity. However, at high shear rates the impact is limited. At low shear rates, the difference becomes more significant. These rheological characteristics allow the applicator to apply thicker layers by reducing the tendency to sag.

FISH EYE PREVENTER

See *Anti-Cratering*

Additive that prevents the wet film defect manifested by the formation of a pattern of small 'dimples' or 'fish eyes.'

FLAME RETARDANTS

See *Lubricants (Solid)*

Chemicals or chemical preparations that will reduce flammability or retard the spread of flame.

Combustion occurs when a substance is heated to its flammable temperature in the presence of oxygen. As it is being heated it starts to decompose, and, as it does so, it produces flames. Over the years we have become increasingly conscious of safety and, as such, are concerned about the materials that are used in the construction and finishing of buildings. This includes coatings. The application of a flame-retardant coating can help to reduce the combustibility of that coated surface.

Flame retardants are compounds that are decomposed by heat into nonflammable fragments. These fragments have the ability of slowing flame spreading and may even retard or suppress the combustion reaction. This is accomplished by suppressing oxygen availability, the building up of protective layers of char at the surface, inhibiting the combustion reaction within the flame area, or by other mechanisms.

Inorganic compounds that are used as flame retardants include aluminum trihydroxide [Al(OH)₃], magnesium hydroxide [Mg(OH)₂] and boric acid. Organic flame retardants tend to fall into two categories: (1) phosphorus compounds such as phosphoric and phosphonic acid esters, such as long-chain ammonium polyphosphate products; and (2) halogenated compounds such as chlorinated paraffins, dibromoneopentyl glycol, tetrabromophthalic acid anhydride, brominated diphenyl, chlorine and bromine containing polyols or diphenyl oxide compounds together with antimony trioxide. Also chlorinated paraffins have been added to latices to impart flame retardance.

Liquid chlorinated paraffins improve the flame resistance of coatings, are cost-effective extenders of most resins and can be nonvolatile plasticizers. They also improve adhesion, water and chemical resistance, and oil and gas resistance. Dispersions and emulsions of resinous and liquid chlorinated paraffins are available and are useful in both cationic and anionic emulsion systems because of their non-ionic bases. In addition to contributing to flame retardance, they improve adhesion, impart chemical and water resistance, and allow the user to formulate aqueous rather than solvent systems. Applications include rubber coatings, paper and fabric coatings.

Compounds that will cause char formation, particularly those with a large number of carbon-carbon double bonds or those that swell (intumescent systems), such as cellulose and sugar derivatives and melamines, are also used to enhance flame retardation.

Zinc borate is used in many fire-retardant and intumescent coatings, usually in combination with chlorowax or some other halogenated source. Other fire-retardant additives, such as antimony oxide and/or alumina trihydrate, are also used to provide synergism leading to a high degree of fire retardance. Zinc borate behaves as a fire retardant and smoke suppressant.

Certain monomers – copolymers of vinyl chloride and vinylidene chloride – tend to be less flammable than non-chlorinated polymers, but because chlorine is less effective than bromine or phosphorus, additive flame retardants are still needed.

Work has also been done in this area using dibromostyrene-based latices. These are copolymers of dibromostyrene with various monomers, depending on the desired Tg of the final coating. Dibromostyrene-based butadiene and acrylic latices have the desired physical properties

for use in coatings, adhesives and sealants.

Fire-retardant coatings that are non-intumescent provide retardance through the presence of special additives. The most commonly used is antimony trioxide used with halogenated materials such as chlorinated paraffins. Antimony trioxide alone is not effective; mixed with a halogenated species it is very effective.

Zinc borates and barium metaborates are also used to improve the performance of antimony trioxide. When they melt, they form a glass-like material that seals off the substrate from the flames.

Phosphates are also good retardant additives, and during a fire they will release phosphoric acid that will break down cellulose into a char and lessen the amount of material evolved and released. These have been used quite effectively.

A new, low-load-level flame retardant, FlexB™, is a boron-based, non-halogenated additive for nylon, epoxies and water-based coatings. Material testing has achieved UL-94 V-0 ratings with loading levels as low as 3%. FlexB is targeted at high-performance materials where traditional high load levels negatively affect weight, strength and other physical parameters. FlexB shows increased flame retardance over the more traditional additives due to its ability to bind into the backbone of the polymer, thereby providing four levels of protection: off-gassing, water production, charring and thermal shielding.

Intumescent coatings are particularly interesting because when subjected to the extreme heat of a flame these agents expand to nearly a hundred fold of their initial volume. In the process they prevent the flow of oxygen.

Intumescent coatings are fire-retardant coatings that protect the substrate by puffing up when exposed to high temperatures and forming an insulating protective layer over the substrate. Initially this type of coating, when exposed to high temperatures, will char and expand greatly to retard the spread of the flame by essentially forming a foamed barrier. The expanded coating is often over 100 times the thickness of the original coating.

FLASH RUST INHIBITORS

See *Corrosion Inhibitors/Anti-Rust*

Chemical compounds that prevent the phenomena of rust formation immediately upon the application of a waterborne coating to an oxidizable metal substrate. This occurs before the coating film has dried and usually appears as small circular rust spots. Flash rust inhibitors are typically water soluble or dispersible and are added to the coating to prevent rust from occurring during the drying stage. To prevent flash rusting, proper control of pH is very important. In addition to pH control, the use of flash rust inhibitors such as sodium and/or ammonium nitrites, nitrates, phosphates and benzoates, barium metaborate, etc., in small quantities (typically about 0.1%) will eliminate and prevent a problem from occurring. Amino materials such as morpholine and AMP also may help.

FLATTING (MATTING) AGENTS

A wide variety of natural and synthetic materials that are added to coatings to primarily affect gloss are called flattening agents. When light is reflected from a smooth surface, the surface appears to be glossy. When light is scattered as it hits the surface, instead of being reflected, a matte appearance will be created.

Gloss is one of the key properties of a coating. The observed gloss of a film is dependent upon the angle and intensity of incident and reflected light from a surface. It is a function of the smoothness of the coating's surface. A very smooth surface will reflect most of the light rays, so that the angle of incidence is the same as the angle of reflectance. As a surface becomes less smooth, incident light rays are reflected at various angles, and the surface is perceived as being less shiny and of lower gloss. In order for light to be reflected in many directions instead of at the same angle, it is necessary to introduce some degree of micro-roughness to the surface of the film. The reduction in gloss to give satin, semigloss, flat or matte finishes can be controlled by adding pigments and extenders – or materials called flattening agents.

Any tiny irregularities in a coating film will cause light to scatter. Flattening agents reduce gloss by imparting micro-roughness to the paint surface as it dries and cures. The rough surface diffuses light rather than reflecting it; the result seen by the eye is a matte surface. These agents include particles with dimensions that range from 1 to 50 microns in diameter. Thermoplastic flattening agents are being increasingly used for this application and, interestingly, the smaller particles reduce gloss to a greater extent than do the larger particles.

Gloss is also affected by conditions under which a film forms, such as the coating application method, drying temperature, humidity, rate of solvent evaporation and solvent composition. These factors can cause an increase or decrease in gloss, depending on the particular coating formulation. Factors such as high temperature or slow solvent evaporation rate, which allow the polymeric resin to relax and find the most thermodynamically favorable position, tend to give the smoothest surfaces and highest gloss. The method of applying a coating (spray, brush and roller) has an influence on the gloss as well.

The components in a formulation can also affect gloss. As film formation proceeds, volatile or nonvolatile leveling aids are sometimes required to assist relaxation of the polymeric film former to minimize the surface area of the coating and give a smoother surface. Other materials such as slip and anti-blocking aids can be used; these are meant to migrate to the surface of the film to perform their intended function. These materials change the characteristics of the surface and hence the gloss.

Flattening agents are available in different chemical compositions and particle sizes. Common inorganic materials include silicas for clear coatings, and extender pigments, such as clays, talcs and carbonates, for pigmented systems. Hydrophilic materials, which include some silicas, must be stored under conditions that prevent moisture pick-up by hydration. The inadvertent addition of moisture to solventborne systems can be detrimental, while the additional water of hydration in waterborne systems might have to be compensated for to retain the desired solids level.

Silicas

Silicas have typically been used as the traditional flattening agents in the industry. Silicas with large particle size generally improve flattening efficiency; surface smoothness and clarity of the film will decline. Small silicas improve surface smoothness but are therefore less efficient at flattening.

The performance of silica flattening agents is also influenced by surface treatments such as organic wax treatment and inorganic surface treatment. Surface treatment is used to prevent settling and also to improve mechanical properties and often adhesion.

Silicas can be used in solvent and aqueous systems, and in virtually all types of resin systems: acrylics, vinyls, polyesters, nitrocellulose, urethanes and alkyds. The reduction of gloss can have a significant corresponding effect on increasing viscosity that makes the job of formulation sometimes difficult. Silicas are available as: precipitated silica, fumed silica, diatomaceous silica and silica gels.

The synthetic silica flattening agents are used to produce low-gloss finishes in organic solventborne systems, waterborne and high-solids coatings. Typically, waterborne finishes cannot withstand high shear that can destroy the emulsion and cause foaming. So the flattening agent must be easy to wet out and incorporate into the coating under low-shear conditions.

Precipitated and Fumed

Precipitated and fumed silicas are not resistant to overgrinding. In some cases, the overgrinding may occur under relatively low shear such as obtained in mixing while tinting a batch of paint. Silica gels are resistant. Fumed silica has a pronounced effect on thickening; silica gels do not. In fact, their impact on viscosity is minimal.

Diatomaceous Earth

Diatomaceous earth (silica, SiO₂) has been used extensively in the coatings arena as a very efficient flattening agent, achieving appearance characteristics from a dead flat to a silky low luster in a range of coatings. It

imparts increased toughness and durability, added 'tooth' for adhesion, and improved sanding properties. Because these microscopic particles are irregularly shaped, they diffuse light and are used to impart degrees of flatness to coating films.

Diatomite consists of the siliceous skeletal remains of single-cell aquatic plants known as diatoms. The diatomite structure is porous with microscopic voids that serve to control vapor permeability and for the reduction of blistering and peeling and faster dry time. The use of this type of material results in uniform gloss and sheen reduction.

Silica Gels

Modern silica gel technology enables the production of highly pure, porous products. A silica gel is an amorphous form of silica composed of nearly 100% silicon dioxide (SiO₂) produced synthetically in a liquid process. Silica gels belong to a class of synthetic silica materials known as hydrated silicas, which have an average water content of 6% to 8% by weight. Silica gels are produced from the acid treatment of an aqueous sodium silicate solution.

Mixing sulphuric acid and sodium silicate under controlled conditions produces the base gel from which all types of silica gels are made. This glass-like, solid gel material is broken down into granules, then washed and dried to produce the highly porous material needed for matting agents. Physical parameters such as porosity, pore size and surface area can be manipulated to produce a range of different silica gel types. The physical properties of silica gel differ from other specialty silicas. The internal structure of silica gel is composed of a large network of interconnected microscopic pores that attract and hold water, hydrocarbons and other chemicals by the mechanism of physical adsorption and capillary condensation. This huge pore volume and extensive surface area gives the silica gel many of its unique properties.

The rigidity of the silica gel particle is higher than that for precipitated silica and thus better resists the shear forces arising during the manufacture and application of the paint. Silica gels can influence rheological properties, although other agents are typically preferred for rheological control purposes.

The efficiency of the matting agent depends on the type of silica, particle size distribution and porosity of the particle. A high porosity is a key feature of a modern matting agent as it enables the formulator to limit the addition rate of a matting agent in a formulation. Unfavorable viscosity effects, as well as limitations in coating surface properties, can be avoided. A new milestone in micronized silica gel technology was reached by achieving a pore volume of more than 2 mL/g for a micronized silica. Today, matting agents for industrial applications are available in a variety of particle sizes.

The application segments for silica gel matting agents include coil coatings, industrial wood coatings, general industrial and automotive coatings as well as printing inks, leather/textile coatings and decorative coatings. Coil, wood and furniture coatings are the applications with the largest volumes, but radiation-cured coatings and other coating systems as well as printing inks also employ silica gels. The solventborne paint sector has been more important for silica gel than waterborne coatings. However, the pressure to reduce VOC emissions and formulate solvent-free paints has led to the development of grades of silica gel, which are suitable for formulation in powder, ultraviolet, and waterborne coatings.

Surface-treated silica gel flattening agents for high-performance OEM and DIY wood coatings and other clear finishes are available. They contain an organic additive that aids in dispersion and suspension, and imparts mar- and burnish-resistance to the finished surface.

Silica gels are more resistant to overgrind compared to precipitated silica or fumed silica. This resistance provides gloss stability for demanding applications such as coil coatings. Synthetic silica gels contain internal voids – thereby giving pore volume or void volume. As pore volume increases, the specific volume of the particles increases while maintaining a constant weight. The result is more particles per unit weight, which yields higher flattening efficiency. The increase in pore volume must be balanced against application viscosity.



Selection and Applications

It is not easy to select the best flattening agent. It depends on the end use of the coating, as well as dry film properties required: clarity, smoothness, mar resistance and weatherability. Also the choice of flattening agent can make a significant difference in application characteristics such as viscosity, re-dispersion and gloss stability. Optimum flattening efficiency results when a flattening agent is selected that has optimum pore volume – that is, more particles per unit weight.

Particle size is also important, as it will affect flattening and surface clarity and smoothness. In general, the larger the average size of the flattening agent, the rougher the surface and the lower the ratio of sheen:gloss. For certain markets this becomes very important and formulators need to determine which agents to use depending on this consideration.

Average particle size can affect the flattening efficiency and loading level at constant film thickness. Silicas are available in a variety of particle size ranges. In general, the larger sizes generally give higher flattening efficiency and are also less sensitive to variations in film thickness. Larger sizes also give rougher surfaces.

In some cases, the flattening agents yield a smoother surface than the full gloss coating does, which indicates that thin film coatings can retain the features of the substrates. This can be important in paper coatings and wood sanding sealers, where it is desirable to obtain a smoother surface by filling voids in the substrate.

Silicas are used in architectural coatings and varnishes, coil coating and general industrial finishes, industrial wood finishes, topcoats and primers for corrosion resistance, and textured and suede effect finishes. Some coatings segments need very high-quality synthetic silicas – coil coatings in particular. Coil coatings are also very dependent on gloss stability.

Clear coatings for fine furniture and other wood products are flattened to obtain a satin finish. The satin finish is a desirable aesthetic feature, obtained by lowering the 60° gloss while maintaining a relatively high 85° gloss, or sheen. Clarity is a very important criterion for wood finishes and cannot be obtained with naturally occurring flattening agents, due to their high index of refraction compared to the resin system in the coating. This difference in refractive index creates internal haze. Therefore flattening agents must be used that have a similar refractive index to the resin system for both solvent- and waterborne systems. The silica gel technology enables these flattening agents to be used in waterborne clear wood satin finishes.

The clarity of the coating can be achieved by matching the refractive index of silica and the resin system and controlling the particle size. Surface treatments, or lack thereof, can influence this property significantly.

Settling is a bigger problem in waterborne coatings than it is for conventional solventborne systems. As such, wax-treated silicas may sometimes be used because they provide better suspension properties. But great care has to be taken during the dispersion because if the wax is separated from the silica, it will tend to cause craters in the final film. For solventborne systems, silica dispersion is always post additive. Hydrous silica has water-filled pores and does not cause coagulation problems.

To incorporate porous silica into waterborne systems, the silica should be pre-wet by dispersing in water, coalescents, cosolvents and thickeners prior to addition to the polymer dispersion.

Micronized Biopolymer

Biotechnology opened the door to an entirely new matting additive with an unprecedented combination of properties compared to conventional matting agents, such as waxes and silicas. The new additive is based on a biopolymer, which is obtained by bacterial fermentation from sugars. The biopolymer-based product originates from renewable resources, is fully biodegradable and GMO (genetically modified organism) free.

The matting performance of the new biobased product was tested in three different solvent-free UV systems: a polyester acrylate, a polyurethane acrylate and an epoxy acrylate containing a photoinitiator and DPGDA as reactive diluent. Untreated and treated silica were tested for comparison.

The matting efficiency of the novel micronized biopolymer, commercially launched as CERAFLOUR® 1000, showed excellent matting with

no detrimental influence on viscosity. Compared to treated silica, the matting efficiency of the biopolymer was higher or equal in common UV systems. In polyester acrylate and urethane acrylate systems the gloss could be reduced to 10-20% at an angle of 60° with 7.5% of added biopolymer-based additive. This is comparable to non-treated silica and better than treated silica.

The haptic properties of an object describe the sense of feeling and are a popular field in research. It is becoming increasingly important from a product's competitive point of view. The haptic properties can be adjusted by the properties of the coating. Good haptic is a smooth surface with a soft touch effect. The biobased additive has been consistently judged as the smoothest and most pleasant. It is noteworthy that improved haptic properties don't generate an increase in slip.

In general, applied films containing the biopolymer-based additive show good leveling. In addition, the additive may improve the scratch and abrasion resistance of a coating. Regarding the enhancement of the mechanical film properties, the biopolymer-based additive performs better than silica and polymer matting agents, but is inferior compared to a modified HDPE wax. Combination with modified HDPE wax is recommended to achieve additional improvement of mechanical resistance. With the biopolymer-based additive, burnishing or polishing effects and finger marks are not observed.

This biopolymer-based additive is 100% based on renewable resources and is completely biodegradable under normal conditions, such as landfills, with zero toxic waste, as it is ultimately converted into carbon dioxide and water. The key benefits are excellent matting efficiency, especially in UV systems, combined with high transparency and a warm, smooth haptic feel without influence on slip. The additive improves scratch, abrasion and blocking resistance. It can be used in solvent-free, solventborne and waterborne systems without detrimental influence on viscosity. Easy incorporation without dust formation and foam stabilization is combined with good storage stability of the coating systems.

CERAFLOUR 1000 biodegradable polymer can be used for aqueous, rad-cure, solvent-free and solventborne systems providing wax-like properties to improve matting efficiency and haptic (soft-touch).

Other Agents

Organic Particles

More recently, spherical organic particles are finding increased use as flattening agents in coatings. These particles are smooth spheres and have a much-reduced effect on viscosity than inorganic particles. These particles can be reproducibly prepared to specific particle sizes. Some examples are: crosslinked poly(methyl methacrylate), crosslinked poly(butyl methacrylate) and crosslinked polystyrene. The different levels of crosslinking control the amount of swelling the particles undergo in 'good' solvents for the particles.

Thermoplastic particles do not form aggregates. Thus they are readily dispersed and are not affected by typical shearing forces in preparing master batches, although procedures that minimize high shearing conditions are recommended. Organic thermoplastic crosslinked spherical particles offer a cost-effective alternative to the more conventional inorganic flattening agents. The spherical particles are readily dispersed, do not significantly affect viscosity of the coatings formulation, and are available in specific particle sizes and distributions. High-melt-point polypropylene waxes are also used to control gloss in a variety of coatings. They may also contribute to a number of other properties such as anti-mar, anti-block, abrasion resistance and metal marking resistance.

Stearates

Metallic stearates improve suspension of solids, modifying viscosity and imparting flatness. Fine particle size and limited solubility in solvents make calcium stearate a highly suitable flattening agent for paints, varnishes and lacquers. It is especially useful when low viscosity is desired. Because of its low solubility in vehicles and solvent, thickening action is minor despite heat encountered during the manufacture or application of coatings.

Calcium stearate also aids in pigment suspension and viscosity control. It produces a mild thickening effect and provides a good means of controlling body, sag and flow characteristics. Its fine particle size permits mill grinding with other pigments to obtain fine dispersions.

Zinc stearate is used in the production of lacquer sanding sealers. It imparts the necessary sanding characteristics to nitrocellulose and ethylcellulose-based films, seals the pores of wood and gives a flat, hard finish. Zinc stearate is used for grinding of fluid pastes that can be discharged from mills even where high temperatures are encountered, and for lacquer films that have the maximum degree of flattening consistent with good film hardness. Zinc stearate is used as a flattening agent and sanding aid. Its low gelling characteristics give excellent flattening to paints since they can be subjected to high temperatures that develop in some dispersion operations without danger of excess viscosity increase.

Wax Dispersions

Wax dispersions aid in imparting a matting effect to most aqueous coatings, while enhancing properties such as abrasion resistance and water repellency. Some of the new wax additives are characterized by large particle size and are designed to highlight the positive properties of large-particle-sized wax and minimize unnecessary interaction from dispersing agents.

As a coating film dries, wax particles are transported to the film surface as a result of the turbulence flow induced by water evaporation. Because of the large particle size, protruding wax particles create a certain degree of micro-roughness, induced as the film shrinks. As a result, the incident light is scattered instead of being reflected, conveying the impression of low gloss or a matte appearance. The degree of micro-roughness is determined by the number of particles present at the surface and this depends on wax properties such as: particle size and particle size distribution; particle density; and amount of matting agent incorporated.

Unlike wax emulsions, where the particle size is much lower than 1 μm , large particle size wax dispersions modify the optical properties of coatings. They reduce gloss but also significantly impart other surface properties such as enhanced scratch, mar and abrasion resistance; improved barrier properties such as water repellency; enhanced slip and anti-blocking; and enhanced soft-feel. In addition the new wax dispersions are totally solvent-free; do not contain APE; have a reduced amount of surfactant; high solids content; and are easily incorporated by single mixing. Typical application areas include wood coatings, decorative and industrial coatings.

Low-Energy Cure

For low-energy cure systems (such as UV or EB), flattening is more difficult because it does not depend on solvent evaporation and film shrinkage. As a general rule, slow-curing systems and slow response at the film surface will lead to a situation where flattening is easier. For example, unsaturated polyesters are slow to cure and are easy to flat.

The combination of specific amorphous, synthetic silica combined with a specific polydimethylsiloxane surface treatment has been used successfully to improve matting efficiency and provide high transparency and low viscosity.

Powder Coating

Flattening, or matting, concepts for powder coating generally involve either (a) the addition of gloss reducers, which are not supposed to interact with the curing mechanism such as extenders or waxes; (b) the addition of matting agents that influence the curing mechanism in terms of acceleration or inhomogeneous crosslinking (amine salts of carboxylic acids and multifunctional cycloaliphatic carboxylic acids); or the dry-blending of formulated powder coatings with different reactivities. New matting agents are being developed that are free of waxes and amines, and therefore can provide non-yellowing characteristics to many coatings.

Nanoparticles

One of the more interesting applications of nanoparticles is in matte coatings, a particular challenge in the 100% solids market. Most matting agents substantially increase viscosity, a problem that is usually addressed by the addition of either organic thinners or water. This solution however cannot be used in a 100% solids formulation. Dispersed amorphous nanoparticles in a variety of monomer components are available through proprietary production methods. This methodology produces a family of additives for the formulation of matte coatings with a nearly zero increase in viscosity.

FLOCCULANTS

Flocculants are chemical compounds that cause controlled flocculation in a coatings system to give the formulator the ability to optimize color development and adjust pigment mobility. As a paint film dries, flow currents transport solvent to the surface. Smaller pigment particles may be transported with the solvent and result in a higher concentration of smaller sized pigments at the surface. This is called flooding and can be controlled through the use of flocculating additives.

FLOW AND LEVELING AGENTS/ FLOW MODIFIERS

Flow and leveling agents are chemical compounds that increase a coating's mobility after application, thus enabling the process of leveling. They reduce the surface tension of the wet coating and, more importantly, maintain a uniform surface tension over the entire surface area. Flow is the resistance to movement by a liquid material. Leveling is a measure of the ability of a coating to flow out after application so as to obliterate any surface irregularities such as brush marks, orange peel, or craters.

Surface tension holds a liquid together and causes it to take the smallest possible volume. A drop of liquid on a solid surface will cover a larger or smaller area depending on both the surface tension of the liquid and the surface tension of the substrate. For example, a drop of water, which has high surface tension, will bead up as small as possible on a clean and waxed automobile. The same drop of water will tend to completely spread out and 'wet' another portion of the automobile that is not so clean or waxed. A liquid will 'wet' a substrate when the substrate has an equal or higher surface tension than the liquid itself. Sufficient wet film thickness is also important for a smooth surface.

The wetting of the substrate and leveling of the liquid film depend on the surface tension of the coating. Both processes have opposing requirements in terms of surface tension. If the surface tension is too high, poor wetting occurs, along with the formation of possible defects such as craters. If the surface tension is too low, poor leveling occurs and can cause orange peel.

Because of the recent advances in technology within the industry in areas of powder and waterborne systems, good flow is more important than ever. Some of the resins that are being introduced exhibit poor wetting and flow characteristics. This is such an important area because good flow is necessary to eliminate possible surface defects such as craters, fish eyes, orange peel and pinholes.

Many surface defects develop during the application of the coating. Application methods can influence leveling. For instance, some brushes, rollers and direct roller coaters can produce uneven surface films that require leveling for a smooth finish. Other methods that produce a smooth surface – spraying, curtain coating, reverse roller coating – need to maintain that smoothness during the baking and curing process.

Leveling agents function by influencing the viscosity throughout the film. Solvents with good solvating power and a gradual evaporation rate influence the "open" time necessary for leveling. Leveling agents can also be pigment dispersants that function by preventing the flocculation of pigments.

Flow modifiers can differ greatly in their chemical structure and in their ability to affect surface tension and promote leveling within any given coating system. As such, they need to be evaluated in a formula at several different usage levels to determine the optimum level needed in



any given formulation. Even more importantly, a given flow agent's effectiveness will vary from system to system. The natures of the resin, other additives and application technique will all affect the flow agent. For this reason, great care must be taken when selection is made and laboratory work must be conducted to check on effectiveness and surface defects.

Some flow modifiers are designed as 'general purpose', while some are very specific. Some are more effective at controlling craters while others are better at imparting good leveling. This is why proper selection is so important.

Flow agents are available for powder systems, solvent and waterborne applications. The most commonly used flow agents are: silicones, surfactants, fluorinated alkyl esters, solvents and polyacrylates.

Silicones form an important group of flow control agents. These consist of:

1. Polydimethylsiloxanes (silicone oils). Increasing chain length gives materials with higher viscosities. Higher molecular weight means reduced solubility in coating systems and less compatibility. Lower-molecular-weight siloxanes (dimethyl units <60 for example) are used for surface flow control and to mask floating of pigments. Higher-molecular-weight polydimethylsiloxanes are effective as defoamers. Those products with molecular weight greater than 1400 are incompatible and are responsible for causing craters. They can be used to produce hammertone finishes.

2. Methylphenylsiloxanes.

3. Organically modified polysiloxanes. Organo-modified siloxanes have distinctly different properties than their original polydimethylsiloxane counterparts, with respect to silicone crater formation, and other silicone-caused surface defects. The compounds are derived from low-molecular-weight polydimethylsiloxanes, and rather than having only methyl functionality, various organic chains replace certain methyl groups to increase the compound's compatibility with coatings and inks. The organic portion of the molecule can be polyether, polyester or a long alkyl chain.

The most important modification is the polyether chemistry derived from ethylene oxide and/or propylene oxide. Hydrophilic character, i.e., water compatibility, increases as a function of the ethylene oxide content so that it is even possible to synthesize water-soluble silicone-based additives. Factors influencing the properties of modified siloxanes are silicone content, and the type and location of organic groups on the molecule.

Polyether-modified siloxanes simultaneously influence the following effects in coatings. Evaporation of solvent from an applied film causes differences in temperature, surface tension, solvent concentration and density within the film. Solvent-rich material rises in the center of these cells, while material having a lower solvent concentration moves downward from the edges of the cells. As a result, the surface tension in the center of the cell is lower than at the edges. Material flow occurs from the lower surface tension to the higher surface tension areas, forming valleys in the center of the cells and ridges at the edges. Bénard cells can be particularly problematic in systems containing mixed pigments. In clear coatings containing a matting agent, the larger pigment particles are forced out of the zones of higher flow-rate to the center of the cell. Bénard cell effects can be suppressed with modified siloxane-based flow additives. The addition of modified siloxane compounds to a formulation suppresses the surface tension of an uncured film to a uniformly low level, which is altered during solvent evaporation. Therefore, no differences in surface tension occur on the coating surface. Uniform drying and uniform flow are achieved, due to the elimination of surface tension variations. Another benefit, the requirement of good flow, is maintained because low surface tension facilitates complete substrate wetting.

Silicone and acrylate additives are typically used in combination in standard coating formulations. Acrylates improve the flow and leveling while the silicone contributes enhanced substrate wetting and prevents cratering. A silicone macromer-modified polyacrylate is available that incorporates both acrylate and silicone characteristics. In high-polarity coatings, the additive brings about a massive reduction in surface ten-

sion, therefore providing good substrate wetting with no significant reduction of the dry surface energy. The silicone part provides good anti-crater properties without increasing surface slip. The acrylate backbone provides excellent leveling.

Silicones are multipurpose additives because, in addition to control of flow, they also assist as slip agents, prevent floating, and in general, are very effective at low levels. One of the most valuable characteristics of silicone flow additives is the prevention of cratering together with the reduction of sagging.

Silicones concentrate at the paint surface and, because they are surface agents, in addition to reducing the surface tension they influence the slip resistance of the coating surface. (For more information, see Slip Agents)

The chemical structure of silicone additives (molecular weight and functional groups on side chains) makes them more or less compatible with the resin solution. Very incompatible silicones will cause surface defects (craters). Compatible silicones will reduce surface tension and slip. Those whose structures cause them to be somewhere between compatible and incompatible will function as defoamers.

Fluorocarbons are the most highly surface-active group of coating additives. Fluorosurfactants aid in wetting and flow because they decrease surface and interfacial tension. Some low-energy substrates, such as polyethylene or metal surfaces contaminated with oil, are very difficult to wet. Fluorochemical agents function quite effectively and do not usually affect other properties such as water sensitivity. Fluorosurfactants are leveling aids because they minimize surface tension gradients between the resin and solvent that resists leveling. They are generally used at very low levels (0.05-0.10%) and excesses can cause severe foaming.

High-solids systems, powder-coating systems and lower-VOC coatings are particularly in need of flow modifiers because the traditional wetting role of the solvents has been greatly reduced or, in the case of powder coatings, totally eliminated. The reduced solvent content of higher-solids coatings causes an increase in surface tension that results in poor substrate wetting, crawling, cratering and sometimes surface defects on the coating. Waterborne coatings in particular are prone to flow defects, particularly when applied over oily substrates or contaminated surfaces. The solventborne systems were quite forgiving of minor amounts of oil or other contaminations. Waterborne coatings are not at all forgiving over substrates such as metal, plastic, glass and concrete. Raw-material suppliers are continuously introducing new products to overcome these problems.

Powder Coatings

For powder coatings, the quality of the final film depends on the film-forming process. This process includes the coalescence of individual powder particles, the wetting of the substrate by the melted but not cured powder coating and the flow of the irregular film into a uniform film. Both viscosity (the resistance to wetting and leveling) and surface tension (the driving force) play a role in the process of film formation.

If the surface tension is too high, poor wetting occurs and craters may form. If the surface tension is too low the leveling is also affected adversely and orange peel may result. Polyacrylates and polysiloxanes are two types of leveling additives in use. Flow modifiers for powder coatings are designed to address the surface imperfections, such as orange peel and craters.

Acrylic powder coatings can be contaminants for other nonacrylic powder coatings. The result is usually some type of cratering formation. Interestingly, acrylic flow agents are also used in powder coatings as leveling aids. These materials are melt-mixed into the powder composition. It is their controlled incompatibility that allows them to equalize the surface tension of the air-to-solid interface. If the acrylic flow agent was dry-blended into the powder coating, craters would surely be a result. The melt-mixing allows this additive to do its job.

The majority of flow modifiers for powder coatings are alkyl acrylates. These modifiers work by enhancing flow and leveling during the bake cycle. There are surface irregularities that must be overcome during the application and cure of powder coatings. In addition, the particle size

and distribution can affect flow. Just as in liquid coatings, incomplete leveling of the surface will result in severe orange peeling. Orange peel for powder coatings is frequently caused by either uneven application, or a nonuniform particle size distribution of the powder particles. Sometimes nonuniform pigment distribution can also cause orange peel. Polyesters, in particular, seem to be susceptible to this defect.

Cratering and trapped air or other volatiles that result in pinholing are also critical. For example, if a powder resin cures too rapidly, it can trap gas and pinholes will result.

Some of the acrylic flow modifiers behave as a plasticizer and lower melt viscosity, and increase the leveling time to produce a smooth surface. Acrylic flow modifiers have been used effectively to provide high-quality surface coatings prepared from a variety of vehicles: epoxy, melamine, urethane, silicone rubber, acrylic, alkyd, phenolic, EVA copolymers, polyester and cellulosic. Certain melamine-formaldehyde resin crosslinkers, such as methylated/butylated coetherified melamine-formaldehyde resins, also provide good flow and leveling and help to prevent pinholes, craters and picture framing in coatings. Levels of use of flow modifiers are different than in liquid coatings, and systems need to be well evaluated by the formulator.

For powder coating, polyacrylates (both homopolymers and copolymers) are the most widely used flow-control agents. These are moderate- to high-viscosity liquids and are usually supplied as a powdered master batch dispersed on silica particles.

Additives based on polyacrylate technology, encapsulated by a solid (silica free) shell, are available as dry powders for powder coatings. These additives promote leveling while maintaining maximum gloss levels.

Silicones are also used and are typically more effective in reducing surface tension. Polyether and polyester-modified polysiloxanes are preferred to poly(dimethyl) siloxane because these are very active and are prone to cause defects such as pinholing, craters, haze, etc. The modified polysiloxanes are provided in a powdered form on silica particles.

The fluorocarbons are very effective in powder coatings but are not often used because they are expensive. They are, however, very effective, particularly on contaminated or oily metal substrates.

FLUIDIZING ADDITIVES

Fumed silica and aluminum oxide may be incorporated into powder to improve fluidization and handling. These materials are small in particle size and are low-bulk-density agglomerates. It is advised to incorporate these materials during the pulverization stage of powder manufacturing. A level of 0.1-0.5% is usually sufficient, and higher levels can affect the electrostatic behavior of the powder coating.

FLUORESCENT ADDITIVES

Fluorescent additives are compounds that emit light when activated by ultraviolet radiation. Fluorescent whitening compounds add fluorescence to a coating and as a result yellowing can be masked or a coating can be brightened. They are also used as tracer or marking compounds that are visible under ultraviolet radiation. The compounds function by absorbing radiation in the ultraviolet region and then emitting radiation (light) in the blue region of the visible spectrum. Care should be used when using fluorescent whitening compounds in ultraviolet cure systems because their absorption in the ultraviolet region may compete with the photoinitiator and reduce cure speed. These compounds are usually used at low concentrations of about 0.05-0.5%.

FOAMING AGENTS

Foaming agents are materials that increase the stability of a suspension of gas bubbles in a liquid medium, or they can also be blowing agents, which generate inert gases causing a cellular or foam structure.

FOAM-CONTROL AGENTS

See Anti-Foam, Defoamer

An additive that is used to eliminate, prevent or control foam in a system. In an aqueous formulation, it is almost impossible (at acceptable use

levels) to totally eliminate all foam. The correct foam-control agent will help to prevent foam but, of most importance, will allow the dried film to be free of foam and any resultant film defects that might result from an air void in a film.

The causes of foam are many. Air can be incorporated into a coating by mixing during the polymer/pigment grinding and letdown steps, by pumping during package filling or by shear or spraying during application. Effective foam-control agents are beneficial in preventing or reducing many common coating problems such as:

- Viscosity increase and loss of mechanical shearing power during milling, resulting in smaller batch sizes and poor pigment/polymer dispersion.
- Volume increase during the letdown and mixing steps, leading to overflowing.
- Slower package filling rates due to inefficient pumping.
- Air incorporation during transport and handling.
- Slower printing press speeds or lower pressures during spraying.
- Surface defects on coated substrates, resulting in poor appearance, reduction in gloss or less substrate protection.

Foam-control agents, or defoamers, must be insoluble in the foaming medium. They function by being more surface active than the surfactant stabilizing the foam so that they are able to enter the surface layers of the potentially foaming liquid and displace it from the gas/liquid interface. The mixed surfactant layers then prevent close association of molecules and exhibit low elasticity. The presence of random, highly surface active, insoluble molecules in the surface film interrupts foam stabilization via the Marangoni effect, and thus foaming is prevented. The four basic processes by which antifoams disrupt aqueous foam are: entering, bridging, dewetting and rupture.

Surfactants orient at the air-liquid interface to create a higher surface viscosity in the lamella than the bulk in which film drainage can be impeded. The surfactant stabilizes foam by hydrogen bonding and electrostatic repulsion between surfactant molecules within the lamella. Increased surface elasticity, created by the thinning of the lamellae, also impedes liquid drainage and subsequent foam collapse. Movement of the surfactant layer can actually pump water back into the lamella causing further stabilization (Marangoni effect).

Most foam-control agents for aqueous systems consist of:

- carrier;
- actives (hydrophobic materials);
- other additives that enhance spreading;
- compatibility, product stability, etc.

The terms 'defoamer' and 'antifoaming' agents are often used interchangeably. In fact, they are not quite the same. A defoamer is a surface-active agent that stops the foam and breaks the bubble once it has been formed. It is a bubble breaker. An antifoaming agent prevents the formation of foam so it never forms. The term 'foam-control agent' is a more appropriate term to use and they function by a variety of mechanisms to prevent or rupture foam.

FREEZE-THAW STABILIZERS

Chemical compounds that impart freeze-thaw resistance to waterborne coatings and prevent coatings from flocculating or coalescing irreversibly when they are subjected to a freeze-thaw cycle. Compounds such as glycols and oxygenated solvents are often used for this purpose. Thickening agents and nonionic surfactant system stabilizers also function as freeze-thaw control agents. Ethylene and propylene glycols are the most widely used. Propylene is preferred because of regulations. In specific formulations, some of the glycol ethers (carbitols) can also act as freeze-thaw stabilizers. These are used where ethylene and propylene glycols have detrimental effects on rheology and/or gloss.

Most freeze-thaw stabilizers are used in aqueous latex systems. To maintain latex equilibrium, these additives are poor solvents for the latex particles and are soluble or readily miscible in water. They function in two ways. First, they lower the freezing point of the aqueous media. Second, they inhibit, or retard, the desorption of water from within the



ADDITIVES REFERENCE GUIDE

latex particles, which maintains intraparticle stability and allows future smooth interparticle coalescence. Some of the additives used in a paint formulation for other purposes, such as the thickener, nonionic surfactants, and similar compounds, also play a positive role in freeze-thaw stabilization. However, they only augment and do not do the entire job.

There are patented zero-VOC, APE-free freeze-thaw additives that protect waterborne low-glass-transition latex-based coatings from freezing during storage, transportation or application. They address the latex coagulation issues of low- to zero-VOC coatings based on low-Tg binders. These additives may be added to the binder or to the coating formulation.

FUNCTIONAL FILLERS

See *Extenders, Microspheres*

FUNGICIDE

See *Biocide/Fungicide/Antimicrobial*

Fungicides are additives that destroy, retard or prevent the growth of fungi or spores. Fungicides are predominantly included in a formula to inhibit the growth of fungi and algae on the dry film of both water- and solventborne paint. Included in this family of compounds are substances such as: copper, sodium or zinc pyrithione; carbamates such as 3-iodo-2-propynylbutyl carbamate; tetrachloroisophthalonitriles; isothiazolones such as 2-n-octyl-4-isothiazolin-3-one; and 1-(3-chloroallyl)-3,5,7-triaza-1-azonia-adamantane chloride. These are but a few examples of fungicidal agents available for coatings.

FUNGISTAT

See *Biocide/Fungicide/Antimicrobial*

Compound that inhibits the growth of a fungus, or prevents the germination of its spores.

GELLING AGENT

A compound that converts a coating from a liquid to a soft, elastic solid with the nature and appearance of gelatin.

GLOSS IMPROVER

A material that increases the amount or degree of specular reflection of a film.

GRAPHITE

See *Lubricant (Solid)*

GRINDING AIDS

See *Dispersant/Wetting Agent*

Grinding aids are compounds, or dispersants, that stabilize deaggregated or deagglomerated particles that have been separated into primary particles by the energy supplied in a grinding operation.

HAMMER-FINISH ADDITIVES

A chemical agent that creates the appearance of a finish having been applied over hammered metal. Where a pronounced hammer finish in solventborne coatings is required, a high-molecular-weight polydimethyl siloxane, can produce a specific incompatibility in the coating system. The resultant surface texture, known as the hammer effect, is further aided by the use of aluminum pigments in the formulation.

HARDENERS

See *Curing Agent/Accelerators*

The term 'hardener' is often applied to the amine or other catalyst used to cure epoxides. Hardeners are single compounds or mixtures of compounds that are added to a formulation to promote, enhance or control the curing reaction and thus aid in property development. The compounds act by taking part in the curing reaction and usually become a part of the final cured product. For example, in the epoxy-amine curing reaction, the amine is the hardener that causes the basic component or epoxide to react and form an epoxy coating.

Blush and bloom are surface defects that need to be avoided in an epoxy coating. They affect the coating performance as they can result in poor gloss retention, discoloration over time (yellowing), poor overcoat-ability and intercoat adhesion. The most important of these effects is the reduced overcoat-ability, i.e., insufficient adhesion of a subsequent coating layer to the system due to surface energy modification. In the case of the final layer (topcoat) the mechanical and chemical properties are altered and the visual appearance is worse.

The propensity for blushing or blooming to occur is related directly to the structure of the amine. Low-molecular-weight (cyclo) aliphatic amines, typically used in combination with epoxy resins, are mostly hygroscopic and have a high vapor pressure. These types of products are very susceptible to blushing or blooming. Aliphatic amines are mainly used as raw materials to prepare "advanced" curing agents or in heat cure applications, but they are also used in room-temperature applications where appearance is not so important. An example of such an application would be grouting compounds (mortars) for anchoring heavy machinery. In priming/sealing applications aliphatic amine curing agents may also be used. Although the initial coating will be affected, the application of a subsequent layer in due time might overcome the problem of blushing.

In order to eliminate the formation of blush or bloom, a wide range of modified amine curing agents has been developed. The two major categories are epoxy-amine adduct hardeners and a special class of adduct hardeners called Mannich bases.

Epoxy-Amine Adducts

Amines and amine derivatives are the most diverse group of epoxy curing agents. The epoxy-amine adduct curing agents are the largest category of products designed to have a reduced tendency to blush. Epoxy-amine adducts are reaction products of liquid epoxy resin with an excess of primary amine. Although epoxy-amine adducts still contain a large excess of free amine, they are less hygroscopic and have a lower vapor pressure compared to the neat amines. Epoxy-amine adducts are less sensitive to blush formation and, as a result, are better suited for coatings/floorings, which cure under high humidity/low temperature. A disadvantage of epoxy-amine adducts is their relatively high viscosity. In order to reduce the viscosity, epoxy-amine adducts are often modified with solvents or plasticizers, such as benzyl alcohol.

The fully polymerized epoxy resins exhibit a very wide range of thermal and mechanical properties. Though other classes of compounds (e.g., anhydrides, phenolic resins, and Lewis acids) are used as hardeners for some applications, the breadth of performance imparted by amine hardeners is unmatched. The terms hardener, curing agent and co-reactant are often used interchangeably to describe compounds that polymerize or co-polymerize with epoxy resins to produce usable materials. The polymerizing resin becomes harder than the starting material, thus the name hardener. Because unreacted groups can lead to property changes over time, a one-to-one ratio of epoxy groups to amine-hydrogen groups is typically desirable, though not always necessary, in epoxy formulations.

Though a variety of epoxy resin products are commercially available, liquid resins based on the diglycidyl ether of bisphenol A (also termed DGEBA or BADGE type resins) have the widest use and availability due to their relatively low price, which is partially gained from economies of scale. Because of this, the epoxy portion of epoxy formulations often remains relatively fixed, and most variations in processing and performance are obtained by making changes to the hardener side of the formulation. The wide variety of commercially available amine compounds, and decades of study and formulation has helped to make this group of hardeners the most versatile and widely used of any epoxy reactants.

The choice of epoxy resin can be used advantageously to affect some processing, thermal and mechanical properties, but the wide diversity of amine curing agents typically allows the greatest latitude in creating formulations to fit a wide variety of applications needs.

The three main use criteria for creating or choosing an amine hardener (or blend) for an epoxy formulation are (in no particular order): cost, processing requirements and performance requirement.

Even greater versatility is available to the epoxy formulator as new hardeners are developed to meet unusual processing and performance requirements. Creative use of amine blends can provide a wide range of processing, thermal and mechanical performance combinations.

Mannich Bases

Mannich base curing agents are adduct-type hardeners formed by the condensation of (aliphatic) amines, phenol (derivatives) and formaldehyde. The phenolic hydroxyl group present in these types of molecules has an accelerating effect on the epoxy-amine reaction rate. Moreover, Mannich bases show better compatibility with liquid epoxy resins than unmodified alkylene amines as well as reduced blush/bloom tendency and improved early water spot resistance.

Special grades of Mannich bases are products using Cardanol, a major constituent of cashew nut shell liquid, as the phenol component. These types of products, often referred to as phenalkamines, are reference materials in low-temperature, high-humidity cure applications.

HASE THICKENERS

See Thickeners

HASE thickeners are a group of polymeric materials whose chemical nature has the form of a Hydrophobe-Modified Alkali-Swellable/Soluble Emulsion. These compounds were among the early associative thickeners and rheology modifiers. In a general sense, HASE thickeners are copolymers of ethyl acrylate, methacrylic acid and a polymeric monomer. The polymeric monomer consists of about 10-100 ethylene oxide units, and is terminated with an alkyl or alkylaryl hydrophobe.

HEAT STABILIZERS

Heat stabilizers are often used with chlorinated polymers to eliminate the abstraction of hydrogen chloride or at least prevent the acid from further catalytic action. A wide variety of basic stabilizers can be used such as: carbonates, amines, alkaline and alkaline earth oxides and hydroxides. Also widely used in coatings are: epichlorohydrin, propylene oxide, epoxy resins, epoxidized oils and plasticizers.

Alkyl and aryl tin esters are another class of heat stabilizers often used. Examples are dibutyl tin dilaurate and dibutyl tin maleate.

Plastisols and organosols often require the use of heat stabilizers to protect the vinyl resin from degradation during bake.

HEUR THICKENERS

See Thickeners

HEUR thickeners are a group of polymeric materials that are in the form of Hydrophobe-Modified Ethylene Oxide-Based Urethane copolymers. These copolymers have hydrophobes coupled by urethane linkages to the ends or sides of an oxyethylene polymer. To facilitate handling and addition to aqueous systems, these thickeners are usually supplied as moderately viscous solutions in an aqueous mixture that contains a solvent such as polypropylene glycol. Coatings thickened with HEURs generally demonstrate excellent gloss, flow and leveling, sprayability, and corrosion resistance. However, they also generally exhibit poor sag and syneresis resistance.

HINDERED AMINE LIGHT STABILIZERS (HALS)

See UV Absorbers and Light Stabilizers

Exterior durability of most organic coatings is highly dependent on the use of light stabilizers. The two main stabilizer categories are ultraviolet light absorbers (UVAs) and hindered amine light stabilizers (HALS).

UV absorbers are not able to absorb all of the UV radiation that a coating is exposed to. Some UV radiation will penetrate the coating surface. Because of this, HALS are incorporated into the coating. These molecules work by scavenging any free radicals that do form – this is different from UV absorbers, which prevent their formation in the first place.

HALS function by removing radicals from the system and subsequently regenerating themselves. Most formulators will use a combination of absorbers and HALS for this reason.

Synergistic combinations of UV absorbers and HALS are optimal for the stabilization of coatings. UV absorbers are governed by the Beer-Lambert Law, thus absorbance is linearly related to the concentration of UVA, its molar absorptivity (extinction coefficient), and path length (coating thickness). For clearcoats, they provide the predominant mechanism for coating stabilization. HALS are free radical scavengers and are not subject to Beer's Law and work anywhere in the coating system. They inhibit the coating binder's photo-oxidative reactions and help maintain their initial film properties such as flexibility and water repellency. HALS are especially effective at coating surfaces, providing better gloss retention, higher chalking resistance in pigmented systems while avoiding crack formation in clearcoats. For pigmented systems, HALS provide the primary mechanism of stabilization because most UV radiation is blocked by pigment from penetrating beyond the first few microns of coating. The selection of the appropriate UVA/HALS combinations and concentration is dependent on the chemistry of the coating system, the presence of pigments and fillers, film thickness and exposure conditions.

When selecting a HALS, the formulator must be very careful regarding the basicity of the compound. A basic HALS is capable of interacting with acid catalysts, metal catalysts and even some organic pigments. In an acid catalyzed paint system, the use of a basic HALS will have the effect of retarding the cure. For coatings systems like this, nonbasic hindered amines (such as a hindered amino ether) can be used. A variety of HALS are available in both liquid and solid form.

Certain pigments, such as carbon black and titanium dioxide, absorb UV radiation and can increase the stability of the coating. But TiO₂ can also eject electrons and undergo a number of reactions to form free radicals. Again this illustrates the wisdom of incorporating HALS into a formulation desired to withstand weathering and provide a quality coating.

HALS do not depend on the thickness of the sample for effectiveness. For this reason they are useful for substrates that have a high surface-to-volume ratio: thin coatings, multifilament and thin thermoplastic films. These additives are outstanding in their effectiveness of protecting and prolonging the coating in exterior exposures – particularly for polyolefins, polyurethanes and acrylics.

HALS materials typically are based on the 2,2,6,6-tetramethylpiperidine chemical structure, with usage levels of approximately 1.0-3.0%. A typical HALS is bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. The total package (UVA + HALS) level is 3.0-5.0% for powder coatings.

Under photo-oxidative conditions, HALS compounds generate stable nitroxyl radicals that can serve as a trap for carbon-centered radicals of the alkyl-type evolving from resin degradation. These hydroxylamine ethers react further with (polymer)peroxyl radicals to form relatively stable (polymer)peroxides, or a ketone and an alcohol, while releasing the effective nitroxyl radical again so that one nitroxyl radical can neutralize up to several hundred radicals. Stabilization with HALS is a chemical process.

The optimal distribution of the HALS in the binder is crucial for its effective use. When sunlight hits the coating, the radiation density is highest right at the surface. Consequently, this is where the formation of protective nitroxyl radicals for light stabilization is most needed. The deeper the sunlight penetrates the coating, the weaker the radiation density, because it is being absorbed by the binder, and, in some cases, by an additional UV absorber. In the deeper layers the likelihood of light-induced decomposition decreases continuously, and so the role of the sterically hindered amines in these areas loses importance. The radical scavengers prevent the photolytic decomposition of the binder, indirectly shielding the substrate below. The coating lasts longer, and the substrate is also protected for a longer time.

New HALS developments include functionalizing to prevent exudation out of films, development of non-interacting materials that are suitable for use with acidic pigments and acid-catalyzed coatings, and encapsulation to accommodate formulating zero-VOC coatings.



ADDITIVES REFERENCE GUIDE

HOMOGENIZER

This term is most often used to describe a piece of equipment, but may also apply to an agent that aids in the formation or maintenance of a uniform mixture of two or more dissimilar materials.

HUMECTANTS

Humectants are compounds that prevent the drying out of a formulated waterborne coating in the storage container. They function by hydration of the polymeric molecule and retaining water molecules that can be supplied to the system. Examples are propylene glycol, polyethylene glycols, polyoxyethylene, ethoxylated cellulose, calcium chloride, diethylene glycol, glucose, glycerin, hexylene glycol, sorbitol, sodium nitrate and urea.

VOC regulations have prompted the development and introduction of a new variety of liquid humectants that is VOC-free and also acts as a dispersing agent. Effects on other paint properties have not yet been fully evaluated. Humectants are sometimes used as a component of antistatic coatings for plastics.

HYDROPHILES

Hydrophiles are molecules, a group on a molecule, or a portion of a molecule, or other moieties that have an affinity for aqueous substances and a repulsion for oil-like substances. Certain hydrophiles can hold or bind water equal to several times their weight.

HYDROPHOBIC AGENT

Substance that makes a paint film not absorb or exhibit affinity for water. Hydrophobes are molecules, a group on a molecule, or a portion of a molecule, or other moieties that have an affinity for oil-like substances and a repulsion for aqueous substances.

HYGIENIC COATING ADDITIVES

See *Enzymes*

AgION™

A silver-bearing zeolite antimicrobial compound, known as AgION, has been incorporated into polymer-based coatings to control the growth of harmful bacteria, mold and mildew. These coatings may be applied to stainless or carbon steel products for use in appliance, food processing and HVAC applications. The active ingredients in the coating are the silver ions that are held within an alumino-silicate zeolite carrier particle. The silver ions exchange with other ions (counter ions) that may be present in nutrients or moisture and in this manner are transported to areas that support microbial growth. The antimicrobial properties of the silver ion have been recognized for a long time.

Ca(OH)₂

Ca(OH)₂-based surface coatings, now available in a variety of pigmented colors, act to prevent infections, in particular influenza, sinus infections, pneumonia, allergic rhinitis, asthma and some indications are it is beneficial for anthrax as well. This is a revolutionary, one-application, antimicrobial-antibiotic surface coating effective against all classes of microbes including bacteria, viruses, fungus and algae. The coating combines calcium hydroxide as its active biocide with a special Bi-Neutralizing Agent (BNA), a biopharmaceutical whose mode of action keeps the coating continuously working year after year.

Calcium hydroxide inhibits the growth of common microorganisms on the coating's surface through its high alkalinity (at levels normally incompatible with the life of microorganisms). Normally, hydrated lime is highly susceptible to atmospheric attack – carbon dioxide in the air quickly converts calcium hydroxide to calcium carbonate, reducing its alkalinity and rendering it ineffective. However, with BNA, calcium hydroxide is safely stabilized by this patented technology – a semi-permeable calcium hydroxide-encapsulated matrix system. This specially engineered matrix system protects hydrated lime from atmospheric degradation, preserving its antimicrobial-biocidal potency long after the coating is applied.

What is unique is its benign nature to humans and its lethal nature to microbes. The active ingredient is coming from a naturally occurring mineral and has been used for centuries as a safe and effective way to kill pathogens.

The end-use product is waterborne, fast drying, virtually odorless and remarkably contains no VOCs. It offers a widespread solution to the problems caused by the presence of the common microorganisms. Using an antimicrobial agent registered by the US EPA this multi-patented technology works by creating a surface coating that resists the growth of microbes on its surface for over six years.

HYPERDISPERSANTS

See *Dispersant*

IMPACT-RESISTANCE IMPROVER

An agent that improves both the flexibility and adhesion of a coating to a degree, which lessens the damage to the film upon direct or indirect impact. These materials usually are rubber and polymeric in nature. They are partially immiscible in the matrix that is being impact modified.

There are also new materials being introduced such as environmentally friendly, actinic radiation-curable coatings for thermoplastic olefin objects, i.e., motor-vehicle bumpers that consist of a mixture of monomers, a free radical photoinitiator, and up to 17% inorganic nano-filler. After curing, the resulting coating provides excellent scratch resistant and high impact-resistant thermoplastic olefin automotive parts.

IN-CAN PRESERVATIVES

In-can preservatives are additives that protect coatings during storage. They prevent microbial attack that would result in gassing and attendant can bloating as well as other spoilage caused by bacteria during manufacture or storage. One additive that is particularly effective against such attack is 2-bromo-2-nitropropane-1,3-diol (Bronopol). It can be used alone or in combination with compounds such as isothiazolinone or dibromodicyanobutane. Such additives are effective against organisms such as *Aspergillus niger*, *Candida albicans*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Other in-can preservatives include an aqueous solution of sodium hydroxymethylglycinate based on glycine, a naturally occurring amino acid. Another recent introduction, this time into the Chinese market, is CANGUARD™ ULTRA BIT Paste, a broad-spectrum bactericide used for the protection of industrial waterborne coatings against bacteria, fungi and yeasts. The paste is a highly pure, solid form of BIT (1,2-benzisothiazolin-3-one) that can be used to prepare additional grades of solutions or aqueous suspensions of BIT. It is a long-lasting, non-formaldehyde-based biocide that can be used under a broad range of pH and temperature conditions. It can be used at higher temperatures and under very alkaline conditions, where other preservatives are often ineffective. It is useful for the preservation of polymer latexes and emulsion systems, waterborne coatings, adhesives, oil-in-water emulsions, and for bacterial control in the paper-making process.

A new generation of in-can preservatives based on the new antimicrobial active ingredient MBIT (2-methyl-1,2-benzisothiazol-3(2H)-one) is called BIOBAN™ 551S. BIOBAN 551S is a synergetic combination of MBIT and MIT which is effective at very low dosages across a broad pH range. BIOBAN 551S, is a water-based and solvent-free solution. It provides paint and latex manufacturers with an in-can preservative for low-VOC and VOC-free water-based systems. It has excellent chemical and thermal stability, does not release formaldehyde and its active ingredients do not contain added organohalogens or heavy metals. BIOBAN 551S has high water solubility and is therefore a good component for new generations of VOC-free, aqueous coatings.

INSECTICIDES

Chemical compounds that kill insects on contact.

In recent years, there have been some EPA-registered insecticide coating additives.

- o,o-diethyl-o-(3,5,6-trichloro-2-pyridyl) phosphorothioate (61.5%)
- o,o-diethyl-o-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate (87%)
- Disodium octaboratetetrahydrate ($\text{Na}_2\text{B}_8\text{O}_{13}\cdot 4\text{H}_2\text{O}$).

Latex insecticidal coatings that contain chlorpyrifos, the active chemical insecticide, are being used in various applications in certain climates. Three-mil-thick coatings provide effective insecticide treatment for a two-year period against roaches, black widow spiders and fire ants, which are fond of attacking wiring and electrical connections.

There is no doubt that the aesthetic appearance of a coating is enhanced by the reduction or elimination of unsightly cobwebs, nests and bugs. The log home industry recognized this because of need, and many other types of structures can also benefit from the technology, such as: farms, public buildings and resorts.

It is thought that insecticide additives behave somewhat like pigment in a coating film and are dispersed throughout the film. Because the insecticide is dispersed throughout the dried film, as the film erodes with aging new insecticide is exposed. The mucous membranes on the bottom of the feet of insects allow them to walk on vertical surfaces with ease. As they crawl along a treated material, they absorb the pesticide through the mucous membrane, and it is then transferred to their central nervous system and they are overcome. Both humans and other animals are able to metabolize these insecticides.

Insecticide additives, while not used to a large extent, do have some applications. The reduction of insects and cobwebs does a great deal to enhance the appearance of buildings – especially in areas where they tend to be more prolific because of the climate.

Also available today is an insecticidal coating composition for use on cellulosic substrates such as packaging materials to provide protection against insects. The insecticidal coating is comprised of a blend of a polyvinyl acetate emulsion and a vinyl acetate ethylene copolymer emulsion, typical additives, and an insecticide having an LD_{50} value of between about 14,500 to 15,500 mg/kg.

INSULATING ADDITIVE

One of the most important applications microspheres were developed for was the Space Shuttle program. When the space shuttle re-enters the earth's atmosphere, incredible heat is generated due to increasing air friction. In order to prevent the space shuttle from burning up during re-entry, NASA scientists developed a superior insulating material using ceramic technology. This technology is now applied to roofs and sidewalls of buildings, piping, ducts, tanks, various storage devices, refrigerated containers, cold rooms, etc., in order to insulate them from the radiant heat of the sun and the atmosphere by using hollow ceramic spheres.

Stagnant air is a bad conductor of heat because heat is transferred by convection currents. Stagnant air inside hollow spheres acts as an insulator for heat and can be used as heat-insulating material in coatings. This characteristic of hollow microspheres allows improved thermal and acoustic insulation properties of coatings or composites. Currently, markets taking advantage of this property include fire-retardant materials, sensitive acoustic equipment and roof coatings.

There is a newer coating additive – Enova™ aerogel – that provides a combination of traditional insulation and flexibility. It is an insulating solid in particle form; each particle is composed of more than 90% air trapped within a network of amorphous silica, making it twice as insulating as still air. This aerogel has exceptionally low thermal conductivity (12 mW/mK), which is far superior to traditional insulation such as polyurethane foam (typically 30 mW/mK) and additives such as glass or ceramic microspheres. When used in waterborne formulations, the coating can achieve a thermal conductivity of 30 mW/mK to 50 mW/mK, which is seven to 10 times more insulative than standard paint. It is easily incorporated into formulations using standard methods.

A combination of physical characteristics, such as high surface area, low density and tailored particle size make the new aerogel product line a key ingredient for high-performance coating applications. As an

additive it is not only effective as a thermal insulator, but also as a matting agent, rheology modifier, absorbent and thickening agent. It also provides operating temperature flexibility, moisture resistance, coating clarity and long shelf life. Usage levels can be adjusted for gloss level, insulation and rheology modification.

INTUMESCENT ADDITIVE

See Flame Retardants, Lubricants (Solid)

Agent that generates inert gas upon heating, thereby causing formation of a foam structure with insulative properties.

Intumescent coatings are fire-retardant paints that protect the substrate by puffing up when exposed to high temperatures and forming an insulating protective layer over the substrate. In the process they prevent the flow of oxygen. Initially this type of coating, when exposed to high temperatures, will char and expand greatly to retard the spread of the flame by essentially forming a foamed barrier. The expanded coating is often over 100 times the thickness of the original coating.

Intumescent coatings consist of various components whose effectiveness is decisively influenced by the mixing ratios chosen. The critical components are the acid source, the binder, the blowing agent, the carbonific compound and the plasticizer. These substances greatly affect the properties of the coating such as tropical- or water-resistance.

LEAFING AGENT

Agent that promotes the action of floating and slight overlapping of metallic or other laminar flake pigments on the surface of a coating.

Due to their manufacturing process, some metallic pigments are covered with a hydrophobic layer of stearic acid, which has a significant influence on the wetting properties and may drive the pigments – especially in waterborne systems – towards the coating's surface. This is called a leafing effect and this 'surface-oriented' alignment gives excellent brilliance and chroma, but the pigments are not always fully embedded into the coating's film. Consequently, they may have poor rub-resistance and are very sensitive to corrosion. The use of surfactants or polar organic solvents provides better wetting, hence pigments turn out to be 'non-leafing'.

LEVELING PROMOTER

See Flow and Leveling Agent

LIGHT STABILIZERS

See Hindered Amine Light Stabilizers, UV Absorbers

LIGNIN STABILIZATION ADDITIVE

There is a new line of coatings additives designed to protect wood from degradation and yellowing caused by UV radiation. It is called SunCare® Lignin Protection and it functions by stabilizing the primary lignin in the wood itself, representing a "first line of defense" against a range of factors that cause wood degradation. The products are based on a UV absorber plus stereochemically hindered amine chemistry. Two of the new products are additives for primer and stain applications, and there is also a product that is a formulated primer for untreated wood. Studies have shown that when SunCare technology is used as a primer or as an additive, it can significantly increase the level of protection for wood coatings and delay yellowing, two important benefits that enable warrantable, long-lasting performance claims on industrial and consumer wood products.

This technology is a fundamentally different approach to wood protection that can work alone or synergistically with other wood protection technologies. By stabilizing the primary lignin, the additive acts as an excellent preventive measure against UV radiation and yellowing. Lignin stabilization makes wood less vulnerable to water, fungal degradation and insect damage. These lignin protection additives are important components of premium wood protection products, working synergistically with other wood protection technologies, for end-use products that will deliver better performance that lasts significantly longer than what is on the market today.



They do not contribute odor to a formulation and are soluble in water. The additive can be used for interior and exterior waterborne primers and stains.

LUBRICANTS (SURFACE)

See Slip Aids

Lubricants are additives that decrease the frictional resistance between surfaces. They make removal of individual sheets from a stack of metal sheets easier when they are used in a production operation, facilitate transport of coated objects, and so on. Lubricants include zinc stearates, castor and sperm waxes, etc.

LUBRICANTS (SOLID)

Graphite

Graphite is one of three common naturally occurring forms of carbon (graphite, amorphous carbon, and diamond). The word graphite is derived from the Greek word *graphein*, to write. Common names for graphite include black lead, plumbago and mineral carbon.

Graphite is effective, low cost and multi functional when used in coatings. Graphite provides chemical inertness, refractoriness, electrical conductivity, thermal conductivity, lubricity, UV stability, and, in the case of 'expandable' graphite, fire retardance. With proper rheological adjustment, graphite is compatible with most aqueous and non-aqueous coating systems. Graphite is available in 'off-the-shelf' purities from 80-99+% carbon, and sizes ranging from large grains to 3 microns. Particle distributions can be tailored to meet almost any liquid system requirement.

Graphite is a hexagonal mineral and crystallizes in the 6/m2/m2m crystal class. Common forms (crystal faces) include the {0001} basal pinacoid, {1010} prism, and {1011} pyramid. Graphite has perfect cleavage parallel to {0001} (perfect basal cleavage). Depending upon the purity, the specific gravity is 2.20-2.30. Graphite is gray to black in color, is opaque to visible light even in thin section, and has a metallic luster. It is soft, having a Mohs hardness of 1-2, and is flexible but not elastic. Graphite has high thermal and electrical conductivity, is highly refractory, and is chemically inert.

The Four Forms of Graphite

Four main types or varieties of graphite exist. Each of these types is used commercially as additives in coating systems; flake, crystalline-vein, amorphous graphite and synthetic. Each type of graphite has attributes, which determine its effectiveness in a given coating application.

1. Flake Graphite

Flake graphite, as indicated by the name, has a flaky morphology. Due to its impervious laminar structure, flake graphite is an effective coating additive. When properly dispersed, overlapping graphite lamella form a tough, impervious coating that is lubricious, inert, and both electrically and thermally conductive. Also, flake graphite is non-photo reactive so it will not be bleached or affected by ultraviolet radiation.

Flake graphite is available in sizes ranging from 0.5 mm flakes to 3-micron powder. The morphology of flake graphite is consistently laminar regardless of particle size. By adjusting the rheology of the system, flake graphite of various sizes can be used effectively in coatings.

Intumescent Flake Graphite

Also known as "expandable graphite," intumescent flake graphite is a synthesized intercalation compound of graphite that expands or exfoliates when heated. When added to coatings, intumescent graphite can act in various ways as a fire suppressant. Suppression may be affected by the following mechanisms.

- Formation of a char layer. Expanded graphite will form a "char" layer between the flame or heat front, and the substrate. This layer provides a shield, which effectively insulates the substrate from radiant heat, oxygen, and direct contact from flames.
- Endothermic absorption. The action of graphite exfoliation is endothermic. Expandable graphite exposed to heat, particularly from a

flame front, will absorb heat during the exfoliation reaction effectively removing heat from the source.

- Out-gassing. The exfoliation reaction is accompanied by out-gassing as intercalation reagents decompose and escape as gaseous decomposition products. Up to 20% of the intumescent graphite mass may be lost as non-flammable gaseous products. These gases may act to displace oxygen in an advancing flame front.

Intumescent graphite is available in purity ranging from 80-99% carbon. Both coarse and fine grades are available. The degree of intumescence, also known as "expandability", generally ranges from 80-300% volume increase. Coarser grades expand more than finer grades. Products can be specified as low (acidic), neutral, and high (alkaline) pH to allow compatibility with a variety of aqueous and non-aqueous systems.

Although intumescent graphite has been used for many years in various applications, it is relatively new to the coatings industry. This unique product may prove to be a keystone in the development of fire retardant coatings to meet the demands of the 21st century.

2. Crystalline Vein Graphite

Crystalline vein graphite is unique, as it is believed to be naturally occurring pyrolytic (deposited from gas or fluid phase) graphite. In coatings applications, vein graphite may offer superior performance since it has slightly higher thermal and electrical conductivity, which result from its high degree of crystalline perfection. Also, vein graphite has good oxidation resistance and is highly lubricious. Commercial grades are available from 85-99% carbon. Sized materials from 1 inch to 3 micron are available.

3. Amorphous Graphite

Amorphous graphite is the least "graphitic" of the natural graphites. However, the term "amorphous" is a misnomer since this material is truly crystalline.

Amorphous graphite tends to be much less reflective in both large- and small-grained sizes. Therefore, it has a darker color, bordering on black, while other natural graphite has a color closer to "silver-gray." This makes amorphous graphite useful in coatings, which require less reflectance. Also, this graphite variety is typically lower in cost than other types but is still lubricious, conductive and chemically stable.

4. Synthetic Graphite

Also known as "artificial graphite," this variety is a man-made product and is available in sizes from 1/2 inch to 3 microns. Synthetic graphite is used in many coatings applications where higher purity is required. It is compatible with virtually any aqueous or non-aqueous system, has excellent thermal and electrical conductivity, is chemically inert, and is relatively low in cost.

Basic Structural Description

Graphite is composed of carbon atoms that are arranged in poly-aromatic, hexagonal ring arrays. Carbon atoms in these arrays are in the sp²-hybridized state. These ring arrays form sheets of carbon atoms, and individual sheets are known as graphene layers. Graphene layers are stacked one on top of another, perpendicular to the "c" crystallographic axis of the hexagonal system. Within each graphene layer carbon-to-carbon bonding is strong covalent (shared electrons) sigma bonding. Individual graphene layers are held in stacked arrangement by weak, secondary electrical bonds resulting from the overlapping pi (π) bonds of the sp² carbon network within each graphene sheet. The high degree of anisotropy (directional properties) seen in graphite is the result of the two types of bonding, covalent sigma and covalent pi, each type acting in a different crystallographic direction.

Anisotropy

Graphite is the classic example of an anisotropic substance. The anisotropic behavior of graphite is illustrated in its ability to act as a solid film lubricant. Graphene layers, stacked along the "c" crystallographic axis,

have high inter-layer strength but low intra-layer cohesion. The weak pi bonding, which holds adjacent sheets in alignment, yields with minimal energy allowing graphene layers to peel away from each other and the crystal. Groups of graphene layers cleaved away from a graphite crystal will provide a tough, impervious, inert, highly lubricious, thin film, which will effectively fill and “cap” disparities between rubbing surfaces. The film forming properties of graphite provide a perfect example of the relationship between microscopic form and macroscopic function.

The anisotropic behavior of graphite is exemplified in virtually all of its physical and chemical properties. For example, thermal and electrical conductivity, which result from various modes of within plane electron or thermal vibration transfer, are very high in the direction parallel with graphene layer planes (“a” direction). However, in the “c” axis direction no “ambient” mechanism of electron or thermal vibration transfer exists, resulting in low electrical and thermal conductivity in this direction.

Platelet overlap, crystalline imperfections and some randomness in platelet location in a thin film result in graphite-containing coatings that in reality do show a degree of through-plane conduction, however parallel plane conductivity is typically higher.

Chemical Inertness

Graphite is composed of carbon atoms so it will react with atmospheric oxygen above about 450 °C to form carbon dioxide. However, most coating systems are composed of binders and other additives, which either oxidize or break down thermally before the oxidation threshold temperature of graphite, is reached. Even in situations where exposure to high temperatures may occur, graphite has excellent short-term resistance to oxidation.

Reactivity between most chemical species and graphite is minimal. This high degree of chemical inertness is a primary attribute of the sp² hybridized carbon atoms that make up the graphite structure. Carbon in this form is stabilized by the so-called “resonance energy” imparted to the structure through the de-localization of the pi electrons of the sp² system. Carbon atoms located within graphene layers have a natural inertness as a result of this resonance stability. However, carbon atoms located at edge sites, especially those bonded to heteroatom substituents, are more reactive. Based on this model chemical reactions typically occur from the “edge in” rather than from the “top down” of graphene layers.

In a reducing atmosphere graphite is one of the most refractory materials known. Graphite is stable to well above 3,000 °C in a non-oxidizing atmosphere. Under ambient to moderately high temperatures graphite will not act as a reducing agent due to the strong interlayer bonding between carbon atoms. The result is that graphitic carbon is relatively unreactive even when finely divided.

LUMINESCENT ADDITIVES

Luminescent compounds are additives that impart fluorescence or phosphorescence to coatings. Examples are: materials based on ZnS and hexagonal wurtzite with bromhexine as an activator. Also used are rare earth aluminates, ruthenium pyrene or meso-tetrakis-(pentafluorophenyl) porphyrin platinum(II).

LUSTRANT

Agent that promotes more mirror-like reflectance. (The ratio of specular reflectance to diffuse reflectance is increased.)

MAR-RESISTANCE ADDITIVE

See *Slip Aid and Anti-Mar*

Chemical compound that enhances or promotes a coating’s ability to resist damage by light abrasion, impact or pressure. A coating must be able to interact with its environment without incurring fine surface scratches that mar or spoil the appearance.

MAR-PROOFING AGENTS

See *Slip Aid and Anti-Mar*

MASKING AGENTS

Masking agents are odorants that cover the distinctive or objectionable odor of specific ingredients in a formulation or a cured coating.

MATTING AGENTS

See *Flattening Agents*

One of the more interesting applications of nanoparticles is in matte coatings, a particular challenge in the 100% solids market. Most matting agents substantially increase viscosity, a problem that is usually addressed by the addition of either organic thinners or water. Amorphous nanoparticles in a variety of monomer components are being used to produce a family of additives for the formulation of matte coatings with nearly zero increase in viscosity.

MICROSPHERES

See *Extenders*

Microspheres are small, spherical particles whose size ranges from 12 to 300 microns in diameter; wall thickness can vary from several microns to as low as 0.1 micron. Microspheres can be solid, porous or hollow; composed of acrylonitrile, glass, ceramic, phenolic or polymeric materials; coated or uncoated. Because most are hollow, the true density of microspheres is lower than that of other non-soluble additives and ranges from 0.60 g/cc to as low as 0.025 g/cc. The spherical shape is one of the unique features that differentiates these products from other non-soluble additives. A sphere has the lowest surface area of any shape and, because of this, microspheres have very low resin demand. Microspheres are innovative raw materials in the coatings industry and are diverse because both solid and hollow formats are available.

Microspheres roll past one another like ball bearings, with no rough surfaces or branches to entangle. At common loadings, there is only a minimal impact on viscosity when they are added to a liquid. Formulators can use microspheres to increase the solid content of a coating while maintaining the proper application and flow characteristics. Higher solids can reduce volatile organic compounds (VOCs), shrinkage and drying time. The large volume that microspheres displace for a given weight is an important attribute in their use. Because hollow spheres will lower the density of materials they are added to, a gallon of coating will weigh less than the same product made without spheres. Lower-density coatings are less expensive to ship and easier to carry up a ladder. A low-density coating will atomize better, give less spatter when rolling, and sag less once applied. And since a small weight-addition of microspheres increases the batch volume significantly, formulation cost can be reduced.

Microspheres that are closed-cell, gas-filled particles are extremely good insulators. This characteristic is imparted to materials that contain microspheres. Thermal and acoustic insulation properties of coatings or substrates can be improved by the addition of microspheres. Makers of roof coatings, fire-retardant materials and sensitive acoustic equipment currently use this property.

Microspheres have some limitations that must be considered. The large particle size, compared to some other solid additives, can result in surface texture or gloss reduction, particularly in thin films. Their low density, the very property that gives them so many benefits, requires proper training and handling equipment so that they do not become airborne when adding them into the batch. Also, there is a tendency for the microspheres to float to the surface of low-viscosity systems. Proper product selection, viscosity modifiers and operator training can overcome these issues in most cases.

Architectural paints containing ceramic microspheres have a lower viscosity, better flow and improved sprayability due to their spherical shape. The surfaces that are coated with ceramic microspheres provide a level of soil and stain resistance typically associated with gloss and semi-gloss paints. These flat, matte paints produce a finish that is easier to clean than conventional flat paints because the surface can be scrubbed without burnishing. These systems are also ideal for large expanses as they reflect light more evenly, thus offering a uniform appearance.



Microsphere technology targeting aerospace coatings can significantly reduce the weight of aircraft paints, thus providing savings in fuel consumption. Weight reduction can have an impact in other coating areas as well.

Current areas under development are hollow glass microspheres coated with metals and pigments for application in various industrial areas. It is expected this technology will continue to grow in importance.

Polyethylene

Opaque polyethylene microspheres act as superior opacifying agents and can provide maximum hiding power with just one monolayer of microspheres as small as 40 microns in diameter. The polymer is pigmented to achieve the exact color and opacity level desired by the customer. Particle size ranges from 10-25 microns up to 850-1000 microns are available and supplied as a dry powder that can be easily mixed into coatings, adhesives and oils. Just like clear polyethylene microspheres, opaque grades are inert in most solvents and have a sharp melting point at 114 °C-120 °C depending on the molecular weight of the material used. Microspheres are manufactured in any color, and even in combinations of two differently colored hemispheres.

When light strikes an interface between two substances, in general, some may be reflected, some absorbed, some scattered and the rest transmitted. An opaque substance transmits very little light, and therefore reflects, scatters or absorbs most of it. High level of opacity becomes more difficult to achieve for microscopic particles, because opacity is proportional to the thickness of the material. An opaque microsphere does not allow any light to pass through, which means every single particle has maximum hiding power.

Opaque microspheres provide superior coverage with one invisible and feather-light layer – revolutionizing coatings products. Microparticles should be guaranteed to be >90% spherical and within specified particle size range. The exceptional smoothness, sphericity and particle size uniformity are responsible for the ball-bearing effect, which imparts the finished product with a silky texture, enhanced slip, glide and omnidirectional spreadability. Outstanding roundness enhances lubrication.

Red, green, blue, yellow or even multi-color microspheres make a product that is not only functional but fun and exciting by adding a hint of color, sparkle or even a color-changing effect, without dealing with difficult-to-disperse pigments.

One particularly interesting and unique feature of these microspheres is their ability to orient themselves in response to an electromagnetic field and show a visual response. This is achieved by making spheres both bipolar and bichromal, with dipole precisely aligned with two differently colored hemispheres. Due to the dipole the sphere will rotate in an electromagnetic field to align more the positive hemisphere to the negatively charged stimuli and vice versa. As the spheres align themselves, the viewer will observe the color of one hemisphere, while the other hemisphere will be hidden from view, providing an obvious strong visible indication of the presence of the field. In an alternating electromagnetic field, these microspheres can spin at hundreds of times per second.

This superior functionality is achieved with a proprietary and patented process that allows extremely precise coating on one hemisphere without affecting the other. Each coating is custom formulated for color; charge; magnetic, electric and surface properties; and solvent resistance per customers' needs. Hemispherical coatings of less than 1 micron with tolerances as low as 0.25 micron have been routinely demonstrated. Color combinations are truly unlimited. White, black, silver, blue, green, red, yellow, brown, purple as well as transparent microspheres have been made. Sphericity of greater than 90% and custom particle size ranges are available.

The spheres were originally developed for very high-tolerance electronic paper-reflective digital displays, where functionalized microspheres are used to create an image that appears to the viewer. To achieve high resolution in display applications it is critical that every single sphere responds to the electromagnetic field in the same way at

the same time and aligns precisely with the other spheres. It is also critical that there are no color gradients in the display.

PPMA

Small spherical beads of polymethylmethacrylate (PMMA) are used as additives in coatings and inks. The size of the beads and the acrylic composition provide immediate and excellent dispersion into solvent and waterborne systems. Sizes range from 20 – 50 µm, which provides visual surface visual effects along with hardness and improved scratch and abrasion resistance. Other advantages include transparency, slip and block resistance, and thermal and UV resistance.

Thermoplastic

Thermoplastic microspheres are compressible, resilient, hollow particles. The extremely thin shell wall possible with plastic spheres results in specific gravities as low as 0.025 and allows just a small weight-percent of these materials to displace large volumes. Because the resilient plastic can deform under stress, there is virtually no breakage when mixing or pumping these products, even with high shear mixing. Additionally, the compressible nature of plastic can absorb impacts that might ordinarily deform the finished product, thereby reducing damage caused by stone chips, foot traffic or freeze-thaw cycles.

Glass

Glass bubbles provide the benefits of high heat and chemical resistance; they are made from water-resistant and chemically stable soda-lime borosilicate glass, similar to the material used to make laboratory beakers. The walls of glass bubbles are rigid. Products are available in a broad range of densities from as low as 0.125 g/cc to 0.60 g/cc. The collapse strength of the glass bubble is directly related to the density, i.e., the higher the density, the higher the strength. For example, a glass bubble with a density of 0.125 g/cc is rated at 250 psi, whereas one with a density of 0.60 g/cc is rated at 18,000 psi. In order to minimize both the cost and the weight of the final product, the appropriate glass bubble is the one that is just strong enough to survive all of the manufacturing processes and the end use of the product.

The 18- and 30-micron hollow glass microspheres offer improved scrub and burnish properties, viscosity control, thermal insulation and sound dampening characteristics, improved performance and other functional properties previously unattainable. Because they are made of colorless glass they do not discolor light or pastel formulations. Their hollow structure, low density (0.60 and 0.34 g/cc) and small particle size make them ideal for use as extenders for paint formulations.

Paint that is extended with microspheres has a lower viscosity than paint filled to an equivalent volume with a non-spherical extender. Spherical particles have a low-energy surface that minimizes friction and drag. As a result, an equal volume substitution of these microspheres for irregularly shaped extenders will decrease the coating's viscosity. Lower viscosity is a significant benefit in solventborne systems as it allows formulators to remove some of the solvent and still maintain a viscosity that facilitates application and spreading properties.

With particle sizes considerably finer than previously available, microspheres can be used in thin film coatings to improve integrity. Glass spheres do not absorb resin and they may be used to improve hiding properties or to replace some TiO₂. The hollow glass spheres redirect the angle of light, imparting opacity. Depending on the formulation, equivalent tint strength can be achieved with 5-10% replacement of TiO₂.

To achieve the best economics with hollow microspheres, attention to formulating and mixing technique is necessary. Although higher density glass microspheres are extremely strong and resist virtually any shear applied, some consideration may be appropriate when hollow glass microspheres are used in paint manufacture. With a smooth glass surface, controlled particle size distribution and low surface area, as well as freedom from agglomerates, the hollow spheres wet out easily in virtually all systems. Adding spheres at the final mixing stage is usually best, and only relatively low shear needs to be applied to get spheres

dispersed. Long periods of mixing employing high shear could result in some breakage of hollow spheres and should be avoided.

Solid or hollow glass microspheres are commonly used to improve the performance of epoxy primers, powder coatings, floor applications, aerospace coatings, heat-reflective and industrial coatings. Hollow spheres are used in thermal insulating coatings for construction and transportation applications, and also for acoustic insulation coatings. Hollow glass microspheres with a density of 0.6 g/cc with a fine particle size distribution can be used in flat wall paint.

Ceramic

Ceramic microspheres offer very high strength and hardness. They are inert and available in fine particle sizes. Because of their hardness they offer formulators improved burnish, scrub and abrasion resistance as well as higher filler loadings because they are inert. They can be used in industrial and architectural coatings and also UV systems.

MILDEWCIDE

See Biocide/Fungicide/Antimicrobial

Microbiostatic agents are additives that will prevent the growth of microorganisms and their spores. It may or may not kill these organisms. A mildewcide is an additive that prevents growth of mildew on painted or coated surfaces. In a more loose sense, they are agents that are added to paints to prevent microbial attack during storage and after use.

MOISTURE BARRIER

Nanoparticles may be used to create barriers to air, water and other vapors, and various solvents. Such barriers work by filling space. A combination of nanoparticles and larger-sized particles is particularly effective for this purpose. By adjusting the percentage of particles or the application of coating itself, the barriers may be fine-tuned to specifically block water, air or solvents. Because these coatings do not work through hydrophobicity, this technique produces surfaces that may be printable and over-coatable.

Nano-enabled moisture barriers are particularly useful as a tool against microorganisms that thrive in a moist environment. This is particularly an issue in the case of flooding where even a few inches of water may be very damaging to drywall. When water is absorbed by drywall, spores landing on the paper surface of the drywall access the moisture and grow quickly. Sealing a porous surface blocks access to water and limits growth. A coating that acts against microbes in multiple pathways may be even more effective in that it is less likely to fall victim to resistant organisms. For example, the addition of a combination of nano-particle antimicrobials that break down cell walls along with larger particle additives (such as mixtures of silver and copper) may create a more effective coating for combating organism growth.

While many organisms may flourish in the presence of moisture, many electronic displays find it fatal. Conventionally, this problem is solved by using glass to protect sensitive components. However, glass has drawbacks; namely it is breakable, heavy and inflexible. Alternatives such as polycarbonate may absorb water. Serving as air and vapor barriers, coatings with nanoparticles can be used as a direct replacement to glass for more porous materials.

MOISTURE SCAVENGER

See Water Removal Agents/Scavengers

Moisture that gets trapped in a coating can be a nuisance and/or have devastating effects on the appearance and performance of the film. Exterior coatings, in general, can have problems with moisture, but certain coating applications are more sensitive to this than others. Applicators who are painting bridges, boats, offshore platforms and so forth are all concerned with moisture-related problems if they are using moisture-sensitive materials. (Some urethane systems are formulated to cure in the presence of moisture.)

Moisture is introduced into the coating in the form of dissolved water in solvents and other raw materials. Often it is adsorbed water in fillers

and pigments. For high-solids coatings this can have a serious effect because these coatings systems are higher in solids content. Humidity is a big factor in creating problems for the applicator using two-component moisture-sensitive urethanes. For urethane coatings this is particularly important because the slightest trace of moisture can react with isocyanates to form carbon dioxide and amines. The amines in turn react with more isocyanate to form ureas.

Low-solids, two-component systems are generally more forgiving to moisture contamination. Higher solids systems are not forgiving because the formed carbon dioxide gas cannot readily escape from the curing product. As a result, entrapped bubbles or pinholes appear which detract from system performance as well as appearance. This is especially true for higher build films that are usually found in industrial maintenance coatings.

If it is desirable to remove or eliminate water from some coatings and raw materials it can usually be accomplished by one of the following methods.

1. Molecular sieves. They provide a physical trapping mechanism to isolate water in the formulation. These materials are synthetically prepared zeolites that are characterized by crystalline cavities or pores that are of extremely uniform dimensions. They are porous aluminosilicates in which silica and aluminum atoms are joined by oxygen bridges within tetrahedral units. Introduction of counter ions of sodium, potassium, or calcium into the system results in negatively charged surfaces that selectively adsorb particular molecules. If the counterion is potassium, molecules with a diameter of less than three angstroms (carbon monoxide, helium, and hydrogen) will be absorbed. If the counterion is calcium, molecules with a diameter of less than 5 angstroms (ethane, methane, and propane) will be absorbed. The compounds are used in a variety of ways. Zeolites are naturally occurring aluminosilicates.

2. PTSI (p-toluenesulfonyl isocyanate) is a low-viscosity, reactive additive useful as a water scavenger in the formulation of specialty urethane products such as coatings, adhesives and sealants. The reaction of PTSI with water generates carbon dioxide and the corresponding toluenesulfonamide, which is generally inert to further reaction with alkyl and aryl isocyanates. The sulfonamide is usually soluble in common coating solvents and presents no significant toxicity hazards. The reaction of PTSI with water introduced from pigments and solvents in the paint formulation generates carbon dioxide and soluble inert chemical products. Experience has demonstrated that 13 grams of PTSI effectively scavenges 1 gram of water, however compatibility with the binder should always be tested.

PTSI provides the formulator of specialty urethane products with an expedient and efficient alternative to physical methods of dehydration in common use. It is also recommended for the storage stabilization of purified diisocyanates against deterioration or discoloration. It can be used for: moisture-curing prepolymers, catalyzed prepolymers, prepolymer and polyol systems, urethane alkyd production and urethane lacquer production.

Both one- and two-part systems can be formulated with PTSI as a scavenger for water introduced with solvents, pigments and fillers. The reactivity of PTSI toward active hydrogen atoms makes it useful as a scavenger for water and other isocyanate reactive groups such as free acid in powdered aluminum alkanoates and active hydrogen present in carbon black pigments, which causes polyurethane coatings to thicken during storage.

3. Oxazolidines. These ketone-based compounds chemically react to eliminate water. Oxazolidines remove the microbubbles without creating haze. In addition, gloss development and gloss retention is good, as well as distinctness of image (DOI) even under humid conditions.

4. Moisture scavengers in the form of hygroscopic silicas are used to scavenge water and prevent the oxidation of aluminum pigments and resulting instability, appearance and gassing problems in aluminum paints.



MOLECULAR SIEVES

See Moisture Scavenger

Molecular sieves are also used as water scavengers. They are composed of crystalline aluminosilicates that have cavities that are interconnected by common openings or windows. Their function of water scavenging is independent of temperature.

NANOTECHNOLOGY

See UV Absorbers/Abrasion Resistance

In the industry, the terms 'smart' and 'nano' are no longer buzzwords. Both terms appear with regularity and bring very innovative technology to the world of functional coatings.

Nano means one-billionth and, by definition, for nanotechnology we are looking at particles whose size ranges from 0.1 to 100 nanometers. It is hard to get our mental image around the concept of a billionth. By way of reference, the human hair is approximately 50,000 nanometers across and a bacterial cell is a few hundred nanometers across. A nanosecond is one billionth of a second and is a common measurement of read or write access time to random access memory (RAM). Time is currently measured in even lower increments such as picoseconds, femtoseconds and attoseconds – a 1 followed by 18 zeros.

At the nano level, the traditional physical and chemical properties of materials, as we know and understand them, all change. For example, all the properties we might attribute to the element gold, for instance, would not be true at the nano level, including its color, which, at ~5 nm, would be red. The implications of course are that we can construct and build whole new systems with different properties when dealing with nano-sized material.

This change in physical properties is attributed to a change in the electronic properties of matter. Electrons are confined in a smaller space causing these changes to occur. Nanotechnology deals with those electronic effects. At the same time the surface area of nanomaterial is enhanced by orders of magnitude so that surface effects become a critical aspect in nanotechnology. Stabilization of individual units as well as the surface activity becomes important when using nanomaterials.

There are examples of nano materials around us in use today. For the most part we are not even aware of them. One example is zeolites, which are very common and have been in use for quite some time, particularly as water softeners. Their nanopore structure accounts for their capability and success. Some companies have been developing and using multilayer films where each layer (10-20 nanometers thick) is applied at the nanoscale level. The layers create an almost perfect reflective mirror and are used inside LCD displays today – for example in the laptops. This technology has been on the market for years.

Coatings with nanoparticles can be used to increase the scratch and abrasion resistance of the surface, used to increase corrosion resistance and used for anti-reflective coating properties. There are applications for furniture coatings and flooring coatings. Nanoparticles can have a significant advantage over traditional fillers. The impact on polymer design may also be of great significance as properties such as heat resistance, stiffness, strength, electrical conductivity etc., can be engineered and controlled. In fact polymers can be custom made and tailored to fit the need.

One of the most advanced markets in the field of nanotechnology is in the area of modifying surface properties using nanotechnology.

Only well-dispersed individual units of nanomatter behave like nanomaterial in the best way. Even slight aggregation can cause the loss of all nanoeffects. For that reason pre-dispersed nanoparticle master batches are an ideal way to utilize nanomaterials in coatings. By using only small amounts of the active ingredient and by achieving very high active ingredient contents in the master batch, nanoadditives provide a smart way to introduce new or enhanced coating properties.

Certain nanosized oxides, well dispersed into a coating formulation, can significantly impact the mechanical properties of the coating. Nanosized alumina and silica is of great interest because high-gloss high-transparent coatings can be achieved by using nanosized fillers instead of micron-sized materials.

The past few years have witnessed a significant increase in the adoption rate for nanotechnology, and in particular, nanoparticles, by the coatings industry. Examples are numerous and include such applications as the use of nanoparticles to: improve the hiding power of latex paint pigment; increase the UV protection of wood stains; enhance the crosslinking of water-based emulsions; absorb IR radiation to control heat flow; enable electrical conductivity; improve binder strength; and provide barrier properties, to name just a few. Perhaps one of the most established applications for nanoparticles is their utility in enhancing the wear resistance of coatings. The most common particles used for this purpose are aluminum oxide and silica, and both materials have benefits and drawbacks. Alumina is much harder than silica, and thereby it provides greater wear resistance at a similar usage level in a coating; however, the higher refractive index of alumina has traditionally restricted it to opaque applications or to systems where coating clarity is not critical.

Perhaps the greatest challenge encountered when attempting to incorporate inorganic nanoparticles into a coating formulation is related to ensuring compatibility of the particles with the resinous matrix so that there is sufficient stabilization to resist agglomeration. Because of their small size, high surface area and numerous reactive surface sites, nanoparticles have a strong tendency toward agglomeration, and, eventually, flocculation from the formulation. To combat this, stabilization of the particles in a formulation typically requires the application of a surface treatment to the particles. The design of the particle surface treatment is critical and is typically customized based on the specific coating application. To be effective, the surface treatment must satisfy the following three criteria: (1) stabilization of the nanoparticle dispersion concentrate (product shelf life); (2) compatibility between the nanoparticles and the other components used in the coating formulation; and (3) prevention of agglomeration during the coating curing process.

An effective surface treatment will allow the nanoparticles to be dispersed to their primary particle size at high concentration in a carrier solvent while still maintaining a low viscosity. The surface treatment must also stabilize the nanoparticles from re-agglomeration to prevent irreversible flocculation and gravimetric settling of the material in the product container over a period of months to years in storage before application. Such dispersion stabilization is achieved with surface treatments based on charge stabilization or steric repulsion or, in some cases, both. Designing the appropriate surface treatment depends on knowledge of variables such as nanoparticle size, surface area, porosity, composition, surface chemistry, zeta potential and solvent properties. Understanding how each of these properties contributes to the overall negative free energy of the dispersed system is often the key to optimizing the surface treatment system.

The second role of the surface treatment on the nanoparticles is to provide compatibility between the discrete particles and the myriad different components in a particular coatings formulation. This can represent a substantial challenge as resins systems, surfactants, defoamers, thickeners, surface tension control additives, pH stabilizers, pigment concentrates, etc., all contain various reactive or interactive groups that can interfere with the nanoparticle dispersion to cause destabilization and flocculation of the particles from the formulation. Compatibility can be particularly difficult in water-based emulsions, owing to ionization and solubility effects, acid-base reactions, and the sensitivity of electrostatic charge on the particles to ionic strength and pH.

Nanoparticle dispersion stabilization must also remain active through the curing process of the coating. As the solvent evaporates, the surface treatment must continue to provide for compatibility with the resin system and any coalescing solvents to ensure homogeneous dispersion of the particles in the final film. Any agglomeration of particles during this stage will lead to increased light scattering and contribute to higher haze, and likely damage the desired uniformity of the coating. Again, for the reasons already cited, water-based coating formulations pose the greatest challenge in this regard.

Scratch Resistance

New nano silica and alumina particles can also be incorporated into pigmented coatings. The nano silica and alumina particles not only offer scratch resistance but can assist in wear resistance, better adhesion, staining and corrosion resistance because the nanoparticles create a denser coating structure. The nanoparticles have a synergistic effect with silicone, acrylates, silica and waxes.

Silica nanoparticles are used in UV-curable systems primarily to promote scratch and abrasion resistance, but also to provide a variety of other mechanical and surface properties. The anionic, hydrophilic surface chemistry of silica is imparted by the silanol groups that dominate the surface of silica nanoparticles, and it creates challenges for the end user of silica in UV-curable polymer systems. The conventional availability of silica nanoparticles in either organic solvents or a limited range of monomers also limits the versatility of these products in UV-curable systems. End users can overcome some of these problems through treating the surface of silica particles with silane coupling agents, however, commercially pretreated silica particles, silica particles dispersed in more versatile system components and carrier-free monodispersed silica promise to increase ease of use of silica nanoparticles in UV-curable systems.

Recently introduced additives containing alumina nanoparticles can provide improved scratch resistance for solvent, waterborne and UV coatings. These new nano alumina particles of 20 - 80 nm diameters are dispersed in different media and easily incorporated with low shear into aqueous, solventborne, or solvent-free UV-curing systems. Typically, low dosages of 0.5 - 2.0% provide significant and long-term scratch, mar and/or abrasion resistance without adversely affecting gloss, color, clarity or other physical properties of the coatings.

The inclusion of surface-active modified poly(dimethylsiloxanes), acrylates, or waxes due to their orientation and crosslinking at the coatings surface as well as throughout the coating enhances the performance of the nanoparticles. Where high gloss is not desirable, combinations of the nano alumina particles with flattening waxes and matting agents allow the formulation of semigloss to flat coatings.

When incorporating a small amount of nanoalumina in a UV-curable coating system the resistance against mechanical scratching can be increased significantly. If the combination of alumina nanoparticles and polysiloxane-based additive is used, the scratch resistance is improved dramatically. Just 1.5% alumina nanoparticles in combination with 0.2% surface-active polysiloxane-based additive is sufficient to reach an excellent scratch resistance. The specific combination of nanoparticles and additives gives the best scratch resistance. The extent of this effect depends on the chemical nature of the matrix and on the additive structure and composition.

Currently the focus on the use of nanomaterials besides scratch resistance includes UV stabilization, anti-microbial activity, IR absorbance, or conductivity/anti-static properties of coatings.

Overprint Varnishes (OPVs)

In an effort to reduce the degree of light scattering, and thereby broaden the potential for alumina particles to be used in coatings, several products have been recently commercialized that consist of dispersions of sub-micron and nanoparticle-size alumina that are specifically designed for use in coatings formulations where both gloss and clarity are critical. These dispersed alumina products have found applicability in a variety of diverse industry areas and coating formulations. One application in particular that is ideally suited for such wear-resistant technology is that of overprint varnishes (OPVs). OPVs are very thin, flexible coatings applied over ink and paper substrates and are used to prevent degradation resulting from rubbing, scratching or abrasion. These coatings must retain a high level of clarity and, very often, high gloss. Because they cure to a very thin film thickness, any particle used for wear protection must be small in size, well dispersed, and stable with respect to agglomeration so as not to impact the surface finish of the OPV.

For OPV coating formulations it has been demonstrated that the combination of sub-micron size alumina particles with nano-size wax particles

provides a level of wear protection that exceeds that possible using either of the additives alone. The behavior has been observed in different OPV formulations and with different wax compositions. The mechanism that drives the synergistic behavior is still under investigation.

Fumed Silica

Fumed silica is an example of a nanoscale inorganic additive that can be particularly enabling in polymer film and coating systems, especially in waterborne formulations. The nanosize provides high specific surface area, and the fractal-like shape provides rheology and viscosity control. (A fractal is a shape such that, if you look at a small piece of the shape, it will look the same as the original, just on a smaller scale. A good example is a Boston fern.) However, this feature of the fumed silica structure, when properly dispersed within a waterborne formulation, can aid in polymer latex film formation. Such particle additives can also help increase drying rates to improve processing throughput times. Unlike VOC organic additives commonly employed as leveling agents, plasticizers and co-solvents that evaporate upon drying, nanoparticles like fumed silica remain in the coating and can fulfill additional functionalities such as mechanical reinforcement, while helping make the overall formulation more "green."

Carbon Nanotubes

Marine coatings formulated with carbon nanotubes have very high abrasion resistance. In addition, the coatings reduce the flow resistance between the ship's hull and the water, thereby enabling reduction in fuel consumption. Carbon nanotubes (CNTs) have been used in this application for sea-going vessels. The coatings are suitable for new vessels and for subsequent repair and maintenance coatings.

Another major advantage of the carbon nanotubes is the reduction of maintenance costs. This is because the ban on organic tin compounds for use as antifouling agents to prevent organic growth necessitated relative frequent cleaning of the coatings surface to ensure cost-effective transport. CNTs provide smoothness and hardness thereby reducing organic growth.

In other application areas, CNTs offer unique mechanical, optical and electrical properties. Coatings containing CNTs are available from many sources today but not all have properties compatible with commercial printing equipment and in high volume. The ability to print CNTs at high volume with commercial equipment without the past negative attributes facilitates a wide range of applications. Printing CNTs is safe and easy to use today with a workable viscosity range, no added surfactants or dispersants and no CNT airborne species. Direct printing means there is no need for subtractive patterning. Certain CNT ink fluids today have been successful on commercial screen printing equipment with relatively high CNT loadings (1 g/L). Commercial applications such as paper lighting, paper batteries, touch pads/screens are currently being investigated.

Carbon nanotubes offer tremendous opportunities for the development of new material systems. Their excellent electrical conductivity combined with their high aspect ratio offer opportunities for the development of functional coatings. To increase the conductivity of coatings, carbon nanotubes can offer an interesting alternative to the classical conductive pigments like carbon black or metallic particles. To get the optimum benefit from carbon nanotubes they should be incorporated into the coating in the form of dispersions to guarantee optimum distribution. In addition, the right wetting and dispersing additives have to be used to enable percolation and compatibility with the coating matrix.

High-Performance Materials

Research chemists at the University of Warwick have devised an elegant process that simply and cheaply covers small particles of polymer with a layer of silica-based nanoparticles. The final result provides a highly versatile material that can be used to create a range of high-performance materials such as: self-healing paints, and clever packaging that can be tailored to let precise levels of water, air or both pass in a particular direction.



The research has created a “soap-free emulsion polymerization process”, which makes colloid particles of polymer dispersed in water and, in one simple step, introduces nanometer-sized silica-based particles to the mix. These silica-based nanoparticles (about 25 nanometers in size) then coat the polymer colloids with a layer, “battering” it almost like a fish is battered in bread crumbs.

This process creates a very versatile polymer latex product. It can be used to create scratch-resistant paints in which the scratches heal themselves. It can be fine tuned to produce polymer-based packaging, which will allow water or air to pass through the packaging in tailored ways. The resultant rough-textured spherical shapes also lend themselves to the creation of sheets with polymer that present much more surface area than usual, allowing more-efficient interaction with other materials. By exposing the material to a second simple step, which deposited another polymer layer on top of the already silica-based nanoparticles—“battered” polymers the researchers were able to produce particles with an even greater range of properties and uses. This new process dramatically cuts the time needed to create such materials, and its single step can already be produced on a mass scale with currently used industrial equipment.

Improved Chemical Resistance

Nanoparticle dispersions as functional additives can be an alternative to improve the performance of waterborne coatings. Specifically, processed ZnO nanoparticle dispersions can increase the chemical resistance of waterborne coatings. Dispersion quality is critical to obtaining good transparency and chemical resistance. These properly used nanoparticles are very efficient compared to wax additives.

Inorganic UV-Absorber

Inorganic UV-absorbers are frequently used in coatings. Three different materials are under intensive development: nanosized titania, nanosized ZnO and nanosized cerium dioxide.

The materials differ in price, performance and absorption characteristics. The most expensive material is cerium. In addition, cerium is an oxidation catalyst – a property currently used in the field of mechanical-chemical planarization (CMP) of semiconductor wafers. The catalytic activity combined with the high cost of raw materials are the two major drawbacks when thinking about the use of cerium dioxide in coatings. Titania is less expensive than cerium, but as pure rutile it is photoactive under UV-radiation. The formation of radicals leads to a decomposition of organic materials. For that reason titania must be coated and doped in order to quench the radical formation. Looking at the absorbance characteristics of nano titania, the absorbance edge is around 320-350 nm which is in the UV-A region.

Compared to ZnO the last of the three inorganic UV absorbers, titania has a higher absorption coefficient but is more transparent in the near UV-A region. ZnO very effectively blocks radiation below 400 nm while being less expensive compared to the two other oxides.

Among inorganic UV absorbers, zinc oxide and cerium oxide stand out with their almost complete adsorption of UV-A, B and C. Reduction of particle size from micron to nano enables the formulator to formulate clear coatings that can both enhance the appearance of wood substrates as well as provide long-term protection for the wood metal and plastic substrates against UV degradation.

There are advantages of inorganic nanosized UV absorbers. Due to the nanosize of the particles, the gloss and the color of the coating are not affected when adding less than 2% of, for example, ZnO. Even with initially equally good performance of the inorganic and organic UV absorbers, especially over a long lifetime, the inorganic will out-perform the organic absorbers simply because they do not decompose by photochemical reaction induced by UV light.

Silicone Nanocomposites

In recent years, polymer nanocomposites have received significant attention since nanoscale particles provide an opportunity for enhanc-

ing the mechanical and functional properties of the polymer at relatively low volume fractions, thereby preserving the desirable properties of the polymer, such as flexibility and ductility. The reasons for using nanoscale particles in a polymer matrix are outlined in the following points.

1. Incorporating nanoscale particles, particularly those with a high aspect ratio (e.g., platelet-shaped clay nanoparticles) in a polymer matrix, leads to several beneficial features, including low percolation threshold (< 2 vol%), high interfacial area, and a size scale that is comparable to that of polymeric molecules.

2. The interface between surface-modified nanoparticles and the polymer matrix will be smooth, resulting in effective load transfer to the matrix and a smooth surface finish to the final nanocomposite. Conversely, coarse particles, because of their large size and particularly when added in large volume fractions, do not bond well with the polymer matrix. Consequently, coarse particles degrade the mechanical properties of the base polymer.

3. Incorporating solid particles (or nanoparticles) in a polymer matrix or in a polymer-based coating formulation can give rise to processing issues such as a significant change in viscosity, inhomogeneous mixing and reduction of shelf life.

All these problems can degrade the final properties of the nanocomposite. Nanoparticles present less of a problem than micron-sized particles because nanoparticles can be added in much smaller quantities to achieve a similar reinforcing effect. Additionally, when nanoparticles are modified with a suitable organic molecule/oligomer, they become compatible with the matrix and ameliorate processing problems.

Silicones, also referred to as polysiloxanes or PDMS, have the repeating unit $[\text{Si}(\text{R})_2\text{-O}]_n$, and are prepared from chlorosilanes. Depending upon the number of repeating units in a polymer chain and the degree of crosslinking, several different types of commercial silicone products can be produced: fluids, emulsions, compounds, lubricants, resins, and elastomers or rubbers. Nanoscale additives in silicone coatings offer the opportunity to improve physical gas barrier properties, in addition to enhancing mechanical properties. Some data indicates that oxygen transmission rates for nanocomposites of silicone are usually less than half that of the unmodified polymers.

The demand for such materials is expected to grow as research and development continues in the areas of inflatable habitats, sunshields, aerodynamic decelerators, and other deployable space structures (e.g., antennas, trusses, solar arrays).

Antimicrobial Nano Silver

The key to nanoscale silver's antimicrobial advantage is found in how it works. Ionic silver is the active form of silver that is most effective at eliminating bacteria, mold and fungus. Moisture activates silver nanoparticles, which release silver ions that attack microbes. These silver ions inhibit bacteria by stopping bacterial energy metabolism and electrolyte transport, by slowing or stopping DNA replication or by binding to the bacterial cell wall causing it to collapse or burst. As such, silver ions are active against a broad range of gram-positive and gram-negative bacteria, have a low risk for bacteria resistance, and are effective in low concentrations.

Reducing silver to nanoscale sizes provides several important benefits not found in silver's bulk form. The first is related to antimicrobial performance. The key to optimizing the use of silver as an antimicrobial is to maximize the production of the silver ions that target and eliminate microbes. This is achieved by reducing the average size of the silver particle, which exponentially increases the collective surface area available for silver ion production. Hence, unlike bulk silver-based antimicrobial solutions that depend on adding increasingly more silver to be effective, nanoscale silver can achieve the same or better levels of efficacy using considerably less silver, thereby reducing cost and the potential for environmental impact.

Nanoscale size brings other advantages to silver. Silver nanoparticles can be covalently bonded to molecules in the products in which

they are integrated. In this way, the silver particles are less susceptible to being washed out or worn off over time. Under the proper application techniques, their antimicrobial capabilities are effective for the expected life of the host material. In addition, silver nanoparticles are so small that they don't impact mechanical properties. And because silver nanoparticles are metallic, they retain a number of key attributes of bulk silver, such as thermal stability during processing and UV-color stability. Nanoparticle silver additives can be produced in integration-ready formulas, compatible with virtually any manufacturing process across a wide variety of host materials, including coatings, foams and engineered plastics as well as natural and synthetic fibers and fabrics. Specific to coatings, nanoparticle silver additives for liquid systems enable formulators to "just add and mix" at numerous steps during the manufacturing process. Powder additives are also available for integration with other performance additives typically compounded into powder coatings, such as flame retardants and colorants.

SmartSilver™ Antimicrobial

Designed for dispersion in water-based or organic solvents, SmartSilver antimicrobial additives are stabilized silver nanoparticles incorporated into coatings to inhibit microbes. See *Biocide/Fungicide*.

Nanoclay

Nanomaterials have a relatively large surface area, and it is believed that replacing larger-size extenders with nanosize extenders could provide improved coating properties and corrosion resistance. Incorporating nanoclay into polyurethane coatings significantly improves dry adhesion as well as high-pressure hot water spray test properties. The nanoclay also improves humidity resistance, VDA cyclic corrosion over mild steel and acetic acid corrosion over aluminum.

Cellulose Nanotechnology/Thickener

Curran®, a material developed from the extraction of nano-cellulose fibers of root vegetables such as carrots and sugar beets, is a high performance cellulose rheology modifier with unique characteristics. The material is composed of cellulose, organized into a unique physical form that imparts properties that are different from other types of cellulose. The plate-like structure of Curran fiber has many of the characteristics of a nanomaterial, but without the presence of free nanofibers. The nanofibers that make up Curran have very high mechanical properties with strength similar to carbon fiber. The physical form of the material means that there is a huge surface area for interaction with water and/or polymers, and the shape of the particles imparts unique viscosity profiles and crack-stopping capabilities.

The chemistry of the material results in a large number of OH groups. These can be used to interact with a wide range of materials, or they can be chemically modified to enable specific reactions with polymers such as epoxies and acrylics. As a rheology modifier, Curran is designed to give very efficient thickening with strong shear thinning characteristics. At the same time it provides enhanced reinforcement/toughening of both curing and cured films. Because of the crystalline nature of the cellulose it can enhance the hardness of polymer systems.

Curran exhibits thickening efficiency greater than other cellulose thickeners and in fact other thickeners in general. Also the viscosity vs. rate profile shows extreme shear thinning, which means that the material is very good at providing sag resistance and is an effective anti-settling agent. When used to thicken water-based epoxy formulations, Curran is just as effective in the absence of an associative thickener.

In the future nanotechnology will influence our life more and more. Simply by changing the size of currently existing materials, new, improved, or enhanced properties occur that can be taken advantage of.



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NEUTRALIZING AGENT

See *pH-Control Agents*

Multifunctional neutralizing agents, inorganic or organic, can provide formulators the flexibility to optimize performance characteristics. Inorganic neutralizing agents are used in paint formulations only for pH adjustments. Organic alkanolamines are used as neutralizing agents, but they also bring multifunctional characteristics through the stages of a coating's life. The multifunctional benefits of alkanolamines can be listed as co-dispersancy, neutralization, rheological performance improvement and VOC reduction through formula optimization. Additional in-can performance attributes include benefits like flash rust corrosion inhibition, improved shelf life and enhanced freeze-thaw resistance. Alkanolamines also can improve the pigment dispersion efficiency and dispersion stabilities in paint formulations.

ODORANTS

Odorants are chemical compositions that confer a specific odor to a formulation.

ODOR-REMOVAL AGENT

Healthier indoor air is critical – especially for those who are susceptible to respiratory ailments, colds, viruses and bacteria. Innovative green technology provides a way to improve air quality and remove offensive odors and pollutants in a way that is safe, clean and effective.

Through the use of nanoionic technology, far infrared rays and a special manufacturing process, a natural (non-manufactured) paint additive has been developed to permanently remove embedded odors caused by smoking, pets, cat urine and bacterial proliferation. Negative ions occur in all sizes and are electrically attracted to airborne particles such as mold spores, odors, allergens, even viruses and bacteria. They attach to these and precipitate them onto the nearest surface, thus cleaning the air of pollution and germs.

Air-ReNu is a proprietary blend of naturally occurring polymeric matrix materials that are used in water purification to detox and remove impurities in drinking water; they are inorganic, natural, nontoxic and environmentally safe. These same matrix materials ground into a fine powder then mixed with paint and applied to interior walls produce a continuous flow of healthy negative ions and IFRs, thereby detoxifying the air while removing offensive odors.

EPA studies indicate that Americans spend billions of dollars yearly on spray and medications to help remove odors, breathe better or cure respiratory illnesses, including ailments such as asthma, hay fever and other allergies. Many physicians believe that a solution is in reducing indoor air pollutants.

Independent studies have confirmed that the inclusion of this innovative technology is effective in reducing and diminishing various pathogens, including MRSA bacteria (*Staphylococcus aureus*) and Black Mold (*Aspergillus Niger*).

The product and technology are non-toxic and will not break down into hazardous materials. It is not harmful to pets, children or plant earth, and no drugs or chemicals are used. It is also passive, which means no consumption of electricity is necessary for the technology to work. It is a green solution.

OILS

Oils have various functions depending on their ability to form films or alter a variety of paint properties. Drying oils from vegetable oil or animal sources have been used as sole binders and modifiers for other resins [linseed, tung (Chinawood) and fish oils]. Over the years tung oil seems to have been the preferred drying oil for coatings and inks as well as a finishing agent for wood and concrete. Linseed oil is one of the oldest known drying oils and like tung oil has been used in the manufacture of coatings, inks and furniture polishes.

Semi-drying vegetable oils are used primarily in the manufacture of other oxidizing resins (soya bean and safflower oils).

Non-drying oils are used in plasticizing alkyds and in blends with other resins in baking systems (raw castor, coconut and cottonseed oils).

Castor oil is a natural oil obtained from the seed of the castor plant. It is unique among naturally occurring oils in that it is the only commercially important oil composed of approximately 90 percent of a hydroxy unsaturated C18 fatty acid – ricinoleic acid. There are four different grades of castor oil. The industrial grade is used extensively in the manufacture of textile chemicals or as a wetting agent for inks, coatings and adhesives.

Mineral oils are used as basic building blocks in defoamers for latex paints or as a VOC-free non-volatile portion of water repellants.

Silicone oils are used in surface lubricants, anti-blocking additives, and scratch/mar resistant additives. Pure silicone oil is very effective, but often causes many other problems due to contamination. See specific additives for more information.

OPACIFYING AGENT

See *Microspheres, Extenders*

OPTICAL BRIGHTENERS

See *Brightener*

Optical brighteners are fluorescent compounds that absorb near ultraviolet radiation and then reemit it as violet-blue light that gives yellowish-white coatings a brighter, whiter appearance. Small amounts of blue dyes are also used to achieve the same result.

ORANGE PEEL PREVENTER

Chemical compound that prevents the occurrence of the surface defect characterized by irregular waviness in the film resembling the texture of an orange skin. Orange peel is usually caused by improper or insufficient flow of the coating on the substrate surface. There can be many causes for this ranging from improper atomization of the coating during a spray operation, excessive coating thickness without adequate flowout, improper drying conditions or the surface of the substrate itself may be dirty or not properly prepared. Adding a surfactant to a waterborne system can often help eliminate orange peel; certain silicone additives may also be effective in solventborne systems.

ORGANOCLAYS

See *Thickeners*

Organoclay is a modified clay such as montmorillonite bentonite clay that has been organically modified to produce an organophilic clay. A variety of organically modified clays are available. These allow the material to be added to a variety of organic solvent systems and to generate thixotropic viscosity and thus control of sag and settling. Typically organoclays are added in amounts of 0.5% to 5%. They allow a gel structure to form under nil and low shear conditions, and when shear is applied to this system, the gel structure breaks down and viscosity decreases. When the shearing force is removed, the gel structure reforms.

pH-CONTROL AGENTS

See *Neutralizing Agent*

Chemical compounds used to raise, lower or buffer the pH of waterborne compositions.

The pH of a latex must be controlled within a certain range for stability. The alkanolamines are most commonly used, in particular: 2-amino-2-methyl-1-propanol (AMP), Advantex™, Vantex-T, 2-amino-2-ethyl-1,3-propanediol (AEPD™ VOX1000), monoethanolamine (MEA) and methylaminoethanol (MAE).

Other than ammonia, alkanolamines play an important role as the primary evaporative neutralizing agents used in waterborne coatings. The adjustment of pH in waterborne coatings is important in order to maintain a stable pigment dispersion, minimize corrosion, reduce biological growth and generally optimize the performance of the coating during storage and application. After application of the wet coating, the pH adjusting agent must, at least partially, evaporate from the film in order to promote the coalescence of the resin binders via a decrease in pH.

Alkanolamines are ideal pH neutralizing agents in a number of ways, including compatibility with latex emulsions, solubility in latex emul-

sions, a sufficiently high pKa value to allow for efficient neutralization to pH values between 8 and 10, and intermediate vapor pressures that allow for evaporation at a controlled rate. The optimum alkanolamine for a given coating formulation will be the one with the best balance of physical properties, allowing for the maximum number of benefits and the minimum number of negative side effects (e.g., odor).

Only certain alkanolamines are exceptional with respect to their ability to improve latex paint through significant positive impact on odor, corrosion properties, adhesion, biostability, pigment stability, coalescence and overall performance.

The influence of alkanolamines on adhesion is significant; comparative waterborne coating formulations that differ only in their alkanolamine content have markedly different adhesion properties on plastics. Better surface affinity of a liquid coating for a solid equates to better overall chemical adhesion of the coating to the solid. Some alkanolamines, despite their low percent composition in the coating, have a significant impact on the interfacial properties of the coating and have a significant effect on the adhesion of dried waterborne coatings on plastics. Alkanolamines with mid-range calculated HLB values yield coatings with lower solid/liquid contact angles and measurably better adhesion.

The pKa of the alkanolamine used in a waterborne coating has an influence on the performance of the coating. Higher pKa alkanolamines allow for more efficient neutralization and higher working pH levels while lower pKa alkanolamines have some utility as reserve alkalinity in open industrial systems.

There are other hindered amines (trifunctional molecule) that are good pH buffers, offer good storage stability, neutralize waterborne resins, improve thickener performance, control viscosity, aid in pigment dispersion, and are able to offer decreased dispersant costs and overall additive cost compared to ammonia in waterborne coatings systems.

Care must be exercised using slowly volatilizing amines because they can cause blocking, early water sensitivity, or after tack problems under poor drying conditions. In some circumstances, ammonia, TEA or DEA are more suitable.

PHOTOCATALYST

Photocatalytic technology has been developed to control atmospheric pollution. CristalACTiV™ is an active, non-pigmenting and odorless photocatalyst that can be added to coatings or building materials. It is derived from titanium and can be formulated into stable, non-toxic coatings systems or added in powder form to standard construction products.

CristalACTiV-treated surfaces draw volumes of NO_x out of the air; NO_x reductions as large as 60% NO and 20% NO₂ in the immediate area of the treated surface can be achieved. This technology is self-cleaning and long lasting (up to 15 years depending on application). This TiO₂ photocatalyst behaves as a catalyst and is not consumed in the reaction. The TiO₂ photocatalyst has also demonstrated anti-bacterial properties against MRSA and *Staph. aureus* bacteria. The product also seems to be effective against fungi and mold.

Photocatalytic powders are available in a wide range of surface morphologies and particle size distributions. The powder form can be formulated into exterior coatings, building and construction materials, transportation and infrastructure projects and can also be applicable to plastics, textiles and roof tiles.

Photocatalytic sols are stable aqueous colloidal dispersions of the ultrafine TiO₂ and are stabilized with acid or base. These sols can either be introduced as components of the formulation to achieve an optimal dispersion of the photocatalyst or they may be applied onto a surface to render it photocatalytic.

PHOTOINITIATORS

Molecules that, when subjected to ultraviolet radiation, generate chemical species capable of initiating polymerization.

Photoinitiators are compounds used in the ultraviolet or visible radiation curing processes. These compounds absorb radiation, are raised to an

electronically excited state, and then photolyze (degrade) into an active species, cations, free radicals, or both, that are capable of initiating polymerization of monomers and functional oligomers in the formulation.

Free-radical photoinitiators are compounds that absorb ultraviolet or visible radiation and photolyze directly through a unimolecular reaction or indirectly through a bimolecular reaction. In the unimolecular reaction, the photoinitiator is split into one or more free radicals. In the bimolecular reaction, there is hydrogen abstraction from a synergist molecule, usually an amine with an alpha-carbon atom, which becomes the actual initiating free radical species. Typical amine synergists are: methyl diethanol amine, dibutyl ethanol amine, triethyl amine and triethanol amine. These react synergistically with hydrogen-abstracting photoinitiators such as benzophenone or isopropyl thioxanthone. The free radicals formed are capable of initiating the rapid polymerization of ethylenically unsaturated compounds such as acrylates. Typical of the direct type is 2,2-diethoxyacetophenone and typical of the indirect type is benzophenone used in combination with an alpha-carbon-containing amine synergist such as triethyl amine.

Cationic photoinitiators are compounds that absorb ultraviolet radiation and photolyze directly into Lewis or Brønsted acids that are capable of initiating the rapid polymerization of compounds such as the cycloaliphatic epoxides, other epoxides and vinyl ethers. Most cationic photoinitiators are of the Brønsted acid type, i.e., chemicals that photolyze into cations – compounds that have a positive charge such as a hydrogen ion, H⁺. These protonic acids are capable of causing very rapid polymerization of epoxides and vinyl ethers as well as copolymerization of cycloaliphatic epoxides with polyols. Most cationic photoinitiators also generate free radicals that are capable of polymerizing ethylenic unsaturation such as is found in acrylates. Examples of cationic photoinitiators are the aryl sulfonium metallic salts, as aryl sulfonium hexafluorophosphate and aryl sulfonium hexafluoroantimonate, and the aryl iodonium metallic salts, such as diaryl iodonium hexafluoroantimonate.

Bis-acyl phosphine oxide (BAPO) photoinitiators are suitable for pigmented systems, thick or UV-stabilized clear coats and daylight curing.

UV Powder Coatings

The proper selection of photoinitiator depends on its adaptability to the powder process and its ability to be photoactive in clear and pigmented systems. Both solid BAPO and HHMP do not seem to adversely affect the softening point of a powder coating resin. In addition, HHMP exhibits minimal yellowing in a clear system.

UV Waterborne Coatings

In recent years waterborne UV-curable coatings have become more significant in the coatings industry. A particularly effective strategy for photocuring is to use two or more photoinitiators. The individual photoinitiators target specific regions (surface and bottom) of the coating. Short-wavelength-absorbing photoinitiators effectively cure the top coating surface. A long-wavelength-absorbing and photobleachable photoinitiator can be effective for deep through-curing. Examples of the common photobleachable, long-wavelength-absorbing photoinitiators are mono-acylphosphine oxide (MAPO) and bis-acylphosphine oxide, BAPO.

Common surface-cure photoinitiators are aromatic *α*-hydroxy ketones (AHK) and mixtures of benzophenone/AHK. To ensure good through-curing, arylphosphine oxide photoinitiators are often used. Deep through-cure is critical for coatings that contain UV-blocking materials such as light stabilizers and/or pigments/fillers. Water-dispersible benzotriazole (BZT) and polar hindered amine light stabilizers (HALS) have also been used. Today, newer high-performance waterborne UV-curable resins are available which put more stringent requirements on the photoinitiator and light stabilizer packages. The higher durability requirements are often not met using traditional light stabilizer packages.

Part of solving the light stabilizer problem is getting high-performance and hydrophobic additives into the resin system. A new way of doing this is to use an encapsulation technology for the high-performance additives. The so-called Novel Encapsulated Additive Technology



(NEAT) provides a way to easily incorporate the materials into aqueous paints without using co-solvents and without requiring high-energy dispersion equipment. Liquid photoinitiators based on arylphosphine oxide have worked well in some systems.

PHOTOSENSITIZERS

Photosensitizers are organic compounds used in combination with photoinitiators. The photosensitizers are capable of absorbing radiation of a particular wavelength and thus being raised from a ground state to an excited state, and then emitting radiation of a wavelength that can activate a photoinitiator present in a formulation. After the excited photoinitiator emits radiation, it falls to either a lower energy level or to its original ground state. Photosensitizers are used when radiation of a particular wavelength is available and though the compound is excited by the radiation, it is not capable of photolyzing. However, it can emit radiation to the photoinitiator at a different wavelength and cause its photolysis.

PIGMENTS

Pigments are ground materials that are dispersed in paints to provide bulk, color and hiding. The primary pigments are used to add whiteness and color. Titanium dioxide is the most widely used white pigment. Colored pigments are of two types – organic and inorganic. Organic pigments provide brighter colors but are less durable than inorganic pigments. There are a large number of colors available and these might be exemplified by copper phthalocyanine blue, thioindigo reds, and azo-based oranges. Inorganic, colored pigments are compounds such as iron oxide reds, iron blue, chrome yellow and green and the umbers.

PINHOLE PREVENTATIVE

A chemical agent used to prevent the occurrence of small pore-like flaws extending entirely through a film having the appearance of pin-pricks. Pinholes are often the result of trapped solvents, air, moisture, or improper surface preparation. Improper spray application may also cause pinholes.

PLASTICIZERS

A material used to increase the flexibility or elongation of an inherently brittle film or to improve flow and processability or reduce brittleness in plastic compositions. Great care must be taken in the choice and level of plasticizer due to possible unwanted side effects such as after-tack, blocking, dirt pick-up and finger printing.

Plasticizers are used in the coatings industry to increase the flexibility or distensibility (elongation) of a polymer or coating and thus minimize film cracking. This can often be recognized in films as offering greater impact resistance, toughness and adhesion. The organic plasticizers are usually moderately high-molecular-weight materials (liquids) or low-melting solids.

The mechanism(s) by which plasticizers actually work has been theorized by many. There is general belief that smaller molecules have surrounding them a higher proportion of “free volume” than larger polymeric structures, which tend to be rather resistant to movement. By adding smaller, plasticizer molecules into the resin blend the free volume within the blend is increased and, thereby, permits easier internal motion of macromolecules – resulting in a more flexible film. The action of the plasticizer is such that it appears to actually solvate various points along the polymer chain. It is also felt that this is a very dynamic condition – in other words that the plasticizer molecules are attached to a given group and then are displaced and replaced by other groups and so forth.

The addition of plasticizer lowers the softening point – T_g – of the resin. This can give elongation properties to the resin and subsequent coating, such that the film can withstand shock or impact resistance. Some emulsions are very hard and a plasticizer is required to ensure proper film formation.

Primary plasticizers are those which are highly compatible with a given resin system. Secondary plasticizers are those, which upon aging, tend to form droplets or give internal cloudiness or bloom as a crystalline surface.

In general, the phthalic anhydride esters – or phthalates – have been used widely throughout the coatings industry as general-purpose plasticizers. The most commonly known are the dibutyl phthalates, dioctyl phthalate [di(2-ethylhexyl)phthalate], diisooctyl phthalate, diisononyl phthalate, diisodecyl phthalate and benzyl phthalate. Obviously, whole arrays of plasticizers exist and are chosen for use based on specific performance and/or price considerations.

Examples of plasticizers are: abietates, adipates, benzoates, castor oil, epoxidized soybean oil (which can also act as an acid scavenger), phosphates, phthalates, polymeric phthalates, sebacates, trimellitates, and so forth. Acrylic esters of aliphatic dicarboxylic acids, in particular adipic, azelaic and sebacic acids, provide excellent elasticity in coatings even at low temperatures. They are often mixed with the phthalate plasticizers.

In selecting the proper plasticizer for a given resin system, the following factors will influence the effectiveness of the plasticizer:

- presence or absence of specific functional groups in the resin;
- polarity and hydrogen bonding ability of functional groups;
- stearic hindrance;
- molecular weight.

Plasticizers are not permanently bonded to the resin in a coatings system; therefore they can often be extracted in part from a coating for purposes of analysis. Many types of plasticizers will extract with water as a polar solvent. Nonpolar solvents such as hexane are also often used.

Plasticizers have been known to migrate from one polymeric material to another if there is compatibility between them. Plasticizers are very mobile compounds and can easily diffuse. Adipates and phthalates have been known to migrate from vinyl upholstery, handbags and so forth to lacquers and soften or destroy the surface coating. They can migrate into food and beverages, and sometimes affect odor and taste. Some plasticizers tend to migrate to the surface under conditions of high temperature and humidity. A type of water-plasticizer blend occurs that makes the surface feel sticky.

In recent years, ortho-phthalate plasticizers such as BBP and DBP have become targets of consumer groups that have demanded the removal of these additives in products that range from toys to coatings. In December 2005, the California Office of Environmental Health Hazard Assessment (OEHA) added BBP and DBP, along with di-n-hexyl phthalate (DnHP) to the Proposition 65 list of chemicals as being “known to the state to cause reproductive toxicity,” prompting manufacturers to seek alternative products.

As a result, formulators are looking for non ortho-phthalate alternatives for their coatings. While there are several plasticizers on the market that are compatible with solventborne systems, there are very few that are compatible with both solvent- and waterborne systems. Fewer still have a boiling point over 300 °C to ensure that the plasticizer will remain in the film over an extended period to maintain film flexibility.

Over the last few years, several new plasticizers have been introduced, positioned as alternatives to the ortho-phthalate plasticizers (DEHP, DINP, DIDP, DNOP, DBP, and BBP) that have been restricted in the EU and more recently in North America. Alternative chemistries include conventional esters (such as adipates and citrates), naturally derived plasticizers that are vegetable based, diisononylcyclohexane-1,2-dicarboxylate, terephthalates (such as DOTP and DEHT), and alkyl sulfonic ester derivatives.

There are newer, non-phthalate alternatives, such as some newer coalescents, on the market today with similar boiling points that are compatible with both solvent- and waterborne systems. In addition, they can help formulators meet a number of environmental regulations.

Another benefit of this type of additive is that it not only keeps the films flexible but it also aids in film formation of latex systems. This is an important benefit to formulators who are under constant pressure to reduce VOC in coatings. Additives such as co-solvents, thickeners, preservatives and lower-boiling plasticizers can add to the VOC level of the coating. Solvents are also used as fugitive plasticizers.

For powder coatings, the purpose is to reduce the viscosity of a binder to enhance flow and leveling. The types used are mainly derivatives of benzoic

acid; others used include toluene sulfonamide, dicyclohexyl phthalate and epoxidized soy oil. The levels are usually 1.0-5.0% of the binder.

Aqueous fumed silica dispersions are a new form of a well-known, long-standing additive that can improve a variety of performance attributes in waterborne coatings. Its liquid, water-like form overcomes the challenges of using traditional powder versions of fumed silica.

Due to their unique ability to prevent cracking and lower MFFT, aqueous fumed silica dispersions serve as a unique tool for the waterborne coatings formulator. Pre-dispersed fumed silica provides the potential to lower VOCs by improving film formation and the possibility to reduce co-solvent with a number of acrylic resins. They also serve as a potential way to gain enhanced durability of waterborne coatings by helping to replace plasticizers commonly used to improve film formation.

POLYMERIC DISPERSANT

See *Dispersant*

POLYMERIC LIQUID CRYSTALS

Polymeric Liquid Crystals (PLCs) are synthetic versions of natural cholesteric nematic liquid crystals. They are available in a translucent, off-white powder form that has little if any color. However, when these materials are added at about a 3% level to conventional colored pigments, i.e., in combination with the pigments, in a coating formulation, they create a change in color when the coating is viewed from various angles. PLCs are nematic liquid crystal materials that are attached via a crosslinking mechanism to a chiral compound that acts as a template to form a helix structure. This process fixes the optical and physical properties of the molecules and makes a chemically and thermally stable structure.

PRESERVATIVE

See *Biocide/Fungicide*

A substance used to prevent the growth of microorganisms in or on any kind of substrate. Preservatives are compounds that will slow down the biodeterioration of a material that will result in loss of viscosity and/or putrefaction during storage. They are used to "preserve" aqueous formulations that are susceptible to attack by bacteria and fungi such as yeast as well as filamentous fungi. Such attack can cause discoloration, gassing, gelation, odors, slime formation and viscosity loss. Metal salts are among the compounds used as preservatives.

Copper-8-quinolinolate is the active ingredient that has been used in wood preservatives for years. Copper-8-containing preservatives have demonstrated outstanding control of mold, mildew and wood decay in a host of environments. The copper-8-containing preservatives are finding increasing acceptance as environmentally acceptable alternatives to such commonly used preservatives as chromated copper arsenate (CCA) and pentachlorophenol. Copper-8 chemistry is unique in that it has earned the approval of the U.S. FDA for use in indirect food contact applications.

PROTECTIVE COLLOIDS

Materials such as gums, starches and proteins, polyacrylates, and cellulose and cellulose derivatives that are effective agents for protecting charged colloidal particles in aqueous media against flocculation.

PUFFING AGENTS

Materials added to paints to increase the apparent (low shear) viscosity, usually post-added to correct viscosity of production batches under low-shear mixing.

REACTIVE DILUENT

A viscosity reducer, which becomes a permanent part of the coating through chemical reaction with other constituents of the formula, and does not significantly increase the VOC of the system.

Reactive diluents are used in a variety of coatings such as waterborne, high-solids and radiation cure. Their main function is to decrease application viscosity and to become an integral part of the final protective or decorative coating by chemical reaction with itself or with other compo-

nents of the formulation. It does this without significantly increasing the VOC of the system. Basically, a reactive diluent functions as a solvent but does not cause VOC increases as a solvent does.

In waterborne coatings, reactive diluents are mainly used to replace co-solvents and coalescing agents. In high-solids and radiation-curable coatings, the main function of reactive diluents is to decrease viscosity for ease in application. They can also act as crosslinking agents as well as flexibilizers and hardness modifiers.

Ideally reactive diluents will have a narrow molecular weight distribution (often they will be a single compound), low viscosity that will impart maximum viscosity reduction, and miscibility with a variety of other compounds, including polymers and crosslinking agents. Functionality will vary, but it is usually greater than one, and the nature of the functionality will depend on the particular system being modified.

The epoxy reactive diluents are commonly mono- or di-epoxides derived from aliphatic alcohols or glycols, or phenols. Most diluents decrease the glass-transition temperature (T_g), the chemical resistance, the water absorption and other physical properties of the cured resin. However, when used in moderation, the limited reduction in properties is usually acceptable.

The most commonly used epoxy reactive diluent is probably Epoxide 8, derived from a C12-C14 alcohol. While this additive is effective in reducing viscosity, it has two drawbacks in addition to those applicable to diluents in general. It slows down the reaction with the curing agent and tends to facilitate solidification of the epoxy resin.

Two reactive diluents that are less known but possess interesting properties are p-tert-butylphenyl glycidyl ether (p-TBGE) and cardanol glycidyl ether.

p-TBGE reduces the solidification of epoxides, has good reactivity and does not reduce the heat resistance to the same extent as other reactive diluents. A 20% addition of this diluent will still give a heat distortion temperature of 74 °C to a bisphenol-A resin cured with triethylenetetramine while a 20% addition of a C8-C10 alkyl glycidyl ether will give a heat distortion temperature of just 56 °C.

Cardanol glycidyl ether is derived from a phenol with a C15 chain in the meta-position. It has very low volatility and imparts good flexibility to the cured resin.

Glycidyl epoxides crosslink into thermosetting materials by combining with various hardening agents such as amines, anhydrides, and polyamides in the presence of catalytic curing agents. The desired properties in the ultimate finished products are obtained by selecting the appropriate combination of epoxide(s) and hardener. Excellent chemical resistance, good electrical properties and toughness are common to nearly all epoxy systems.

Epoxy systems of the bisphenol A-epichlorohydrin type and epoxy novalac type generally lack flexibility. There are a number of proprietary, flexible, low-viscosity epoxides that can be used to modify the above types to provide better impact resistance, elongation or flexibility. These flexible epoxides react completely with epoxy curing agents and become a permanent part of the cured system. However, they do not contribute toward lowering costs.

It is often necessary and desirable to alter an epoxy formulation for one or more reasons:

- to alter viscosity of the epoxide; increase the level of filler loading;
- improve pot life and reduce exotherms;
- improve certain physical properties such as impact and adhesive peel strength;
- flexibilize, reduce surface tension, improve system wetting action; and reduce cost of the formulation.

Diluents and viscosity modifiers for epoxides may be classified as: reactive diluents; viscosity modifiers; plasticizers, extenders and non-reactive diluents; and organometallic esters.

Some of the most widely used reactive diluents are based on derivatives of glycidyl ethers. To be effective, the diluent should react with the curing agent at almost the same rate as the epoxide, contribute substantial viscosity reduction at low concentrations, and be nonreactive with the epoxide under normal storage conditions.



ADDITIVES REFERENCE GUIDE

Butyl glycidyl ether is most acceptable because maximum viscosity reduction is obtained with a minimum concentration. It contains reactive glycidyl groups that react with the epoxide, and it is therefore incorporated in the binder portion of the cured formulation. A number of proprietary, formulated epoxides are marketed with certain percentages of this reactive diluent to give a lower initial viscosity system. The amount of curing agent used with such systems is calculated on the total epoxide equivalents of the blend. Reactive diluents generally decrease the properties of cured epoxy compounds.

Viscosity modifiers are used to improve thermal and mechanical shock, increase elongation, and obtain higher impact strength and flexibility. Usually, there is some sacrifice of physical strength, electrical properties and chemical or solvent resistance, and elevated temperature performance. Flexible epoxides or monofunctional epoxide compounds are examples of reactive epoxide-type modifiers. They can be used at ratios up to 1:1 to obtain a flexible and rubbery cured epoxy compound. They are shelf-stable when blended with the formulation.

Modifiers that may be reactive as curing agents are often used. Among these are triphenyl phosphite, liquid polysulfide polymers and various polyamides. High-molecular-weight aliphatic polyamines, which are also widely used, cure the epoxide system slowly at room temperatures and usually must be heated to reduce their viscosity for easy blending with the epoxide.

The polysulfide polymers react slowly with the epoxides when used alone. One to three parts of an active catalytic amine, or amine salt, is used to accelerate cure. Triphenyl phosphite reduces viscosity and somewhat reduces ultimate cost of a compound. Although reactive with epoxides, it is not effective as a curing agent by itself. A polyfunctional amine is necessary to effect a satisfactory cure.

Acrylate polymers and certain poly(vinyl butyral), silicone fluids, titanate esters and fluorocarbon compounds are used as flow-control agents in epoxide-based powder coatings to modify the surface tension of the film in the melt stage preventing crater formation and improving substrate wetting.

Vernonia oil is derived from the seed of *Vernonia galamensis*, a plant native to Africa. The oil is chemically similar to epoxidized soybean and linseed oil. Although the two modified seed oils are widely used in coatings, they are highly viscous. By contrast, vernonia oil has a low viscosity and is pourable below 32 °F. It has shown great potential as a reactive diluent in very low-VOC alkyd paint systems.

Illustrative of some systems in which reactive diluents have been used is the following. Functional siloxanes are used to modify automotive clearcoats and provide exterior durability, which often means improved resistance to acid rain. Fatty acid diols are often used to increase the solids of isocyanate crosslinked systems. Monofunctional epoxides and oxetanes are used to reduce the viscosity of cationic radiation-cure formulations. In these systems, the monofunctional epoxide will react into the system and produce a hydroxyl group, which will also react. Thus, in effect the initially monofunctional compound is difunctional in nature. Compounds such as 2,7-octadienol are said to be used as reactive diluents for unsaturated alkyds.

REDUCING AGENT

Emulsion polymerization redox systems have historically used ascorbic acid (AA) or sodium formaldehyde sulfoxylate (SFS) reducers along with t-butyl hydroperoxide (TBHP) oxidizer. These systems are well established and have been used for emulsion polymer production for more than 50 years.

New regulations, market needs and customer requirements demand new emulsion formulations that are low in VOC content. Many of these new formulations use hydrophobic monomers that present significant challenges regarding productivity and monomer conversion. Recent development work with the formaldehyde-free reducing agent Bruggolite® FF6 M (FF6) in emulsion redox systems has shown that it is capable of substantially reducing free monomers, reaction time and yellowing. This reducing agent is more powerful than either AA or SFS, is formaldehyde free and is best suited for lower-pH reactions.

When used in the main polymerization step, more controlled reactions are possible with an FF6 redox system. Polymers can be tailor made with improved physical properties. Slow, controlled initiation of the polymerization is possible with no retardation later in the reaction cycle. Lower-temperature initiation for free radical generation is also possible, avoiding side reactions and crosslinking. This can result in tighter control of molecular weight distribution.

When used in the post polymerization step, physical stripping of residual monomers may not be necessary, resulting in less energy consumption. Recycling of monomer and associated process equipment may not be necessary.

For both main and post polymerization use, FF6 can provide faster reactor throughput and more complete conversion of monomer to higher quality polymer. The biggest advantage, perhaps, is that low-VOC polymers can be made with formaldehyde-free redox agents.

RELEASE AGENT

See *Anti-Blocking*

RETENTION AIDS

Retention aids are compounds that slow down the surface evaporation rate and prevent entrapment of carrier, solvent or water, under a solidified surface layer, prevent pigment flocculation, alleviate blocking of spray nozzles, and alleviate blocking of printing screens. High-boiling solvents and thickeners that have the capability of retaining and holding water are used. Examples of high-boiling solvents used are glycol ethers, propylene glycol, diethylene glycol, polyoxyethylene glycols, sucrose, and some urea derivatives.

All of these compounds are capable of quite strongly associating with water and keep the surface wet. Many of these compounds are adducts of ethylene oxide and an alcohol or glycol, i.e., the glycol ethers and polyoxyethylene glycols. Each ethylene oxide unit is capable of associating with two or three water molecules. These water molecules tend to be retained for reasonable time periods and are only slowly given up, which maintains a wet surface. Thickeners such as polysaccharides and cellulose ethers have similar water retention properties and are used as retention aids. Many retention aids also function as "wet-edge extenders."

Although retention aids are high boiling in nature, they do volatilize at least to some degree that is dependent on the particular compound used, temperature and time. Thus, this may be a factor to consider in the VOC sense and may negate using terms such as "solvent-free" or "no VOC" when discussing the paint product. (See also *Humectants*)

RHEOLOGY MODIFIERS

See *Thickeners, Sag Control Agents*

Rheology is the study of flow and deformation of matter. Rheology modifiers are chemicals that alter the deformation and flow characteristics of matter when it is under the influence of stress. A basic understanding of coatings rheology is essential to the development of acceptable flow properties in a coating. In coatings formulations and manufacturing, rheological additives control rheology.

The rheology (viscosity as a function of applied shear) of a coating determines many of the properties such as in-can appearance, anti-settling of pigments, color stability, application performance (including sag and spatter resistance), brush or roller loading, brush drag, film build, and flow and leveling. Viscosity/shear rate curves are often used to characterize the rheological behavior of coating systems.

It is important to note the three main viscosity profiles used to describe the rheological behavior of resins in solutions: pseudoplastic (shear thinning), dilatant (shear thickening) and Newtonian (shear has no effect on viscosity). Pseudoplasticity is often referred to as thixotropy.

Pseudoplastic systems recover quickly after shear is removed, while thixotropic systems take longer to build viscosity back up and do not recover the same level of viscosity. Because each profile has advantages and disadvantages, combinations of rheological additives are used to optimize final coating properties.

Viscosity is constant at all shear rates for a Newtonian fluid; this flow behavior is typical of solvents and oils. Dilatant flow shows a viscosity increase as the shear rate is increased and is characterized by solutions of PVC (polyvinyl chloride resins) in solvent or plasticizer. This type of flow can damage equipment. The viscosity approaches infinity as the shear rate increases in the same direction.

Pseudoplastic flow is highlighted by a viscosity decrease as the shear rate increases. Such a material is said to be shear thinning. A brush-applied system, for example, needs high viscosity at low shear rates to remain on the brush but must thin out for ease of incorporation. In addition to these effects, pigment settling at low shear rates is minimized with high viscosity formulations. Package appearance and how paint “feels” when stirred are typically low shear-rate phenomena. Rheology control additives are used to impart this flow behavior.

A thixotropic coating exhibits a viscosity decrease as shear rate is increased. The longer this material is sheared the lower the viscosity, until a limiting value is reached. This behavior is due to a loss of structure in the coating system. This loss in viscosity is usually temporary and time dependent in a true thixotropic system. The system will rebuild to its original state given enough time (minutes to hours). The generated curve is commonly called a thixotropic loop or hysteresis loop. The area of the loop is a measure of the degree of thixotropy for the system.

Rheological control additives can completely dictate the paint flow properties in the ultra-low shear rate range (sag, leveling and settling) and the low shear rate range (increased package viscosity). A polymer solution affects the high-shear rate viscosity of a system. Therefore, as molecular weight of the polymer increases, high-shear rate viscosity of the system increases (the converse is also true). High pigment loadings also tend to raise high-shear rate viscosity.

Rheology modifiers for waterborne coatings are polymeric thickeners that are associative, flocculative or hydrodynamic in character and comprise compounds such as hydroxyethyl cellulose, hydroxypropyl cellulose, hydrophobe-modified nonionic surfactants and cellulose, and the like.

Conventional rheological modifiers for solventborne coatings include organoclays, fumed silica, organic thixotropes and over-based calcium sulfonate. Commonly encountered rheological additives in waterborne systems include organoclays, castor oil derivatives, fumed silicas and water reducible cellulose esters.

Ideally, rheology modifiers would have (a) minimal impact on the package viscosity of the coating; (b) provide anti-sag control at elevated temperatures; and (c) not detract from the final film properties.

Basecoats

Basecoat rheology should be carefully designed for a particular application such that the performance of the paint is superior during the entire handling cycle, from storage to spray application and drying. The required rheology should enable the basecoat to have a high viscosity during storage, which leads to minimal settling. Under moderate agitation and during circulation, the viscosity should be low to allow the basecoat to be easily pumped. At the spraying gun or bell, the viscosity should be very low so that the paint can be properly atomized. As soon as the paint is sprayed on to the target, the viscosity should build quickly to prevent paint from running or sagging. However, the viscosity should still be low enough to enable the paint to level off, providing a smooth film.

Another important role for rheology additives in a basecoat is to help achieve desired colors that give the sharpest aesthetics. A properly designed rheology package should prevent floating/flooding and mottling. In a basecoat containing a specialty pigment such as aluminum flakes or pearlescent pigment, along with binder system, rheology additives are the key tools to help control flake alignment during flash-off and drying periods. Properly oriented pigment flakes not only increase hiding and durability of the coating film, they also bring out the maximum beauty of these expensive pigments: sparkling effect, maximum face brightness and high flop.

A paint formulation as a whole defines the final paint's rheological behavior. A polymer solution affects the high-shear rate viscosity. As polymer molecular weight increases, high-shear-rate viscosity of the system increases. Emulsion-type binders often show more thixotropic behavior compared to polymer solutions. Their shear rate versus viscosity relations are impacted more by particle size and solids of emulsion solutions rather than molecular weight of the polymer itself. Heavy inorganic pigments tend to raise high-shear rate viscosity; high pigment loading of organic pigments and carbon blacks tend to raise low-shear rate viscosity.

In solventborne basecoats, microgels, waxes, bentonite and cellulose acetate butyrates (CABs) are commonly used as rheology modifiers.

One of the advantages of using microgels is the low viscosity at higher levels of non-volatile content in a coatings formulation. Since microgels are prepared as non-aqueous dispersions (NADs), this is a category not available to waterborne formulations. Different from other rheology modifiers, a CAB solution in a common solvent exhibits near-Newtonian flow behavior. At the moment a basecoat is spray-applied to an object, the Newtonian characteristic of CABs help flow and leveling. Due to a rigid cellulosic backbone, CABs possess extremely high glass transition temperatures (T_g) compared to other polymers used in coatings. High T_g of CABs results in a rapid viscosity build-up within a short period after a basecoat is applied, leaving no time for coated film to sag, as well as no room for pigment to swim. The combination of these unique properties provides a basecoat formulation with excellent flake orientation and color uniformity, which leads to quick dry-to-touch time and improved strike-in resistance in a wet-on-wet application. This will enable the basecoat to have superior flow and leveling without compromising sag resistance.

For waterborne basecoats, instead of microgel, there are a variety of alkali-swellaable emulsion-type rheology modifiers available. Wax dispersions and bentonites are also available. New technology in the form of cellulose nanofibers are available that provide unique rheological functions and enhanced film properties. (See thickeners for more information.)

Alkali-Swellaable Emulsions

Commonly used are hydrophobically modified alkali-swellaable acrylic emulsions (HASE) and hydrophobically modified ethoxylate urethanes (HEUR). Viscalex™ HV30 is a very efficient thickener in this category. Another type in this category are rheology-modified acrylic core/shell dispersions such as Setalux™ 6803 AQ-24. The dispersed particles consist of a hydrophobic core and an acid functional alkali-swellaable shell. Upon neutralization with amines, the resin develops its unique, strong pseudo-plastic or thixotropic character essential in a waterborne basecoat.

Wax Dispersions

There are polyamide-based aqueous dispersions such as Disparlon™, and modified polyethylene dispersions such as Aquatix™ 8421. In general, wax dispersions are not as effective as alkali-swellaable types, and they often increase high shear viscosity, which is undesirable.

Bentonite

Bentonite refers to a family of layered silicate clays. Silicate clay is insoluble in water but hydrates and swells to give clear and colorless colloidal dispersion. At very low concentration in water, highly thixotropic gels can be produced. A well-known product in this category is Laponite™ RD.

Waterborne Cellulose Ester

A recently commercialized waterborne cellulose ester, Solus™ 3050 performance additive, provides superior flow and leveling, optimal metallic flake control and better redissolve/strike-in resistance.

Selecting the right rheology package is the key to formulating optimized waterborne basecoats that possess desirable application fitness and best finishing appearance.

See *Thickeners* for more detail about these additives.



ADDITIVES REFERENCE GUIDE

RUST INHIBITORS

See *Corrosion Inhibitor/Anti-Rust Agent*

SAG CONTROL AGENTS

See *Rheology Modifiers, Thickeners*

Glossy coatings, such as automotive clear coats, require a perfectly smooth, high-quality appearance after curing. It is necessary that surface irregularities arising from the substrate, created during application and/or curing and drying, be eliminated. Paint thixotropy is critical in increasing sag resistance, thus improving coating appearance and providing a wider application window. Thixotropy can be introduced by the addition of sag control agents (SCAs).

Sag control agents based on the reaction product of 1,6-hexamethylenediisocyanate (HDI), and benzylamine yielded the so-called 'opaque' SCA, named after its opalescent appearance in paint. The opaque SCA crystalline particles form a weak 3-D network in the paint, which is disrupted under shear and when shear is decreased will build up again in a certain period of time, thus providing thixotropic behavior. At higher temperatures (>100 °C) these HDI-BA crystals completely melt or dissolve and become fully transparent in the final coating and therefore applicable in clear coats.

There are two key properties of SCAs: (1) the ability of the crystal particle to form weak, 3-D networks and (2) the ability to completely disappear (for di-urea type SCAs to melt and/or dissolve at higher temperatures). New SCAs have been developed based on optically active (chiral) amines, which are more efficient (the percent SCA needed to obtain a given amount of sag resistance) than the opaque SCAs. Mixtures of SCAs can have a wide range of melting temperatures and offer process efficiency advantages. These new SCAs allow tuning of the paint fluidity during the different stages in the flash-off drying and curing process.

SCRATCH-RESISTANT ADDITIVE

See *Abrasion-Resistant Additive*

SEAL COATING ADDITIVE

Seal, or barrier, coatings are asphalt or coal tar emulsion-based coatings. They are used to protect airport, driveways, parking lots, and similar surfaces. Particular latex additives are used to increase usage lifetime by improving chemical resistance and mechanical properties.

Additives are used for: thickening; altering drying characteristics; skid resistance; salt and other chemical resistance as from jet fuel; deicing chemicals; oil, grease and the like; color uniformity in sunlight and shade; exterior elemental resistance to rain, ice and snow; texture, and physical properties such as elongation, flexibility, and toughness. Specific additives include the following.

- Latexes that produce thickening and bulk, which improves suspension of sand or other aggregate to alter texture and/or skid resistance and improve drying time by a water exclusion process, which in turn improves uniform dry color. Depending on the particular latex selected, the polymeric materials may improve low temperature flexibility and toughness as well as reduce tack at elevated temperatures, plus provide improved resistance to a variety of chemicals.
- Acrylic polymer and copolymer latexes have the capability to provide all of the performance characteristics. Butyl, natural and styrene-butadiene rubber latexes have been used for many years to improve most of the above properties. They fail if used in areas that have major contact with oils, grease, hydraulic fluid, etc. As might be suspected, they impart excellent water resistance. Acrylonitrile-butadiene latexes impart excellent chemical and water resistance as well as enhance the other properties described above. Neoprene or chloroprene latexes impart excellent water resistance and fairly good chemical resistance; improve mechanical properties, thickening, etc.
- Poly(vinyl acetate)-based latexes are mainly used for improving drying, dispersing and thickening. They have poor water sensitivity, ultraviolet radiation resistance and chemical resistance.

SLIP AID

See *Waxes, Surface Modifier, Abrasion Resistance*

A compound that migrates to the surface of a coating during, and immediately after, application and curing. The compound coats the surface and provides the necessary lubricity to lower the coefficient of friction and improve slip characteristics.

Slip represents the ability of two surfaces to glide over each other without causing any mechanical damage. Many slip aids also function as anti-mar agents and abrasion-resistant agents, although this may be dependent on the type and concentration of resin.

Nature supplied a model for us to use in protective situations. There is a wax-like water-repellent film on leaves and blossoms; many animals, like ducks, are provided with water-repellent coats. We learned from nature that waxes can provide a protective thin film and that they can offer excellent slip and surface feel. There are many such additives available to the formulator today. Slip aids are available as solids or liquids. Solid additives are conventionally used in dry, dispersed and emulsion form.

Many of the liquid slip additives are silicone based; the solid slip additives tend to be waxes. The term "wax" does not actually describe a class of chemical substances. It is a collective term for all materials that display the typical "wax properties." A distinction is made between natural waxes (beeswax and carnauba wax), fossil waxes (montan waxes, paraffins) and fully synthetic waxes (polyolefins). Carnauba wax (naturally occurring) is made from the leaves of Brazilian palm trees and is used as a polish for automobiles and floors. Waxes are chiefly esters in which both the acid portion and the alcohol portion have very long chains. The following are commonly used: paraffin waxes (alkanes with 25-50 carbons), microcrystalline waxes, polyethylenes, polypropylenes, fluoropolymers and polytetrafluoroethylene (PTFE, commonly called Teflon™).

Using a combination of PTFE and polyethylene provides good properties to high-gloss applications as the PTFE imparts good slip, scuff and antiblocking properties. For low-gloss coatings either polyethylene or polypropylene can be used by themselves or with silicas. Silicas are used as flattening agents but in combination with polyethylene or propylene the mar resistance is improved and a smoother feel is achieved. Small amounts of these waxes also aid in sanding sealers. These materials also assist as anti-settling agents for the silicas. As a general rule, wax emulsions are added last in the coating formulation, although in each formula this should always be tested and not assumed because order of addition is always important in a formulation. Normally, levels of 3-5% wax solids on a vehicle solids basis are used in coatings.

Modified names are used for other substances that have waxy properties. Paraffin wax is really a mixture of long-chain hydrocarbons. It is one of the higher-molecular-weight petroleum distillates having 25-50 carbons; as such they are quite soluble in non-polar hydrocarbon solvents. The paraffin waxes are often used in solvent-borne wood coatings and stains.

Polyethylene waxes are unsaturated (containing carbon-carbon double bonds); this is unlike the paraffin waxes, which have no double bonds (saturated). Polyethylene waxes are high molecular weight – generally between 1000 and 3000. These waxes are frequently used as anti-slip aids and mar aids because of their general insolubility. The polyethylene waxes can be used for most applications in both water- and solventborne systems. They are available as dispersions and emulsions in micronized or un-ground forms. The micronized have very fine particle size and can easily be incorporated into the coating and applied by means of a spray gun.

During baking conditions, if the bake is higher than the melting point of the wax, the wax will melt, migrate to the surface and recrystallize as the coating cools to form a continuous film. In some cases this is desirable. The wax will bloom to the surface and form a thin layer that can help provide resistance properties. Sometimes there is a partial migration of the wax to the surface. Localized wax coverage results.

If having a layer of wax on the surface of the film is not desirable, then the baking temperatures should be kept below the melting point of

the wax. Combinations of PTFE (polytetrafluoroethylene, or Teflon) and polyethylene are also used for high-gloss applications.

Choice of particle size depends on the property desired in the coating. The particle size of the wax should be slightly larger than the film thickness of the dried coating to maximize abrasion resistance, block resistance and coefficient of friction reduction. Usually waxes are available in ranges of sizes and sometimes the same results can be obtained from smaller particle sizes at higher concentrations. Some waxes of large particle size and type can act as physical spacers that inhibit another surface from contacting the coating. (This is also dependent on concentration.)

Waxes decrease blocking so that unwanted transfer or adhesion to a contacted surface is prevented. This can be very important for materials that are coated, dried, and stacked for storage and shipping. Waxes can be used in any type of coating that could benefit from mar resistance and/or a slip aid. Both water- and solventborne metal coatings benefit from added lubricity and abrasion resistance.

Micronized waxes are available in a variety of grades and can be added using high-speed mixing equipment or, for larger particle size waxes, by pre-dispersing. Some companies provide micronized waxes in liquid form, which are designed for ease of dispersion in aqueous systems.

Many waxes are modified for uses in water-reducible systems and waterborne systems. Micronized waxes are added to powder coatings to impart better flow and a smooth surface on curing. Harder waxes improve hardness and the scratch resistance of the coating film. For fingernail mar and heat resistance, the PTFE waxes perform best.

Many types of wax emulsions are available for waterborne systems, including the following:

1. Carnauba and Carnauba-blend emulsions: These are available as both anionic and nonionic emulsions and offer additional slip, mar and block resistance.
2. Microcrystalline and microcrystalline-blend emulsions: These are petroleum-based emulsions and can be used when low-temperature block resistance is desired.
3. Polyethylene and copolymer waxes: Polyethylene waxes are synthetic, provide a variety of melting points and hardness and are desirable for high-temperature conditions.
4. Paraffin and paraffin-blend emulsions: These are straight-chain hydrocarbons derived from petroleum oil and are desired for their ability to repel water.
5. Polyolefin emulsions are used where slip and hardness are desired.
6. Ethylene acrylic acid (EAA) dispersions are heat sealable at low temperatures and offer water and solvent resistance.

A study with microcrystalline waxes demonstrated that the harder the wax, the better the slip properties. This can be explained by the fact that a softer wax would tend to be more easily liquefied, and as a consequence, there remains less of it in a solid state to impart slip. In other words, the harder wax would have a relatively higher proportion of crystals in the solid state to impart slip.

Specialty waxes are also available. There is a wax for UV coatings that, in contrast to conventional wax types, can be firmly anchored in the paint film through radiation energy. This is due to the modification of the wax with recently introduced reactive double bonds. These lead to additional bonds between wax and other substances in the coating during curing. The result is a two- or three-dimensional crosslinkage, which fixes the wax in the paint and prevents migration to the surface. These systems provide extraordinary solvent resistance, and lasting matting through the anchoring of the wax in the coating.

The silicone additives are available for both solvent and aqueous systems. Frictional forces must be overcome to allow an object to slide across a coating surface. Possibilities for reducing the frictional force include reduction of surface roughness of the film, application of a thin lubricant film on the coating surface, through which the uneven voids are filled and the sliding body is kept at a distance. Additives based on modified siloxane can produce both effects. Through a positive influ-

ence on flow and leveling, the surface of the film is smoother. During drying, the additives become increasingly concentrated at the surface. A closed film is formed, facilitating dynamic lubrication when a solid body slides over the surface.

Slip additives are especially effective in solventborne systems. The additives are quickly carried to the air interface during the drying process, in which a lubricating film is formed. In solvent-free systems, the additive is insoluble during the crosslinking process and is pushed to the surface. This mechanism is particularly effective in the case of UV-curing systems. In waterborne systems, the effectiveness of the slip additive depends strongly on the resin. In crosslinking a resin, less additive is required than in physically drying systems to achieve good slip properties. In addition, in waterborne systems the effectiveness of slip additives can be influenced by the selection of an emulsifier.

A customary test method for measuring dynamic (gliding) friction is the "Horizontal Pull Test". It is accurate in testing crosslinking systems. It involves a sled that is made to move by means of an electric motor. This method is quite accurate and reproducible in differentiating slip values. The best lubricants are silicones and modified siloxanes with a high polydimethylsiloxane segment content because of the low interaction of these segments.

Scratches are the result of surface deformation by a sharp object, damaging the coating surface irreversibly or even penetrating into the coating film. Increasing the smoothness of the surface with slip additives can make a film more scratch resistant. A slip additive on the surface of the film provides hydrodynamic lubrication between sharp objects and the coating surface and so protects against damage.

In general, silicone fluids exhibit the following properties: low surface tension, water repellent behavior, thermal resistance, floating inhibition, flow improvement, and improve gloss and surface smoothness. In addition, they have an almost unchanged viscosity over a range of temperatures. Care must be taken in formulation to avoid instability problems.

Some reactive silicones can be incorporated into the system to enhance gloss, adhesion and mar resistance. These types of products are di-functional silicone polymers with both ends of each silicone chain-modified with an organic functional group capable of undergoing further reactions. For example, various polyalkyleneoxide-modified silicones allow the modified thickener to be lower in surface tension and hydrophilic.

Manufacturing the end piece of an aluminum two-piece can is an example of a coating application that puts severe stress on the coating and demands flexibility and surface lubricity. The end piece in these cans is formed after the coating is applied. The baked coating has a wax component that will bloom to the surface during the curing cycle. Usually a layer of wax is then sprayed over the cured coating prior to re-rolling the stock. Aluminum discs are punched from the precoated flat stock, shaped into ends and a tab attached. There is tremendous stress on the coating in this process as the metal is elongated and the wax must protect the coating from abrasion. Generally carnauba and paraffin waxes are used in these applications.

Coil coating applications need to be resistant to blocking and abrasion. After coil stock is coated it is rewound for storage and handling. Wax in the coating reduces or eliminates marring and blocking. Post formation of the coil involves stamping, bending and handling, and wax in the coating also helps here. If the coil is to be recoated, a wax is selected that does not contribute to poor intercoat adhesion. Many grades of polyethylene satisfy this condition.

PTFE is used in the topcoat layer for marine application on wood, fiberglass and metal hulls of ships. Fluorinated polyurethane coatings containing micronized PTFE are effective antifouling coatings.

In summary, slip agents are available as solids or liquids. The liquid slip aids are usually either polydimethylsiloxane – either diluted with solvent, or in the form of an emulsion for use in waterborne systems. These silicones will migrate to the surface of the coating and impart excellent slip resistance and lubricity. If not properly used, they can also



be the source of surface defects such as cratering. Loss of adhesion is also possible if other interfaces are affected.

Slip-resistant or anti-skid additives are compounds that function directly opposite of slip additives or lubricants. They make it more difficult to move one surface past another surface. Compounds such as the colloidal silicas are used for this purpose. In the marine coating segment, antislip or antiskid coatings are those that reduce the sliding and slipping of humans and cargo on decks.

SOIL REPELLANTS

A chemical agent that improves a coating's ability to resist soiling by foreign materials, other than microorganisms, deposited on or imbedded in the dried film.

SPREADING AGENT

A chemical that either reduces the surface tension of a liquid coating to enhance flow, reduces the viscosity or resistance to spreading, or aids in the wetting of the substrate.

STAIN-RESISTANT ADDITIVE

A chemical agent that improves a coating's ability to resist defacement by foreign materials, other than microorganisms, deposited on the surface of the film. There is an aqueous fluorinated polyurethane dispersion (PUD) on the market that, when formulated as a penetrating sealer, adds stain resistance and release, and water and oil repellency characteristics to porous surfaces such as concrete, grout, unglazed tile, granite, clay, slate, limestone and terra cotta. It may also be used as an additive to many general coating formulations, and to various construction materials. It is suitable for both indoor and outdoor use.

STATIC PREVENTIVE

See *Anti-Stat Agent*

SUBSTRATE WETTING AGENTS

See *Wetting Agent*

SURFACE-ACTIVE AGENTS

See *Surfactants*

Surface-active agents are compounds that when added to a liquid alter its properties when it comes in contact with another liquid, solid or gas. These additives alter the interfacial characteristics of the liquid. Surface-control additives are multifunctional, improve leveling, slip and scratch resistance, and prevent craters, orange peel, fish eyes, pin holes and pigment flotation.

SURFACE ADDITIVES/DEFECTS

Additives are often used to prevent surface defects that can mar the appearance of the coating and/or the protective properties of the coating. Some of the more common surface defects that appear at the coating-air interface are: orange peel, craters, fish eyes, picture framing and popping. Surface defects that occur at the substrate-coating interface are: crawling or cissing (poor wetting), and telegraphing.

There are additives, which have been discussed in other sections of this handbook, which are typically used to prevent and/or eliminate the above mentioned defects. These additives typically fall into the following types of categories: solvents, silicones (polysiloxanes), polyacrylates, fluorosurfactants and a variety of other chemical types.

SURFACE MODIFIER

See *Surfactants, Surface-Active Agents, Slip-Aid, Waxes*

A surface modifier is an additive intended to modify a particular surface property. Typical functions of surface modifiers are to:

- reduce the effect of friction/surface tension of the film;
- improve abrasion resistance;
- alter a coating's "feel";
- modify surface appearance; and

- enhance other performance properties.

For example, an easily cleaned surface is an important target of new developments in architectural coatings and general industrial coatings (such as household appliances), wood coatings (kitchen and bathroom cabinets), plastic coatings (coatings for consumer electronics), marine coatings and so forth. Fluorinated resins are well known for superior durability and for excellent dirt-releasing properties. A specialty application coating in the architectural market utilizes a very hydrophilic surface that is easily cleaned by rain. This easy surface cleaning property, or cleanability, is typically a function of the specific binders selected to form the film. However, good cleanability can also be obtained with conventional binders when they are modified with certain additives. Among those additives, crosslinkable silicone containing polymers provide a unique set of properties.

Silicone additives are well known for their beneficial effects in coatings. Polyether- or polyester-modified silicones not only provide good surface flow and substrate wetting, but also improvement of surface slip and mar resistance. However, the improvement of surface slip and mar resistance is limited because the silicone on the coating surface can be washed or wiped off. Hydroxyl functional polyester or polyether-modified silicones can provide longer-lasting surface slip properties, but improvement of surface cleanability is not completely satisfactory.

A new, special silicone-modified hydroxyl-functional acrylate additive has been developed to enhance the surface cleaning properties (cleanability) of coatings. Crosslinkable via the -OH groups, the additive provides long-lasting significant improvements in cleanability so that adhering dust and dirt particles as well as graffiti can be removed much easier compared to 'normal' surfaces. This new development not only provides easily cleaned surfaces in hydroxyl-crosslinking binders, but also improves surface flow, substrate wetting, slip and mar resistance.

Due to the described properties of this new additive, many interesting coatings with unique surface properties can be developed for new applications. Potential areas for this new technology are in the following applications.

- Polyurethane coatings for buildings, facades and ceramic tiles for tunnels that are graffiti resistant.
- Polyurethane wood coatings for kitchen cabinets.
- Baking alkyd-melamine and polyester-melamine coatings for household appliances.
- Polyurethane coatings with improved foulant-releasing properties due to the low surface energy.
- Polyurethane coatings for consumer electronics with easily cleaned and scratch-resistant surfaces.
- Interior coatings for metal drums/pails/other technical metal packaging containers to provide more complete drainage.

The excellent resistance to graffiti does however severely limit recoat adhesion. This additive (silicone-modified hydroxyl-functional acrylate) is only recommended for those applications not needing recoatability. Recoating is only possible with surface sanding.

Wax-based surface modifiers are used to optimize abrasion resistance, raise or lower coefficient of friction, or improve chemical resistance. For a wax to perform, the material must migrate to the surface and sometimes protrude out of the coating. Surface modifiers rely on two mechanisms to migrate:

- (1) Stacking/ball bearing: this mechanism relies on the wax particle either being similar in size to the coating thickness, or several particles stacking and bridging.
- (2) Bloom/floating: in coating systems where heat is applied, the wax particles become molten or solubilize and migrate to the surface due to incompatibility or lower specific gravity. The wax may form a thin layer on the surface. If the density of the wax is significantly lower than that of the coating, the particles may float to the surface during the curing.

Other variables that effect migration are raw material interaction, coating viscosity/specific gravity, curing conditions, additive chemistry and additive form.

Waxes can be divided into synthetic (produced by polymerization), refined (from fossil fuels) and natural.

Polyethylene (PE) waxes are produced by the polymerization of ethylene. PE waxes have a broad range of physical characteristics, providing a wide variety of performance possibilities in coatings. Melting points of PE waxes are between 100 °C and 130 °C. The features and benefits of PE waxes include good slip and matting properties; improved scratch, and mar and abrasion resistance.

Polypropylene (PP) waxes are produced by polymerization of propylene. They have a higher melting point than most waxes. They are often blended with PE waxes to use their properties of high elasticity and toughness. The benefits include improved scratch resistance, very good antiblocking properties, excellent abrasion resistance and good migration characteristics. Their disadvantages are cost and poor slip qualities.

Mono and bis-amide waxes are semi-synthetic waxes have higher melting points and low penetration hardness and are relatively brittle. The benefits include good matting, excellent sanding, enhancement of silky and soft feel, thickening of liquids, antisetling properties and good migration characteristics. Their disadvantages are reduced gloss, thickening of solventborne paints and they may cause yellowing in light-colored thermoset coatings.

Carnauba wax, an ester of long-chain alcohols and acids, is extracted from the leaves of the carnauba palm tree. It melts below 100 °C and the benefits include excellent slip and good mar resistance, hardness, excellent clarity and it is FDA-compliant. Disadvantages include cost/availability due to crop variation and the color may prohibit use in some applications.

PTFE is not a wax because it does not dissolve or melt at the temperatures used in coatings, however it functions like one. PTFE produces a very low coefficient of friction in coatings and inks, and is usually used in blends with PE. The benefits include excellent slip; promotes antiblocking; improves stability against polishing; and improves abrasion, scratch, mar and scuff resistance. Its disadvantage is its high cost and it may cause intercoat adhesion problems at high levels.

Waxes are available as powders, cold dispersions, and emulsions or precipitations. Particle size of waxes is very important.

SURFACE TENSION REDUCER

Any chemical agent that, when added to a mixture, reduces the property known as surface tension.

SURFACTANTS

Surfactants encompass a variety of compounds that are used in various ways. The term 'surfactant' is derived from 'surface-active agents,' and as the name implies, the compounds are used to alter surface phenomena. These chemicals will reduce surface tension and improve wetting and spreading (wetting agents); aid in dispersion of pigments in formulated products (dispersants); inhibit foam formation (defoamers) although others will stabilize foams; and cause or improve emulsion formation (emulsifiers). These topics will be treated individually, but in each case keep in mind that we are really talking about compounds that affect surface activity – surfactants.

Traditionally, the surfactants utilized in paints and colorants were based on alkylphenol ethoxylates (APEOs or APEs). Due to the unique branched structure, the surfactants provided good pigment and substrate wetting while maintaining a low pour point. In the alkoxylation, a typical aqueous caustic catalyst is added for the EO addition, and water is removed to dehydrate the catalyzed mixture and to form the phenoxide anion. As the phenol group is slightly more acidic than the hydroxyl group on a primary alcohol, the phenoxide anion is easier to form than the alkoxide anion. This leads to a more narrow-range EO adduct distribution compared to base-catalyzed primary alcohol ethoxylates. Additionally, it significantly reduces the levels of free un-ethoxylated phenol, which means the VOCs are much lower for APEOs. Two common APEOs are octylphenol ethoxylates and nonylphenol ethoxylates. These surfactants are excellent in reducing VOCs in coatings and colorants, but due to governmental regulations and end-use customer demands, APEOs are not being utilized as coating and colorant formulations are

re-formulated. The coatings industry is seeking alternative surfactants not based on APEOs.

APEs are suspected of being endocrine disruptors and they are persistent in the environment. This, in addition to increased consumer awareness and a demand for higher-quality product, causes ongoing refinements of existing products as well as the introduction of newer surfactants and new types of surfactants. Formulators need to be vigilant in maintaining updated product information from their suppliers.

Alternatives to APEOs must be able to match the physical properties such as similar gel points, color and low free alcohol content, which are not easily achieved. This is especially true when linear alcohols are ethoxylated with potassium hydroxide, the typical catalyst for ethoxylation. For this reason, branched hydrophobes and narrow-range ethoxylation (NRE) catalysts are employed. The combination has shown significant improvement in generating products similar to APEOs.

There is widespread use of surfactants in waterborne coatings where surfactants play a crucial role, and yet the same compounds can cause problems in the final cured film. In the chemical industry, surfactants have been used for many decades to: emulsify oil and water systems; as wetting agents for dispersion of solids in liquids; as defoamers; and as foam stabilizers in the polyurethane industry.

At times it is difficult to categorize, define or associate particular surfactants in an end-use sense, because the same surfactant can be used as a dispersant in one application and as an emulsifier in another application. Thus, the roles of some of these materials can overlap and complement each other. The quantity of surfactant used can also play an important part in how the compound functions. Sometimes too much of a 'good thing' can turn it into an 'undesirable thing.' For this reason, it is important to discuss surfactant usage with suppliers.

Surfactants, as chemical compounds, have a hydrophilic or 'water-loving' portion and another portion that is hydrophobic or 'water-hating' in nature. Often the molecules are oligomeric in nature. This is particularly true in the case of nonionic surfactants. Usually the hydrophobic portion of the molecule is comprised of long-chain hydrocarbons such as fatty acids; straight, branched or cyclic hydrocarbons; or aromatic hydrocarbons with or without alkyl side groups. The hydrophilic portion of the molecule will contain groups that attract or are attracted to water molecules. Groups such as hydroxyl, carboxyl, sulfonate, sulfate and the like will be found in the hydrophilic portion of the molecule. In other cases, the hydrophilic portion will be an ethylene oxide chain that is relatively short – it is well known that each oxyethylene group will strongly associate and complex with two or three molecules of water, which markedly changes their nature. In addition, other water molecules will less strongly associate with the water/oxyethylene complex that is formed. Oxyethylene/oxypropylene copolymers are surface active and used in specialty areas.

Surfactants preferentially concentrate at interfaces. These interface surfaces or interfacial regions are where one continuous phase ends and another begins. By their chemical nature, surfactants lower the total energy associated with the boundary and stabilize it. For example, consider a container with oil and water. The boundary layer between the two substances will be well defined, and there is a large energy involved in keeping the boundary layer stationary. If the system is shaken, the oil will disperse into the water because energy is being supplied by shaking, and this overcomes the energy holding the boundary in place. However, if allowed to stand under room conditions, the system soon returns to its original condition with a single boundary dividing the substances. If we add surfactant to the system, the oil is broken into droplets and dispersed. However, the process has created a large number of tiny drops of oil that are now dispersed in the water. The system is more or less stable. All of the droplets formed have surfaces that are now in contact with water. There has been a very large increase in the interfacial contact area between the two substances. The only reason this dispersion of oil into droplets can take place and be maintained is because the energy associated with the large surface has been significantly reduced.

It should be apparent from this discussion that surfactants can have a marked affect on the interfacial forces between materials. They modify



the properties of liquid-liquid, liquid-gas and liquid-solid interfaces by changing the interfacial tension. The usual effect of a surfactant is to decrease the surface tension of an aqueous system such as a waterborne coating. In such systems, the surfactant concentrates at the air/liquid interface. Surfactants vary in their ability to cause defoaming. As mentioned above, excessive use of surfactants in aqueous coatings can cause the undesirable situation of foam formation and stabilization.

Emulsion polymerization is a useful technique for preparing waterborne latexes used in coatings and inks. The polymerization reaction takes place in micelles in which the monomer droplet is stabilized by surfactants. The surfactants, usually an anionic or a combination of anionic and nonionic surfactant, together with polymerization conditions, determine the particle size. Anionic surfactants provide shear stability to prevent loss due to coagulation. Nonionic surfactants provide electrolyte or chemical stability to the growing latex particles. The type and structure of a surfactant can have a dramatic effect on emulsion properties such as particle size, particle size distribution and latex viscosity.

Like non-reactive surfactants, reactive surfactants are molecules that typically have a hydrophobic segment and an ionizable and/or polar group. The hydrophobic segment preferentially adsorbs onto the surface of the latex particle during and following particle polymerization. The hydrophilic group extends into the aqueous solution phase and provides a steric barrier or charge repulsion against particle agglomeration and coagulation.

Unlike their non-reactive counterparts, reactive surfactants additionally contain a reactive group on the hydrophobic segment that is capable of covalently bonding to the latex surface. Usually this is a moiety such as a meth(acrylate) ester or a terminal olefin that can participate in free-radical emulsion polymerization reactions.

Once a latex-containing product has been applied to a surface as part of a coating, the surfactant is no longer needed. In fact, the presence of the surfactant often degrades the moisture sensitivity of the coating. Other coating properties can be negatively affected as well. This is largely due to the mobility of the surfactant polymers. For example, locally high concentrations of surfactant molecules can form in the coating from the coalescence of surfactant-coated micelles. When the coating is exposed to water, these unbound surfactant molecules can be extracted from the coating, leaving thin spots or pathways to the substrate surface. This can result in a pinholing effect and substrate corrosion.

A number of reactive nonionic and anionic surfactants are commercially available. Most of these are designed to participate in free-radical polymerizations. However, none of these reactive surfactants incorporates more than one reactive moiety in their structure.

A new class of reactive surfactants, both nonionic and anionic, is being developed for use in both conventional aqueous emulsion polymers and in UV-curable coatings that contain two polymerizable moieties. These new reactive surfactants can be employed either as emulsifiers or as pigment dispersants. These new surfactants are block copolymers of two or more moles of allyl glycidyl ether (AGE) and ethylene oxide terminated on the AGE end with a hydrophobic moiety. The addition of a second equivalent of AGE significantly reduces the amount of non-reactive surfactant in the product so that increases in coating repellency may be achieved.

These surfactants may contain various hydrophobes such as styrenated phenol ethers, alkyl ethers such as tridecyl alcohol, or alkylphenol ethers. Varying the level of ethoxylation and adjusting the size of the hydrophobe results in being able to tune the structure for optimal performance for each application. These nonionic copolymers may be further derivatized to convert them to anionic surfactants. Examples of these include sulfonates, phosphate esters and carboxylates.

Although essential in latex preparation, remember that the hydrophilic portion of the surfactants is immiscible with the polymer matrix, which is hydrophobic in nature. During film formation, this immiscibility results in hydrophilic surfactant domains in the film, and these can have an effect on adhesion, moisture sensitivity and

appearance. New surfactants that are copolymerizable or otherwise non-migratory in nature are being developed.

There are many approaches toward classifying surfactants. Some are based on their end use such as wetting or dispersing agents. Some classifications are based on their hydrophilic-hydrophobic characteristics and balance. Other classifications are based on their chemical structure. Surfactants are also classified according to the electronic charge associated with the molecules and in that regard they fall into four categories: nonionic, anionic, cationic and amphoteric.

1. Nonionic Surfactants. Nonionic surfactants usually refer to polyoxyethylene derivatives although other surfactants are included in this category. They are usually prepared by the addition reaction of ethylene oxide to hydrophobic compounds that contain one or more active hydrogen atoms. Examples of such hydrophobic compounds are fatty alcohols, alkylphenols, fatty acids, fatty amine, alkanolamines, fatty mercaptans, fatty amines and certain polyols. The polyols can include oxypropylene polyols, polyesters, and the like. These surfactants do not carry a charge nor do they dissociate. Their surface-active character comes from the oxyethylene portion of the molecule. Both the nature of the hydrophobe and the length of the oxyethylene chain have an effect on the surface-active character.

Nonionic surfactants are the most common ones used in latex coatings. In such systems, these surfactants do not ionize. Instead, they hydrate in water through association complex formation and hydrogen bonding at the ether-oxygen sites as well as interaction with the hydroxyl groups that usually, but not necessarily, are found at the end of the molecule. Overall, these groups are weakly hydrophilic in comparison to the hydrophobic portion of the molecule. Also present in many nonionic surfactants are weak ester and amide linkages. Because of this difference, or needed balance between hydrophilic and hydrophobic nature, the oxyethylene portion of the molecule is much larger than the hydrophobic portion in a molecular weight sense.

A particular advantage of the nonionic surfactants is that they are compatible with ionic surfactants. For example, many nonionic surfactants function well with anionic surfactants. In such combinations, they impart good freeze-thaw stability to aqueous systems and are less deleterious to mechanical properties than the ionic compounds. Nonylphenol ethoxylate (NPE) is a typical example of such surfactants. Other examples are: octylphenol ethoxylates (OPE), secondary alcohol ethoxylates, trimethyl nonanol ethoxylates (TMN), specialty alkoxyates, and amine ethoxylates.

In emulsion polymerization, alkyl ether sulfates are one of the major surfactants necessary to provide for the stabilization of micelles. Traditionally, these sulfates have been based on alkylphenol ethoxylates (APEOs). Their good cost/performance coupled with their distinctive structural and physical properties led to their widespread use in emulsion polymerization. Typically, emulsion polymerization uses two types of surfactants – one nonionic and the other anionic. Each provides separate stabilization mechanisms for the micelles, but the combination provides better stabilization, especially as temperature increases. The nonionic surfactants bestow a steric separation between micelle groups, while anionic surfactants yield a charged repulsion between the micelles.

Nonionic surfactants generally perform well over a range of pH values, and they will usually foam less than anionic and cationic surfactants. However, nonionic surfactants may not lower the surface tension as well as anionic or cationic surfactants in complex coating formulations.

There are non-ionic polymeric fluorochemical surfactants that provide low surface tensions in organic coating systems. The lower the surface tension, the more effectively a coating wets, levels and spreads. Consequently, these are excellent wetting, leveling and flow-control agents for a variety of waterborne, solventborne and high-solids coatings systems. This is particularly important on surfaces that are not clean, as contamination, surface defects and hard-to-wet surfaces can cause orange peel, cratering, fish eyes and picture framing. When a surfactant is added to a coating, it concentrates at the inter-

face between the liquid and the substrate. That is because surfactant molecules are made up of two groups: a soluble group and an insoluble group. The insoluble end tends to push out of the liquid and the soluble end tends to be pulled in. These combined actions lower the surface energy of a liquid and allow it to better wet, level and flow over a surface.

Most of the fluorosurfactants are soluble and compatible with most polymers and continue to be active throughout the drying or curing process. When used in waterborne systems, they tend to reduce the aqueous/organic interfacial tension and remain surface active in the organic portion of the polymer system.

There is also an anionic fluorosurfactant on the market based on ammonium salt, so it is easily soluble in water and thus mainly suitable for aqueous formulations.

Alkylphenol-Free Nonionics

Alternate surfactants are desired to expand formulators' surfactant options and product materials free of APEOs. Narrow-range alcohol ethoxylates, based on different hydrophobic feedstocks, are effective APEO alternatives as nonionics in emulsion polymerization. New APEO-free ether sulfates have been developed that yield emulsion polymerization characteristics similar to that of the APEO-based ether sulfates. Globally, many areas have banned use of APEOs for applications where surfactants could contact sewer water, and as a result the use of NPEs and NPE sulfates is being phased out.

Because of increasing recommendations to phase out the use of alkylphenol ethoxylates (APEs), new generations of APE-free nonionic surfactants are available. They are based on C12-16 natural fatty or synthetic alcohols and primary and secondary isomeric alcohols. They are APE-free and biodegradable; have low viscosity, low foam, excellent water miscibility, high solids content, low freezing point range and are easier handling at low temperatures.

2. Anionic Surfactants. These surfactants carry a negative charge on the hydrophilic portion of the molecule. They are usually phosphates, sulfates and sulfonates. Anionic surfactants are good emulsifying and wetting agents, but they do not impart good mechanical properties or freeze-thaw stability. These surfactants may or may not contain an oxyethylene chain in their structure. Examples of anionic surfactants are sulfosuccinates, dioctyl sulfosuccinate (DOSS), polyether sulfates, polyether sulfonates, polyether phosphates, sodium lauryl sulfate and phosphate ester-modified alcohol-ethoxylates. Generally speaking, anionic surfactants perform best in alkaline coating systems.

Surface-active phosphate esters are a class of anionic surfactants prepared by the reaction of alcohols with an activated phosphoric acid derivative – including phosphoric acid anhydrides and acid chlorides. Typically, phosphate ester commercial products are composed of a mixture of monoester, diester, free-phosphoric acid and free alcohol used in its preparation. The property of the final phosphate ester product is primarily defined by the starting alcohol used as well as on the composition of the four different species. Conversely, the property of the final phosphate product can be tailor-made by altering the alcohol used in the preparation as well as controlling the ratio of the four different components present in the final product. Phosphate ester surfactants are made in the free-acid form, but can also be neutralized to the salt form using any base including sodium hydroxide, potassium hydroxide, ammonium hydroxide or any organic amine.

As a result of the surface activity provided by combining the alcohol used (hydrophobic component) and the anionic phosphate moiety (hydrophilic component), these products are widely used in a number of industries because of their wetting, dispersing and emulsifying properties – as wetting and dispersing agent, emulsifier, hydrotrope or stabilizer. In addition, the presence of the phosphate moiety imparts some complex interactions with metallic surfaces, thereby exhibiting anti-corrosive and metal adhesion properties. Phosphate ester surfactants have also been found to successfully stabilize reactive pigments

such as iron oxide and zinc oxide. The phosphate ester moiety does not easily hydrolyze upon exposure to extreme pH conditions – phosphate ester surfactant will be present in the application when needed.

General applications of phosphate ester surfactants rely on its surface activity. Initially, phosphate esters were designed for application as cleaners, detergents and scouring agents in textile processing. Over the last 50 years, they have also found wide utility in other industries including emulsion polymerization, agriculture and metal working as wetting and dispersing agents, hydrotropes, emulsifiers, and stabilizers.

For coating applications – including water- and solventborne coatings and ink applications – it has been determined that the introduction of the phosphate moiety into the formulation as a wetting and dispersing agent also significantly enhances the gloss and color acceptance properties, reduces the viscosity buildup of the paint with aging, inhibits rust corrosion (flash rusting as well as long-term corrosion resistance), promotes adhesion to metal surfaces, and provides films that exhibit lower water sensitivity (as compared to coatings with conventional surfactant additives). These phosphate esters are typically used as auxiliary dispersants to result in more stable, more homogeneous dispersions. In addition, supplementing certain phosphate esters to low-VOC formulations to replace glycols and other volatile reagents in waterborne formulations result, in most instances, in improved block resistance, open time and freeze-thaw stability.

Typically, the phosphate ester surfactants are added into the formulation during paint manufacture – added either in the grind or letdown depending upon the formulation. These additives have also been tested as post-paint formulation additives and have exhibited comparable properties. It has been speculated, and is the focus of a number of investigations, that use of the phosphate ester surfactant before the paint formulation stage – use of phosphate esters in emulsion polymerization as well as post polymerization stabilizer or additive in pigment dispersion – should only benefit the final property of the paint as well as reduce the detrimental effects of additional surfactants into the paint system.

3. Cationic Surfactants. These surfactants carry a positive charge and quaternary ammonium compounds are the most common. As a rule, cationic surfactants do not play a significant role in emulsion polymerization. Compounds such as alkyl trimethyl ammonium chloride typify these surfactants. Generally speaking, cationic surfactants perform best in acidic coating systems.

4. Amphoteric Surfactants. Amphoteric surfactants exhibit both positive and negative character. An example of these compounds is lauryl betaine. Amphoteric compounds have been developed for the prevention of flocculation of carbon black and other pigments in high solids systems. They have also been used to prevent viscosity increases where polymer solubility is causing rheology problems.

Contribution to Properties

Surfactants comprise a very minor portion of a system, if the quantity used is based on the total weight of the system. However, even though they are used in small quantities, surfactants make a major contribution to the following properties.

• **Pigment Wetting and Dispersing:** Anionic surfactants are the major type used to improve wetting and dispersion of pigments. They are essential for good dispersion, which allows one to optimize hiding power as well as flow and leveling. Both anionic dispersants and nonionic wetting agents contribute to overcome pigment floating and settling. Each pigment particle requires a particular amount to disperse and stabilize it. Excessive amounts of surfactant should not be used because this can lead to color and other appearance changes and moisture and/or water sensitivity with an accompanying loss of adhesion and poor scrub resistance.

Pigment wetting involves the replacement of the pigment/air interface with a pigment/liquid interface. This replacement is accomplished



by dispersing the pigment in the liquid by mechanical means, which is something that can be done with a high-speed disperser. When a surfactant is present in the mixture, the hydrophobic portion interacts with the pigment particles and the hydrophilic portion with the liquid – often water. Here the surfactant becomes the dispersant by keeping the pigment particles separated, which prevents agglomeration and settling during storage. This is accomplished by one or both of two mechanisms (a) electrostatic repulsion and/or (b) steric hindrance.

Steric hindrance takes place when the hydrophobic portion of a nonionic surfactant is absorbed onto the surface of the pigment particles. The long hydrophilic chain is in the liquid medium, and it acts as a bumper that prevents the stabilized pigment particles from too closely approaching each other. This is the mechanism by which nonionic surfactants function.

When the hydrophilic portion of the surfactant is adsorbed on the pigment particles, the ionic portion of the molecule or hydrophile will be found in the liquid phase. This charged portion of the molecule will repel particles that contain like electrostatic charges on other particles with the result a stabilized system. Anionic surfactants function by this mechanism.

- **Color Development:** This property is achieved or optimized by the proper or correct dispersion of the pigment particles in a coating formulation. The more finely divided the insoluble pigment is in the paint, the more uniform and better (true) will be color development. Color development is a direct result of the efficiency or effectiveness of the pigment dispersion, a factor that is dependent on the type of surfactant used for dispersion. Since the surface character of pigments can be quite different in nature, there is no one surfactant what will be universal for all pigments. It is important that formulators read and use supplier information as well as call on them for assistance. Other factors that play a role in color development are the nature of the latex used, type of thickener used, type and level of defoamer, and type of preservative used.

- **Washability and Cleansability:** As mentioned earlier, nonionic surfactants and other surfactants that contain an oxyethylene segment will have an effect on moisture sensitivity. Nonionic surfactants usually are less severe in causing moisture sensitivity as compared to ionic surfactants. Proper selection of the nonionic used is important to obtaining the best adhesion and scrubability. New non-migrating surfactants may be very useful in improving these properties.

- **Foam:** When foam forms, changing the surfactant or surfactant blend being used can modify the foaming characteristics of the paint being prepared. Low-molecular-weight nonionic surfactants will foam less than high-molecular-weight nonionic surfactants. In general, all nonionic surfactants will cause less foam than anionic surfactants.

While fluorosurfactants are perceived by many as foam generators, certain types of fluorosurfactants act as defoamers in coatings when used at low levels. The grades recommended for most architectural paint applications decrease foam when the formulation also minimizes the use of other foam-causing surfactants. In most cases when fluorosurfactants are used other defoaming agent usage can be decreased or eliminated.

- **Freeze-Thaw Stability:** Ethylene and/or propylene glycol are usually added to paints to obtain freeze-thaw stability. A mixture of nonionic and anionic surfactants properly blended will yield a synergistic balance between the respective properties of the individual surfactants. Properly blended combinations of these surfactants will often provide excellent freeze-thaw stability and allow decreased levels of ethylene or propylene glycol to be used.

- **Volatile Organic Content (VOC):** Usually surfactants are not a contributor to VOC. However, some surfactants are dissolved in or contain organic solvents. An example of such surfactants is those

that have been used to achieve specific colorant stability. Thus, the contained organic solvent must be taken into account when calculating VOC. If one wishes to obtain zero VOC or to decrease VOC, such surfactants might or must be eliminated from formulations. Correct use of surfactants can help decrease the level of glycol, coalescents and other VOC contributors in a formulation.

- **Package or Storage Stability:** Surfactants play an important role in obtaining good coating stability and good in-can or storage stability in particular. They are useful in reducing settling.

- **MFFT and Tg:** Both of these properties can be significantly affected by the choice of surfactant; some families of surfactants can substantially lower MFFT by 10-20 °C and Tg by 5-10 °C for certain formulations. This is due to the unique chemistry of the surfactants and this provides great formulation latitude with benefits such as improved adhesion, lower coating temperatures, and reduced VOCs.

- **Surface Tension Reduction:** With today's diversified coating substrates and waterborne low-VOC coating systems, surface tension reduction is essential for application and good film formation. High surface tension will cause paint film defects such as craters, fish eyes, pin holes, orange peel and poor thin film control. Telomer-based fluorosurfactants are very powerful at very low concentration in reducing surface tension. This allows the use of very small amounts and still achieves wetting and leveling, with reduced foam to achieve defect free coatings on conventional and hard-to-wet surfaces, such as plastics.

- **Emulsion Stabilizer:** Fluorosurfactants work synergistically with hydrocarbon surfactants in resin synthesis during emulsion polymerization. Their main functions are stabilizing the emulsion, controlling particle size and allowing the reduction of hydrocarbon emulsifier surfactants. Reducing hydrocarbon surfactants can also help reduce foaming in the paint formulation. After the polymerization, fluorosurfactants are carried over to the final coating formulation to provide the other properties provided by fluorosurfactants.

- **Open-time Extension:** Open-time is the time that it takes the surface of the wet paint to form a partially dry top layer. Short open time causes coating defects in the over- and cross-painted areas. With low-VOC paint formulations, open time is normally reduced due to lack of slower-evaporating solvents; this causes over-brush defects. Open-time of a latex paint is influenced by the viscosity, rheology, surface leveling and water evaporation rate under a given relative humidity when the paint is applied. Selective fluorosurfactants have demonstrated a positive impact on leveling and slow down water evaporation from the wet film surface, thus reducing the surface defects caused with short open-time for latex paints.

There are patented zero-VOC, alkylphenol ethoxylate-free additives for extended open time in waterborne coating formulations with textured and other similar high film-build finishes. They can provide a two-to four-fold increase in open time without the addition of solvents, and offer additional benefits such as improved gloss, scrub resistance, stain resistance and elimination of wetting agents.

- **Dirt Pickup-Resistance (DPR):** Dirt pickup for low-VOC exterior paint is one of toughest challenges that formulators encounter. Many factors contribute to increased dirt pickup. High-PVC paints have higher surface area allowing a greater area for dirt to accumulate; low Tg resins make the film soft and sticky under heat and moisture; and oil-affinitive surface-active additives attract environmental dirt and stains to the painted surface. There are two approaches that are currently taken by the industry to increase exterior DPR.

One approach is to make the paint surface highly hydrophobic, measured by high water contact angle. This approach often uses a silicone-modified resin or silicone additives in the formulation. The challenge

with this approach is that if the paint does not have high enough water repellency, which has a water contact angle above 130-145°, dirt stains will appear as dark streaks on the wall that are not removed by rain.

A second approach is to make the paint surface hydrophilic, so it will allow rain to rinse the surface. If this surface is also static dissipative it will repel airborne particles from the painted surface. Fluorosurfactants work well with the second approach. Fluorosurfactants serve three functions: allow the reduction of other oil attracting additives; allow the reduction of hydrophobic additives; and add oil repellency to the paint. Because fluorosurfactants migrate to the film surface and enrich the top 25% depth of the paint surface, the amount needed to achieve oil repellency at the surface is very low.

Other Surfactants

In addition to the types of surfactants discussed above, there are other types of surfactants in use. Copolymerizable surfactants offer another approach for formulators to use when improving set adhesion and stabilization of coatings. These surfactant monomers are used during latex polymerization and are incorporated into the polymer that will form the final coating film. These types of monomer must be able to:

- provide sufficient surfactant capability to emulsify or otherwise disperse the monomers;
- be sufficiently reactive to become a part of the polymer – i.e., able to copolymerize and not homopolymerize to any extent; and
- be properly distributed in the growing polymer so their surface-active character can come into play.

Surfactants need to be both hydrophilic and hydrophobic or lipophilic (oil loving) in nature. In addition, copolymerizable surfactants must contain reactive functionality in the region that joins the hydrophilic and hydrophobic portions of the molecule. This functionality, which is usually ethylenic unsaturation, is the portion of the molecule that will allow incorporation of the molecules into the growing polymer chains. These surfactants appear to function better if the unsaturation is located near the lipophilic end of the molecule.

The copolymerizable surfactants can be nonionic or anionic in character. Both types have good surface-active characteristics, and they are available with reactive moieties located near the hydrophobic end of the molecule. These monomers can be used as the sole emulsifier in anionic or mixed anionic/nonionic systems for the preparation of latex products with improved water sensitivity (decreased) and accompanying properties. They also provide improved mechanical properties to the coating films.

Fluorinated compounds, silicone oils and modified siloxanes are surface-active in solventborne systems because of their inherently low surface tension. Fluoro- or silicone surfactants provide wetting to low-surface-energy substrates, and they can impart low equilibrium surface tension reducing capabilities. However, they have poor dynamic performance. The ability to reduce dynamic surface tension is important during high speed coating operations wherein the surfactant needs to diffuse to the interface as rapidly as possible to provide good wetting.

Silicone surfactants are short-chain polydimethylsiloxanes that contain only a few polyether sections as modifying groups. Organo-modified siloxanes have distinctly different properties than their original polydimethylsiloxane counterparts, with respect to silicone crater formation, and other silicone-caused surface defects. The compounds are derived from low-molecular-weight polydimethylsiloxanes and rather than having only methyl functionality, various organic chains replace certain methyl groups to increase the compound's compatibility with coatings and inks. The organic portion of the molecule can be polyether, polyester or a long alkyl chain.

The most important modification is the polyether chemistry derived from ethylene oxide and/or propylene oxide. Hydrophilic character, i.e., water compatibility, increases as a function of the ethylene oxide content so that it is even possible to synthesize water-soluble silicone-based additives. Factors influencing the properties of modified siloxanes are silicone content, and the type and location of organic groups on the

molecule. Polyether-modified siloxanes simultaneously influence the following effects in coatings.

They:

- improve flow and leveling;
- promote formation of a uniformly structured surface;
- prevent floating of pigment and matting agents (Bénard cells);
- reduce coefficient of friction;
- improve scratch resistance;
- promote substrate wetting; and
- prevent craters.

Fluorochemical surfactants are used in waterborne and high-solids systems. Because of the strength of the carbon-fluorine bond, these surfactants can be used effectively in harsh environments such as hot acid or alkali, oxidizing or reducing agents, acid baths, and so forth. By reducing the surface tension gradient, coating defects such as cratering, Bénard cells, edge pull, fish eyes and picture framing can be eliminated. Surface tension gradients can be caused by uneven solvent evaporation or by uneven heating. These defects are caused by these factors because the temperature variations they cause result in the coating having a tendency to flow from the low-surface-energy areas to the high-surface-energy areas. Fluorochemical surfactants can be tailored to function in all types of coating systems including solventborne, waterborne, high-solids and powder coatings.

The multi-functional properties provided by fluorosurfactants include anti-crater, improved leveling, reduced foaming, decreased block, open-time extension, oil repellency and dirt pickup-resistance.

Until very recently, fluorosurfactants were used to address formulation problems near the end of the coating development cycle. Recent research and practice have demonstrated that fluorosurfactants are most useful and cost effective due to the multiple functions they provide in formulating a low or VOC-free architectural coating. The formulator can reduce other ingredients and create high-performance paints by minimizing the use of other coating additives, such as defoamers, wetting agents, leveling aids, anti-block additives and open-time extenders. Oil repellency and other functions that fluorosurfactants provide have also made them attractive to formulators in developing dirt pickup-resistance exterior paints.

Formulators often consider using fluorocarbon surfactants as dispersants in coating formulations. However, fluorocarbon surfactants will not function as dispersants in a coating formulation because they repel essentially any materials except for other fluorocarbons. To function effectively, a part of a dispersant must be attracted to the liquid carrier and a part must be attracted to the material being dispersed. In such a situation, fluorocarbon surfactants could be added to the liquid carrier, thereby reducing the surface tension of the liquid carrier and allowing it to wet the material being dispersed.

Another type of fluorosurfactant has a new fluoropolymer technology platform based on oxetane chemistry that features short fluorinated side chains, stable ether linkages and reactive end group functionality. Unlike conventional, non-polymeric fluorosurfactants that are typically based on long C₈F₁₇ fluoroalkyl groups, those based on oxetane chemistry are short-chain structures that vary from only CF₃ to C₄F₉.

The macromolecular structure of these surfactants makes them less bio-available than typical small-molecule fluorosurfactants. As coatings modifiers, these compounds have proven to perform well despite the moderate surface tension values (25–30 dynes/cm) they provide. The polymeric structure of the fluorosurfactants and the modest surface tension offers performance benefits including improved wetting, flow and leveling, as well as stain- and scratch-resistance in some applications. They also have been shown to prevent defects such as cratering, pinholing, fish eye and picture framing. However, surfactants based on this concept cannot achieve very dense packing because the distance of perfluorinated groups is limited by the oligomeric backbone.

With regard to branched surfactant structures, the molecular distance (distance within a surfactant molecule) between the perfluorinated groups can be adjusted by the choice of molecule segments between the hydrophobic groups and their connecting points.



Therefore, the total packing density of perfluorinated groups per surface unit can be increased with branched surfactants because the distance between perfluorinated groups given by covalent binding is lower than in the case of a self assembly of linear fluorosurfactants where the packing is simply given by the intermolecular distance. This can lead to lower surface tension and has been realized in the market place as a branched short-chain surfactant based on three perfluorinated C2 groups linked to one hydrophilic moiety (Tivida™ FL-2300). This new fluorosurfactant can reduce the aqueous surface tension to 20 mN/m, which has never before been reported for a C2-based surfactant. It is exceptionally fast and prevents surface defects efficiently.

Branched, short-chain fluorosurfactants can be used as a tool to speed up slower fluorosurfactants and achieve synergistic effects. The surface tension that can be achievable with such a mixture would be lower than using the single surfactants alone with the additional speed of the branched surfactant. The concept of branched, short-chain fluorosurfactants not only leads to more environmentally friendly products, but also to one of the fastest surfactants ever measured. Tivida FL 2300 can be used to improve the dynamic properties of other fluorosurfactants and achieve additional synergistic effects in mixed surfactant systems.

In addition to fluoro- and silicone surfactants, the advance acetylenic glycol (AAG) surfactants have the ability to reduce the combinations of equilibrium and dynamic surface tension. These phenomena are important to slow- and high-speed applications, respectively. For waterborne systems, the AAG surfactants impart low water sensitivity, foaming and VOC in combination with good flow and leveling as well as enhanced wetting and surface tension reduction.

Block copolymer nonionic surfactants offer blocks of hydrophilic and hydrophobic groups. A key advantage for these surfactants is obtained from the block structure that provides improved steric stability for the separation of latex particles from each other. This type of surfactant usually displays very low foam generation and has excellent chemical, mechanical, steric, freeze-thaw and electrolyte stability.

Typical organic surfactant technology using alkylphenol ethoxylates is sometimes inadequate in its wetting ability. These may have a tendency to foam plus cause water sensitivity problems. In such cases, the block copolymer alkylene oxide copolymer surfactants offer an alternative approach.

In formulating with surfactants, many people find the Hydrophilic Lipophilic Balance, HLB, system helpful. This is a numbering system for rating the relative hydrophilic nature of a surfactant. The system is based on an arbitrary numerical scale where zero is assigned to a surfactant that is overwhelmingly hydrophobic and 20 is assigned to a surfactant that is overwhelmingly hydrophilic. The number assigned to the surfactant represents a measure of the balance between its hydrophilic and hydrophobic strengths. A surfactant with an HLB of 10 has an equal balance of oil-loving and water-loving groups.

Gemini surfactants have two hydrophilic heads or ends that are connected to two or three hydrophobic tails or ends. This structure difference is in contrast to conventional surfactants that have a single hydrophilic head or end connected to a single hydrophobic end or tail. These unique surfactants, which are named after the twins of Greek mythology, can be used at very low levels because of their high efficiency. They provide improved solids dispersion, wetting, foam control and emulsification, as well as decreased wetting times and reduced surface tension at lower use levels over conventional surfactants. Readily biodegradable versions of these surfactants are available. Multifunctional Gemini-type surfactants can help formulators by improving coalescence and providing excellent substrate wetting and low foam and low-VOC systems.

The Gemini surfactants are highly efficient in reducing surface tension and often have very low critical micelle concentrations. This makes them attractive for the graphic arts industry, and they have been used for decades to improve the performance of waterborne inks. Because their structure is so unique the formulator is often able to solve unique problems without introducing other undesirable side effects. A typical example of a non-ionic Gemini surfactant is 2,4,7,9-tetramethyl-5-decylene-4,7-diol (TMDD).

APE (alkylphenol ethoxylate)-free for waterborne architectural and industrial coatings are also available in the marketplace. Multifunctional, low-foaming, solvent-free additives, designed for pigment and substrate wetting, act as drop-in replacements for APEs or nonylphenol ethoxylates (NPEs). These surfactants are also suited for adhesives, inks, pigment synthesis and dispersion.

Coating Defects

It should be noted that many of the common coating defects are related to poor selection of wetting and dispersing agents (surfactants). Ultimately, surface tension problems and pigment dispersion can cause cratering, telegraphing, crawling, flooding, floating, poor gloss and many other types of defects. In addition, poor substrate cleaning and preparation may also contribute to defects.

Because surfactants affect surface tension and surface activity, they are a KEY additive in any coating. Despite the abundance of scientific guidelines and information, the use of surfactants in formulating borders on being a fine art gained through experience.

SUSPENSION AGENTS

A material used in a coating to improve or increase the resistance to pigment settling.

Fumed silica is frequently used as a suspending or anti-settling agent for the suspension of solids in liquids or liquids in liquids (emulsions). This use can produce complete suspensions over long periods of time and it also eliminates hard settling so that material is readily re-dispersed upon stirring or shaking. Fumed silica in aerosol products maintains the mixture of active ingredients, solvents and propellants.

Colloidal microcrystalline cellulose (MCC) is used in the food and pharmaceutical industries to suspend dense particles, provide stable emulsions and prevent phase separation. Likewise it can be used in waterborne coatings to improve in-can shelf stability, color capability and sag. MCC forms a three-dimensional network in waterborne systems when it is full activated by shear. As a secondary thickener, MCC provides minimum viscosity to waterborne systems at low use levels making its use particularly attractive for stain applications.

SYNERGISTS

Synergists are compounds used in radiation-initiated polymerizations. These compounds have at least one hydrogen atom on a carbon atom that is located in the alpha position to a nitrogen atom. Synergists are used in combination with free radical photoinitiators that function by a bimolecular reaction. The photoinitiator absorbs the radiation and is excited, but it is unable to initiate polymerization. Instead it abstracts a hydrogen atom from the synergist making it a very effective free radical for the polymerization of unsaturated compounds such as acrylates. Synergists are typically tertiary amines (i.e., triethylamine, dimethylethanolamine), but amides and ureas have been used.

Formulators are often able to achieve increased cure rates using conventional free amine synergists such as methyl diethanol amine, dibutyl ethanol amine, triethyl amine and triethanol amine. These amines react synergistically with Type 1 hydrogen-abstracting photoinitiators such as benzophenone or isopropyl thioxanthone (ITX). They enable formulators to overcome oxygen inhibition, which negatively affects the surface cure of coatings. Conventional amine synergists may have odor problems, blooming of the amine to the surface and they may be a source of extractables in cured coatings.

Acrylated amine oligomers present a viable option to conventional amine synergists. They enable UV-cure formulators to increase the surface cure rate and overcome oxygen inhibition as the conventional amine synergists, but they also provide performance and processing benefits that the others do not. Typically they have lower volatility, odor, film extractables, no blooming, and improved color (less yellowing) and solvent resistance.

Synergists have been referred to as accelerators or photoactivators.



TACKIFIER

Chemical agent that will extend the period of time in which an adhesive will remain in the tacky-dry condition after application to an adherend, under specified conditions of temperature and humidity.

Tackifiers are compounds that are used to enhance materials to adhere to each other on contact. These compounds provide for bonds that have a measurable strength when two surfaces, usually termed an adhesive and an adherend, are brought into contact with minor pressure. They are usually used in adhesives and in hot melt coatings. In the coatings industry, they are often a part of a coating that is termed a 'bond coat' or a 'tack coat' that is placed on a substrate or essentially nonporous substrate where it acts as a tie between the substrate and a new coating.

Chemically tackifiers are comprised of natural rosins and their derivatives, such as abietic acid; polymeric materials, such as ethylene-vinyl acetate copolymers, styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymers; as well as oil and waxes.

TEXTURIZING AGENTS

A number of materials are available to cause a texture pattern in a cured powder coating. Most of these materials are based on the impedance of normal flow during cure. As with all coating ingredients, these conventional additives offer a balance between performing their intended function and imparting some negative property.

Conventional texturing additives include a number of high-molecular-weight polymers used to create a pattern in the coating film. Common examples are acrylics, butyl esters, polyethylene and polypropylene. Cellulose acetate butyrate is incorporated at low levels to make "hammertone finishes."

Specialty polymers such as polytetrafluoroethylene (PTFE) are also quite common. PTFE provides texturing when used at very low addition levels of about 0.1% to 0.25%, with the degree of texturing increasing rapidly as the concentration increases. PTFE is also available in blends with polyethylene, which provides a product with a less sharp texturing effect with concentration. More of the blend can be used and thus reduces weighing errors when formulating. Such blends also reduce metal marking and allow a broad variation in texture from fine grades to coarse. Various rheological modifiers are popular as well.

These conventional additives represent obstacles to smooth flow and therefore impart texture patterns. High-molecular-weight materials represent high-viscosity obstacles. They do not flow much before the coating gels and can remain in almost the same geometric shape throughout the curing cycle. Materials that do not melt are solid obstacles. They deliver much the same performance as high-viscosity obstacles i.e. impeded flow. Any material that causes impeded flow will cause incomplete leveling before gelation, leaving the surface contoured.

For the most part, conventional materials impede the smooth flow of the coating. The coating must therefore flow around or over these materials. The geometric shape of conventional texturing compounds changes little with respect to the particles of coating. The texturing particles may partially melt, but flow is restricted compared with the bulk of the coating.

A major problem with conventional texturing additives however is poor uniformity. Poorly dispersed additives affect the uniformity of the pattern. Certain areas of the coating may have higher pattern density than others. The vertical profile may also be uneven.

Using texturizing agents can result in three critical equipment issues. The first, incomplete dispersion, begins in the extruder. The presence of incompatible conventional texturing materials aggravates the extruder's already inefficient dispersion capabilities.

Processing conditions are the second equipment issue as it may be difficult to set extrusion parameters to standard conditions. Because of the incompatible nature of conventional texturing additives and the sensitivity of the highly complex extruder, it becomes necessary to continually change the extruder settings and this is time consuming.

The third issue is equipment contamination. Since conventional tex-

turing material passes through the entire line of production machinery, residue traces will occur throughout the system. Without thorough cleaning of every piece of equipment after every production run, subsequent batches will be contaminated.

Conventional texturing materials can deliver texture that is inconsistent horizontally and vertically. They may also be limited in the variety of texture finishes they can produce individually. Formulators may need to use several different texturing additives to achieve the diversity of special effects they need.

Surfactant texturing uses the difference between the molten surface tension of the additive and that of the powder coating texture base. During the baking cycle, surfactant particles distributed throughout the curing film melt and create areas of low surface tension. The primary difference between a smooth finish and a texture base is the absence of flow agents. In most cases, flow and leveling agents are unnecessary in texture coatings as they contradict the function of a surfactant texturing agent. Flow agents will try to force a coating to become smooth, while the texturing agent attempts to perform the opposite function.

THERMAL CONDUCTIVITY ADDITIVES

Widely known as the world's best insulating solid material, silica aerogel-enabled coatings are redefining the coatings industry with thermal benefits. Recognizing the advantages of a high-performance insulative coating has driven some coatings manufacturers to explore the use of silica aerogel as a paint additive to achieve significantly lower thermal conductivities. This new class of high-performance coatings, called Highly Thermally Insulative Coatings (HiTICs), is also finding opportunities in condensation and corrosion prevention.

Traditional insulation can be used to try to reduce the risk of condensation by increasing the surface temperature above the dew point of the surrounding air, but this method is often met with limited success. Since many insulation systems are porous, condensation still occurs on the surface of the substrate or within the insulation layer, resulting in a higher risk of corrosion under insulation (CUI). In addition to the risk of corrosion, the presence of condensed water in the insulation material dramatically limits its thermal effectiveness, thereby increasing energy consumption. Alternatively, surface heaters can be used to warm the substrate above the dew point, but these tend to be energy intensive and are not always practical.

Aerogel-enabled insulative coatings (HiTICs) are advantageous because of their extremely low thermal conductivity (a measure of a material's ability to transfer heat), as well as their high film build (the thickness that can be applied in each coat). These combined material properties allow for superior insulation performance with minimal coats, resulting in lower installation cost. With this new generation of HiTICs utilizing aerogel with thermal conductivities comparable to bulk commodity insulation, industries can now consider insulating surfaces that have been difficult to insulate due to topography, humidity, chemical exposure, and maintenance or space requirements to minimize or even eliminate condensation, and thereby, enhance corrosion protection. By combining corrosion protection and thermal resistance into a single product, the issue of trapped moisture within traditional insulation forms is effectively eliminated.

THICKENERS

See Rheology Modifiers; Sag Control Agents

A material used to thicken (increase the viscosity of) a liquid. Thickening agents provide the proper consistency to coatings, aid in applying an adequate thickness of coating to a substrate, and inhibit phase separation and prevent pigment settling. Basically, thickening agents increase the viscosity at moderate shear rates and thereby increase the coatings resistance to flow during mixing, pouring and stirring. They are important to all phases of the manufacturing process, storage and application.

The functional importance of thickeners varies from dripless and spatter-resistant coatings to improving film build and spread rate, wet and dry adhesion, scrub resistance, brushability and brush drag, leveling

and sag resistance. Thickeners also contribute to and may improve gloss retention, color acceptance and development and opacity.

Rheology modifiers are often difficult for a formulator to appreciate and work with conveniently. They are necessary additives to prevent excessive sag and spatter during the application process, but they cannot add such a significant viscosity increase to the product such that it affects the package viscosity.

Rheology control is particularly important in products that are sold to the do-it-yourself market. It is not uncommon for cans of house paint to stay on the shelf in small market areas for one or more years. Therefore, it becomes imperative that the formulation is such that the paint in the can will be free from pigment settling and will still apply properly.

Emulsion paints usually require the addition of thickeners so that the paint has the proper application viscosity and so that the pigments and other particulates do not settle

Ideally, rheology modifiers would:

- have minimal impact on the package viscosity of the coating;
- provide anti-sag control at elevated temperatures; and
- not detract from the final film properties.

These additives are carefully designed to promote high viscosity at low shear rates (i.e., in the can for instance) and low viscosity at higher shear rates (during application). Very small amounts of additive are required to affect the rheological properties of a coating – generally amounts from 0.1-5% by weight.

Rheological additives used to be easy to categorize into solvent and waterborne systems. With technological advances in waterborne additives, these categories are no longer logical, as many of the thickeners are applicable to both water and solvent systems.

The literature also is confusing at times as different companies choose to categorize the organic thickeners in a variety of different ways. For example, the organic thickeners and rheology modifiers are often referred to (and sometimes categorized) as follows:

- HEC Hydroxyethylcellulose
- HMHEC Hydrophobically Modified HEC
- HASE Hydrophobically Modified Alkali-Soluble Emulsion
- NSAT Nonionic Synthetic Associative Thickeners
- HEUR Hydrophobically Modified Ethoxylate Urethane
- HMPE Hydrophobically Modified Polyether
- PEPO Polyether Polyol

NSATs and HASEs are divided into two major categories: low-shear effective, which increase Storrmer consistency, and high-shear effective, which increase ICI viscosity.

High-shear effective types interact more weakly with latexes. For this reason, a high-shear effective NSAT may not be the best choice to increase ICI viscosity in high-PVC/low-latex flat paint. It will do the job, but only at very high levels. A more strongly interacting low-shear effective product may be the better choice.

In low-PVC/high-latex paints, a low-shear effective product may inter-

act too strongly to be the primary thickener – it will deliver the KU target at such a minute concentration that ICI viscosity will be unacceptably low. In this type of paint, a high-shear effective product will be the better choice for a primary thickener.

The following major types of thickener additives that are used to control rheological properties in coatings are discussed in more detail and categorized as follows.

- Associative Thickeners
- Non Associative Thickeners that interact with the water phase
 - Cellulosics
 - Cellulose Nanotechnology
 - Acrylics
- Inorganic Thickeners
 - Clays
 - Swelling
 - Non-swelling
 - Fumed Silicas
 - Overbased Calcium Sulfonate
- Mixed Mineral Thixotropes
- Organic Thixotropes (includes cellulosics, acrylics, etc. as well as castor oil derivatives/polyamides)

Associative Thickeners

Surfactants are typically characterized as: hydrophile – hydrophobe. Associative thickeners can be characterized as: hydrophobe – hydrophile – hydrophobe. In other words, a long hydrophilic center with two hydrophobic ends. One hydrophobic end would be attracted to the resin surface and the other end plays a role in the thickening mechanism. This other end can associate with another resin particle or it can associate with another hydrophobic end of another thickener molecule.

Associative thickeners are polymers that are based on water-soluble polymers. These can be acrylate polymers, cellulose ethers or, for the top-quality nonionic products, poly(ethylene glycol). These are capped with water-insoluble hydrophobic groups such as fatty alcohols, for example. In aqueous media or in emulsion, these polymers form a network that increases the viscosity. The water-soluble backbone polymer is dissolved in water. The hydrophobic caps are adsorbed onto the hydrophobic emulsion polymer particles, or they form micellar structures with hydrophobes from other polymers. As each associative thickener polymer contains at least two hydrophobic caps, the result is a three-dimensional network within the emulsion. This increases the viscosity. Mainly high- and mid-shear viscosities are affected. Therefore, it improves anti-spatter and brush drag more than many other thickeners.

Because the thickener interacts with the polymer surface, consideration must be made of the particular polymer when choosing the appropriate thickener. Factors to be evaluated are the following: polymer particle size, polymer volume solids and polymer surface hydrophobicity.

As the polymer particle size changes, the total surface area can

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change dramatically – this becomes very important in terms of the associative thickener.

Because associative thickeners are surface active, they function by associating with the surface of the emulsion binder particles. The particle size and size distribution of the emulsion, as well as the surfactant system, can have major effects on the efficiency and performance of thickeners. Other wetting agents can also affect the thickener behavior. Sound experimental design is appropriate for looking at wetting agent alternatives and levels as well as particle size and distribution of the emulsion. Sometimes a combination of thickeners will provide a synergistic effect and increase efficiency.

As a class, the associative thickeners offer excellent scrub resistance and flow. Diminishment of spattering is a major advantage. They are sensitive to surfactants.

By association of these hydrophobes with other components of the paint such as latex particles, pigment particles or other thickener molecules, they impart a rheology to the paint that is significantly different than the traditional high-molecular-weight cellulotics.

As shear forces are applied to these materials, there is thought to be a disruption of the associative bonds causing a temporary decrease in viscosity. Upon removal of the shear force, the hydrophobes reassociate, causing an increase in viscosity. Paints containing associative thickeners generally exhibit higher viscosity at high rates of shear and lower viscosity at low rates of shear than paints formulated to comparable Storrer viscosity with cellulosic thickeners.

The primary thickening mechanisms have been described as providing viscosity by intermolecular association and by association with disperse phase components. These thickeners have terminal hydrophobic groups that have been drawn into solution by the water-soluble backbone. The number and type of hydrophobic groups determine the viscosity of the solution. Under ideal conditions, coatings containing associative thickeners are highly dispersed and show little evidence of depletion flocculation. This improves the rheology of the coating and also may impart improved hiding and gloss. Decreased spatter is also obtained with the use of associative thickeners.

The features of associative thickeners are: impart flow and leveling; give very little roller spatter; give better sag resistance; usually give better gloss than HEC; give higher film build; are cost effective with HEC; are easy to incorporate (usually liquid); are resistant to enzymes; and provide one-coat hiding.

The problems with associative thickeners are: pH sensitive; sensitive to surfactant HLB; sensitive to type of surfactant, and this is dependent on the total paint formula (anionic, non-ionic, nonylphenol, octylphenol are the types of surfactants commonly used); sensitive to latex particle size; sensitive to type of coalescent; sensitive to type of glycol; and water sensitivity is increased.

The water sensitivity is due to the increased use of surfactant necessary to stabilize the thickener emulsion. Increased water sensitivity causes a decrease in scrub resistance.

Heat stability is also not very predictable and can present problems if the formula is not properly tested. The right surfactants and dispersants can help here, but again the formula needs to be tested.

Associative thickeners are usually supplied as a latex dispersion or a viscous solution. When using these thickeners, initially it is wise to follow suppliers' recommended formulations until one becomes experienced with how the thickeners function. Compared to water-soluble thickeners such as cellulose or acrylic copolymers (i.e., alkali-swellable emulsions), paints made with associative thickeners show better performance in sag and leveling, moisture resistance, spatter resistance and coverage. In addition, mixtures of associative thickeners allow one to tailor the rheological profile to provide superior paint performance.

Associative thickeners and rheology modifiers are often referred to as ATRMs.

1. Hydrophobically modified acrylic thickeners, often referred to as HASE are often used. HASE stands for Hydrophobically modified Alkali Swellable Emulsion.

2. Among the very best thickeners used for rheological purposes are those in the class known as HEURs – or Hydrophobically modified Ethylene oxide Urethane Rheology modifiers. Sometimes these are merely referred to as PU thickeners. These compounds provide excellent high film-build, leveling, reduced spatter and a non-flocculative thickening mechanism. These types are nonionic and exhibit poor sag resistance in most instances. Urethane type associative thickeners network with themselves and the binder and sometimes even with the pigment.

New technology significantly reduces the viscosity loss upon tinting. These HEUR, non-ionic-type thickeners deliver excellent flow and leveling, are free of both solvent and tin for compliance and offer viscosity stability. The viscosity stability is achieved through a new viscosity-building mechanism. This technology is designed to have a lower molecular weight than the high-shear thickener and for tinted paints offers improved resistance to viscosity loss, improved sag resistance and preservation of excellent flow.

3. HEURASE Thickeners – These alkali-soluble addition terpolymers are produced by the emulsion polymerization of a carboxyl functional monomer, a water insoluble monomer, and a hydrophobic-terminated urethane functional ethoxylate monomer. Different products and characteristics can be achieved by varying the ratio of the three monomers and the type of hydrophobe, degree of ethoxylations and so forth. These materials are supplied as aqueous emulsions of water insoluble polymer. When a base, such as ammonium hydroxide is added, the polymer swells, becomes soluble and strongly associates with water – hence its thickening action.

The HEURASE types of thickeners (water-soluble polymers) have relatively long chains within the polymer. There are also many carboxyl anions scattered along the polymer backbone, which repel one another. The

Thickener performance, especially for synthetic associative thickeners, depends on interactions with latexes and surface-active paint ingredients such as surfactants and dispersants. However, each of the four types of organic thickeners in the following table may be characterized by several attributes that are fairly independent of paint type and composition.

PROPERTY	HEC	HMHEC	HASE	NSAT
Spatter resistance	Poor - Fair	Good - Excellent	Good - Excellent	Excellent
High-shear viscosity	Poor - Good	Fair - Good	Good - Excellent	Excellent
Sag resistance	Excellent	Excellent	Good - Excellent	Poor
Leveling	Poor - Fair	Fair - Good	Fair - Good	Excellent
Gloss	Fair	Fair	Good	Excellent
Viscosity retention on tinting	Excellent	Good	Fair	Poor
Water resistance	Excellent	Excellent	Poor - Fair	Good
Robustness (insensitive to other ingredients)	Excellent	Good - Excellent	Poor - Fair	Poor
pH insensitivity	Excellent	Excellent	Fair	Excellent

hydrophobe interaction is what is responsible for the thickening mechanism in this type of polymer. The HEURASE family of thickeners can also be blended so that the rheology of the coating can be fairly unique.

4. Aminoplast Associative Thickeners – There is a new class of associative thickeners called HEAT – Hydrophobically modified Ethoxylated Aminoplast Thickener. The aminoplast linkage is done by use of an aminoplast instead of a diisocyanate. The aminoplast linkage in most cases is more hydrophilic and more water-soluble than the diurethane groups. The ability to add very high levels of hydrophobe is a special property of aminoplast chemistry, and it allows the production of associative thickeners that resist viscosity loss when glycols or surfactants are added to coating systems, as happens during tinting of paints with concentrated colorants.

5. Hydrophobically Modified Polyether (HMPE) – There are new high-shear modifiers on the market based on HMPE that are VOC and APEO free that are easy to incorporate and handle. They have a high degree of efficiency in building high-shear viscosity but also provide medium-shear viscosity contribution. Consequently, lower incorporation levels are needed to achieve the same viscosity target as compared to some currently existing HMPEs or HEURs.

6. HMHEC – The hydrophobically modified cellulose (HMHEC) are cellulosic thickeners, which have a hydrophobe modification on some branches – several long chain alkyl groups have been introduced along the backbone of the structure. These molecules build viscosity by association of the various hydrophobic groups. These paints have higher viscosity at high shear rates, and therefore get better film build and hiding. See the discussion under Cellulosics.

Non Associative Thickeners That Interact With the Water Phase

1. Cellulosic Thickeners (Cellulosics)

Cellulose is a naturally occurring polysaccharide that can form many water-soluble ethers. The cellulose ethers are nonionic water-soluble polymers. Cellulosic ethers have been available for over 30 years, and they continue to be used as thickeners in nearly all latex paints. Cellulosics are efficient for aqueous systems because they thicken the water itself.

In the coatings industry, the most commonly used cellulosic thickeners are as follows:

- Methyl cellulose (MC);
- Hydroxyethyl cellulose (HEC);
- Ethyl hydroxyethyl cellulose (EHEC);
- Sodium carboxymethyl cellulose (CMC);
- Hydroxypropyl cellulose (HPC);
- Hydroxypropyl methyl cellulose (HPMC); and
- Hydrophobically modified hydroxyethyl cellulose (HMHEC).

Hydroxyethylcellulose (HEC) is a water-soluble polysaccharide widely used for thickening many types of flat to semigloss architectural latex paints. It is available in a range of viscosity grades, and paint thickened with HEC exhibits excellent colorant compatibility and storage stability. Coating properties that depend on the molecular weight of HEC include: thickening efficiency; flow and leveling; spatter resistance; film build; and sag resistance. HEC and other non-associative water-soluble polymers thicken the water phase of paint, and the viscosity achieved is related to the hydrodynamic volume of the water-soluble polymer (WSP) and the degree of chain entanglement of these polymers in solution.

Cellulosic thickeners may be used by themselves or in combinations with other thickeners to achieve specific rheology characteristics. Cellulose ethers are produced in a variety of molecular weights and a number of viscosity grades ranging from the very low molecular weight with a 2% aqueous solution viscosity of approximately 10 cps to the highest molecular weight grades approaching 100,000 cps.

The low-molecular-weight grades are usually used as protective colloids in emulsion polymerization of paint latices. The most common grades that are used as thickeners range from 4,800 to 50,000 cps.

Various degrees of hydroxyl substitution are also available and so it is important that the formulator be aware of the various options and associated effects when picking thickeners of this type. It is through the action of hydrogen bonding that the mixture actually starts to build and gain in viscosity. The effect is quite powerful.

Most suppliers of cellulose ethers offer versions that have been surface treated to allow the powder to disperse in the water before it begins to dissolve or hydrate. Without such treatment, the outer layer of the particles would immediately begin to hydrate and gel when added to water, causing large agglomerates to form. These surface-hydrated agglomerates would be difficult to dissolve. The surface treatment temporarily insolubilizes the surface and permits complete dispersion of the powder before dissolution begins. The time between initial wetting of the powder and the onset of dissolution is referred to as 'hydration time'.

Hydration time depends primarily on two factors:

1. The temperature of the water. The higher the temperature, the faster the hydration.
2. pH – Higher pH means accelerated hydration time.

The traditional cellulose ethers are high-molecular-weight polymers that thicken primarily by chain entanglement. Under high shear the polymer chains become oriented, resulting in lower viscosity and exhibiting shear-thinning behavior. When the shear force is removed the chains, being highly viscoelastic, immediately recoil causing the viscosity to increase rapidly, resulting in less than satisfactory leveling.

Application characteristics such as brush-drag, film build and roller spatter are directly related to the choice of thickener. Also flow properties such as leveling and sag resistance are also greatly affected by the thickener.

Formulators need to be aware of one caution in using cellulose ethers. They are susceptible to attack by cellulose enzymes, which can result in a significant loss of viscosity.

The hydrophobically modified cellulose (HMHEC) are cellulosic thickeners, which have a hydrophobe modification on some branches – several long chain alkyl groups have been introduced along the backbone of the structure. These molecules build viscosity by association of the various hydrophobic groups. These paints have higher viscosity at high shear rates, and therefore get better film build and hiding.

HMHECs can provide excellent sprayability, sag resistance, flow and leveling, gloss and good resistance to pigment settling. They allow for a wide range of application techniques and have no negative impact on the film formation of small particle size latexes. Good film formation results in good water and corrosion resistance and good gloss.

This particular type of associative thickener has gained favor with the vinyl acetate copolymer systems. Performance is quite close to associative thickeners, but without formulating complexities.

2. Cellulose Nanotechnology

Curran[®], a material developed from the extraction of nano-cellulose fibers of root vegetables such as carrots and sugar beets, is a high performance cellulose rheology modifier with unique characteristics. The material is composed of cellulose, organized into a unique physical form that imparts properties that are different from other types of cellulose. The plate-like structure of Curran fiber has many of the characteristics of a nanomaterial, but without the presence of free nanofibers. The nanofibers that make up Curran have very high mechanical properties with strength similar to carbon fiber. The physical form of the material means that there is a huge surface area for interaction with water and/or polymers, and the shape of the particles imparts unique viscosity profiles and crack-stopping capabilities.

The chemistry of the material results in a large number of OH groups. These can be used to interact with a wide range of materials, or they can be chemically modified to enable specific reactions with polymers such as epoxies and acrylics. As a rheology modifier, Curran is designed to give very efficient thickening with strong shear thinning characteristics. At the same time it provides enhanced reinforcement/toughening of



both curing and cured films. Because of the crystalline nature of the cellulose it can enhance the hardness of polymer systems.

Curran exhibits thickening efficiency greater than other cellulose thickeners and in fact other thickeners in general. Also the viscosity vs. rate profile shows extreme shear thinning, which means that the material is very good at providing sag resistance and is an effective anti-settling agent. When used to thicken water-based epoxy formulations, Curran is just as effective in the absence of an associative thickener.

3. Acrylics

Acrylic emulsion polymers are used as thickeners for some systems. Water-soluble acrylates are used for this purpose – either the acid or salt form of the polymer. Care must be taken here because these soluble thickeners will remain part of the finished film and are always sensitive to water.

Polyacrylic acids are quite successfully used as thickeners. They have an advantage because they are emulsions that thicken by adjustment of the pH of the batch. But because they are pH sensitive, the viscosity of the batch will be dependent on any changes in pH. Formulators using these as thickeners must take great care, since they are sensitive to many other formulating additives in addition to system pH.

When aramid pulp is added to coatings, the degree of reinforcement will depend on the length of the fibers used and loading level. Viscosity build and sag resistance are largely unaffected by fiber length; however, reinforcement increases with length, allowing formulators to engineer strength without impacting thixotropy. Other factors such as moisture level and degree of fibrillation also affect fiber performance in coatings. For waterborne coatings, wet versions of the pulp provide improved dispersion and application properties. When reinforcement is desired with minimal effect on viscosity, short fibers are recommended.

Inorganic Thickeners (also see Organoclays)

1. Clays

Clays can be discussed as follows:

A. Swelling (smectite) – Smectite refers to a family of layered silicate clays that undergo an increase in effective volume during incorporation in the coating. These clays have a unique structure that allows them to swell in water and form stable gel structures that impart various physical, performance and rheological properties. Despite these advantages, the smectite clays pose some challenges. They must be pre-dispersed with high shear to use them effectively. Improper dispersion can cause high levels of post thickening, and loss of key performance characteristics. Additionally, the water demand of the clay during the pre-gel phase can be excessive, reducing the feasibility in higher solids systems.

(1) Bentonite – (colloidal clay, colloidal hydrated aluminum silicate). The primary component of this clay is montmorillonite. Other components include quartz, feldspar and pyrites. The crystal structure of bentonite contains aluminum and magnesium in the lattice. The montmorillonite type provides superior viscosity build and suspension.

(2) Hectorite – similar chemically to bentonite containing montmorillonite as the primary component, and quartz, feldspar and pyrites. Its crystal lattice contains magnesium and lithium in the crystal lattice in place of aluminum and magnesium. Hectorite is often used in the more demanding coatings such as automotive because it provides extraordinary thixotropy. This in turn provides improved sag, metallic pigment orientation and appearance as well as improvement in the application window.

Smectite clay minerals give excellent rheological properties to solvent and waterborne systems. The benefits stem from the three key properties of smectites: particle size, particle shape and particle charge.

Smectites are platy crystals with large aspect ratios and high surface area. The face dimension ranges from about 0.2 to 1 micron across the widest part. The edges are less than 10 angstroms thick. They are irregular in shape. The interior of the crystal is negatively charged while the edges are positive at low to neutral pH. Ions of opposite charge are

attracted to the face and edge, but due to the large face to edge ratio, the net charge of the crystal is negative.

The polyionic nature of the natural smectite is the basis for the mineral's ability to gel aqueous systems. The smectite come to us from nature in packets of platelets, or aggregates. The aggregates are readily wet by water and large aggregates disperse initially into smaller aggregates. Upon shear conditions, the crystals will disperse to their primary particle size. This dispersion, in aqueous systems is governed in part by the ionic, or electrolytic, concentration of the water medium. Under appropriate electrolytic concentrations, due to osmotic pressure, the sodium ions will diffuse away from the crystal surface, forming the electronic double layer forms. Under low shear conditions, the oppositely charged face and edge of the particles will align and the gel structure is formed. These are weak bonds, so upon shear the bonds break and the system becomes shear thinning. Release the shear, and the viscosity builds again based on realignment of the particles. For any smectite-based system, whether water or solvent, two conditions must exist: dispersion of particles from their natural aggregate form, and particle-to-particle interaction.

In solventborne systems, the gelation mechanism is a bit different. The two key criteria, dispersion and interaction, are still necessary, but the interaction bonding is through the exposed hydroxyl groups on the edge of the crystals. Well before the application, however, the smectite must be modified from its natural, water-wetting state, to be compatible in solvent systems, or oil wetting. The counter ions on the surface of the smectite were sodium. Another name for these counter ions is exchangeable cations, because that is just what they can do – exchange with other cations such as a long chain organic cation, rendering the surface oleophilic. The cation may be from a quaternary ammonium salt, such as dioctadecyl dimethyl ammonium chloride. The ion exchange is a hydroprocess and after the organically modified crystal is dried, aggregates of platelets are formed. Just as in the waterborne system, these aggregates must be well dispersed prior to gelation. After dispersion, at low shear, particle-to-particle bonding ensues, but this time through hydrate bonding at the edge hydroxyl sites. This hydrogen bonding is weak, so when shear is increased, the bonds break and shear thinning follows.

Clays rely on hydrogen bonding to establish a network structure. To a large extent, the efficiency of these materials as rheology control agents depends on adequate dispersion of the additive. The greater the amount of surface area available for hydrogen bonding, the greater will be the strength of the structure.

The structural and chemical properties of the smectite lead to many benefits: anti-settling, improved hold out, pigment spacing, pigment extension, improved wet edge, sag resistance, and improved flow and leveling.

Clays are often used with organic thixotropes and anti-settling additives. The organic thixotropes provide excellent flow and leveling properties but are very temperature sensitive. That is why they function so well together with the organoclays, which are not temperature sensitive. It is important to keep the level of organoclay use to a minimum because it will cause a loss of gloss. Excessive levels can also affect adhesion.

While some recent modifications to organoclay products have created more easily dispersible types, many products still require the preparation of pregels and the use of polar additives. Particular care must be taken when incorporating organoclays with low-to-moderate shear dispersers into unpigmented systems. The addition of organoclays to solventborne coating systems contributes to reduced gloss due to the oil absorption effects of organoclay.

B. Non-Swelling Clays

These clays swell either very little or not at all.

(1) Kaolin (china clay)

Kaolin is the common name for products comprised of the aluminum silicate clay mineral Kaolinite. It is a non-swelling clay that has a platelet structure in which layers of alumina octahedral are joined to layers of silica rings through shared oxygen atoms. When well formed, kaolin

platelets have a hexagonal structure with an oxygenated surface on one side and a hydrophilic hydroxyl surface on the other side. When used in coatings, the optical properties that contribute to opacity are more important than any physical property improvements. The clay is hydrophilic in nature and readily dispersible in water. Surface treatments are used to improve its dispersibility in organic media.

There are various grades of kaolin, with 'hydrous clay' and 'calcined clay' being the common types used in the coating industry. Hydrous clay is basically an unmodified product that is prepared by a water-washing process in which impurities are removed and specific particle size fractions are obtained. The refined clays may be further treated to improve brightness by chemical bleaching and/or magnetic fields to remove iron and titanium impurities. Typically water-washed kaolin is used in interior and exterior latex and alkyd coatings, E-coat primers, and wood primers.

When water-washed kaolin is delaminated by attrition milling of large particle fractions, it is known as 'delaminated clay'. The milling breaks down the stacks of kaolin platelets into thin individualized plates, which improves barrier, brightness and opacity properties of the clay. Delaminated kaolin clay is used in exterior house paints including porch and deck enamels, interior wall and ceiling coatings, and stain-blocking primers.

When kaolin clay is dry-ground and air-separated to control particle-size distribution and further reduce impurities, it is known as 'airfloat' clay. Such clay does not have the color and is more abrasive than water-washed clay and is not widely used in the coatings industry.

Calcined kaolin clay is prepared by thermally treating water-washed and bleached kaolin at about 650 to 700 °C. Higher temperatures are used if highly refined products are desired. This process removes structural hydroxyl groups and forms amorphous 'metakaolin', which has improved brightness, oil absorption, and opacity. Calcined clay is used in interior alkyd and latex coatings, interior primers, and exterior acrylic paints.

Other types of kaolin clays include chemically treated versions in which the treatment improves dispersibility in aqueous systems, treatment with stearates or silanes to improve dispersibility in organic media, and treatment alkaline silicates to further improve optical properties. The later type are referred to as 'structured' kaolin clay and mainly used in interior paints. Other surface treatments are used for products used in high-solids polyester baking enamels, marine coatings and two-package polyurethane enamels.

(2) Mica

Mica is a term used for a group of silicates that have a varied chemical structure, but that have similar atomic structure and physical properties. They all have excellent cleavage properties and can be split into thin, flexible sheets. They all have hydroxyl functionality and are silicates of aluminum and an alkali metal such as potassium, sodium or lithium. Natural color varies and mica that is transparent, black, brown, gray, green, rose-red, violet or yellow can be found with the color depending on metallic impurities.

The most common form of mica is the mineral Muscovite (white mica), which is a non-swelling, hydrated potassium aluminum silicate. In a wet- or dry-ground form, mica is, or has been, used in the coating industry for decorative purposes in paints, wallpaper, water- and oil-based artists' colors, and certain printing operations. In 2002, the paint industry accounted for 15% or almost 15,000 metric tons of the ground mica produced. It is used as a pigment extender and suspension aid and to reduce chalking, decrease shrinking and shearing, improve the resistance of dry paint films to water penetration, promote adhesion, and improve the brightness of colored pigments. Overall, the paint industry is the second largest user of ground mica. The largest user is the tape-joint compound industry segment where almost 60,000 metric tons were consumed in 2002. In this industry mica acts as a filler/extender, improves smoothness, and improves the resistance to cracking.

China clay (kaolin) and mica, which are basically non-swelling types of clays, are used primarily as extender pigments. Kaolin differs from both bentonite and attapulgite because its particles range from colloidal size to 5-10 mm in diameter. It is a very white and platy mineral that accounts for its desirability as a pigment. Although these are not used as thickeners, they do provide some body to systems, particularly at low pH or for highly pigmented systems.

(3) Colloidal interaction network

These clays function by a mechanical entanglement and absorption mechanism. Typical of such clays is the mineral attapulgite.

An important type of thickener that is very useful in paint formulating is the colloidal inorganic, clay-like mineral thickener called attapulgite. It has a variable composition that consists mainly of hydrous magnesium aluminum silicates with traces of calcium, iron, potassium, sodium, titanium and manganese oxides. Attapulgite products are sold under a variety of trade names such as Attagel®, MIN-U-GEL®, EZ GEL, and so on. Typically, attapulgite is dried, milled and separated into specific particle size ranges for sale. It may or may not be formulated with other products depending on the particular end use.

Attapulgite products are one of the least expensive and commonly used co-thickeners. They provide thixotropic thickening to waterborne and solvent formulations used in paint, adhesives, inks, sealants and other liquid products. Their function is to reduce the amount of sag and prevent settling of pigments and other materials. Many formulators combine attapulgite clays with hydroxypropyl methylcellulose. They are also used in conjunction with HEURS to control syneresis.

Attagel thickeners and suspending agents are made from specially processed attapulgite, a hydrated magnesium aluminosilicate and a principal member of the fuller's earth family of clay minerals. Attapulgite occurs as tightly packed bundles of submicron particles whose lathe-like structure gives it unique colloidal and sorptive properties. Attagel thickeners and suspending agents provide benefits, including easy dispersion, formulating latitude and long-term stability.

Electron microscopy indicates that attapulgite exists as randomly oriented single units and bundles of needles and/or laths that are crystalline in nature. The shape and random nature of the structure leads to high absorptivity and porosity of the mineral, which are characteristics that lead to easy wettability in liquid systems.

This inorganic mineral is essentially inert and non-swelling in aqueous applications. It is the network of myriads of finely dispersed colloidal particles that cause these thickeners to develop their desirable properties, which include liquid separation (syneresis) control, pigment suspension, thixotropic thickening, spatter resistance, good film build and sag control, and improved hiding and tint strength in coatings. The impartment of thixotropy to coatings allows them to appear gelled (high viscosity) when at rest and yet become thin (low viscosity) when agitation or shear is applied.

Attapulgite-based thickeners are popular because they are easy to use and the powder can be added to the 'grind' or high-shear phase of formula preparation. No dispersants are needed in aqueous applications, but appropriate surfactants are added to impart thixotropic characteristics to oil-based products.

2. Fumed Silicas

Fumed silica is referred to as fumed silicon dioxide and is produced by the vapor phase hydrolysis of silicon tetrachloride in a hydrogen oxygen flame.

Degussa's Dr. Klopfer discovered fumed silica in 1940 while searching for highly active, light-colored filler pigments to replace carbon black in rubber formulations. In 1941, Degussa scientists successfully completed the high-temperature hydrolysis of silicon tetrachloride in an oxy-hydrogen flame to produce fumed silica. Most commercial grade fumed silica contains reacted organophilic groups on the silica surface.

Fumed silica forms extensive 'networks' or 'structures' in coatings systems by virtue of its ability to hydrogen bond via the silanol groups.



Silica relies on the ability to create relatively large particle chains (structures) by establishing an association between particles of similar chemistry. Proper incorporation of the fumed silica is essential to provide adequate dispersion and maximum surface area, yet prevent destroying the particle chains by mechanical separation and solvation of the discrete silica particles. As with organoclays, fumed silica also exhibits oil absorption and lowers the gloss of a solventborne coatings system. The density of fumed silica is very low so dusting and handling concerns are a factor for consideration.

Cab-O-Sil® fumed silica is generally considered unique because of its extremely small particle size and its enormous surface area. This is why it is an excellent rheology-control agent for numerous applications.

The surface chemistry of fumed silica is important because of its ability to thicken non-polar and semi-polar systems. During the formation of Cab-O-Sil, hydroxyl groups become attached to some of the silicon atoms on the particle surface. This makes the fumed silica surface hydrophilic and capable of hydrogen bonding with suitable molecules of materials in vapor, liquid or solid form. The ability of this fumed silica to adsorb moisture is one of the properties that makes it an excellent free-flow agent for lumpy or hygroscopic solids.

Three groups should be noted: isolated hydroxyl groups, hydrogen bonded hydroxyl groups and the siloxane group. The isolated hydroxyl groups attached to surface silicon atoms are hydrophilic. So also are the hydrogen-bonded hydroxyl groups attached to silicon atoms hydrophilic. The siloxane group is non-polar and accounts for the hydrophobic characteristics of that part of the silica surface.

When heated above 110 °C, the surface undergoes reversible dehydration. This is restored by exposure to humidity.

Because the surface hydroxyls form hydrogen bonds, they form a network of silica. Rheology control is dependent on this tendency of the aggregates to link together through hydrogen bonding. The network increases the viscosity of the system and produces thixotropic behavior. Thixotropic behavior is the time-dependent recovery of viscosity after shearing. The addition of fumed silica results in this behavior because the shear forces from mixing are able to break the inter-aggregate hydrogen bonds, causing the apparent viscosity of the system to drop. The apparent viscosity will decrease in proportion to the length of time of mixing or the intensity of the mixing. Once the shear force has been removed, the bonds rebuild over time and the viscosity approaches its original value.

A major determinant of the effect of fumed silica in a system is the nature of the liquid phase of the system. Network formation is determined to a large degree by the ability of the liquid to form hydrogen bonds. Common solvents within the coatings industry vary from highly polar (water) which are apt to readily form hydrogen bonds to non-hydrogen bonding solvents.

It is in the non-hydrogen bonding systems that Cab-O-Sil fumed silica displays its greatest efficiency in rheology control. The silica particle has no choice but to hydrogen bond with the silica particles and the greatest degree of network formation is achieved at the lowest concentration of silica. Concentrations of 3-6% fumed silica by weight are usually sufficient to provide gel formation in these systems. In highly hydrogen bonding systems, the interference with the silica-to-silica bonding from the medium is very prominent. In this case a larger concentration of silica will be required to produce a given increase in viscosity and thixotropy.

Fumed silica is sometimes dry blended into protective powder coatings up to 2-3% by weight to aid in fluidizing the powder during application. The silica also acts as a thixotrope, reducing flow-out when the powder melts on a hot melt surface.

Hydrophobic fumed silica used with anticorrosive pigments can improve the anticorrosion properties of waterborne systems as well as solvent systems. Hydrophobic fumed silica is made by processing fumed hydrophilic silica through an in-line hydrophobic treatment. Treatments can vary from silanes, siloxanes or silazanes.

Examples of types of hydrophobic fumed silica:

- dimethyldichlorosilane (DMDS);
- trimethoxyoctylsilane (TMOS);
- silicone oil (SO); and
- hexamethyl-disilazane (HMDS).

Hydrophilic and hydrophobic fumed silicas are used in solventborne coatings to improve rheological properties, and as flow control agents and anti-settling additives for pigments.

Because of the silanol groups, these structures can now undergo a large degree of hydrogen bonding and create large particle chains and structures.

Aqueous Fumed Silica

Aqueous fumed silica dispersions are a new form of a well-known, long-standing additive that can improve a variety of performance additives in waterborne coatings. Its liquid, water-like form overcomes the challenges of powder versions of fumed silica. As an anti-settling agent, fumed silica dispersions are efficient, show good flow and leveling, improved heat age stability, improved matting in matte systems, improved König hardness in water-based coatings.

The aqueous fumed silica dispersions can lower VOCs as they are solvent and surfactant free and, by improving film formation, they offer the possibility of reducing co-solvent with a number of acrylic resins. Performance enhancements include improved sag resistance, reduced cracking in highly filled systems, and improved film hardness along with reduced dirt pick-up and film tack.

3. Overbased Calcium Sulfonate Gels

These gels are a complex matrix of colloidal calcium carbonate in the calcite crystalline form stabilized by dispersants. Overbasing is a way to provide a colloiddally stable form of basicity in an organic medium. In overbased calcium sulfonate gels, the basic component undergoes a change in crystalline structure to act as a substrate from which alkali metal sulfonate dispersant hydrophobes project. The polar heads of the dispersant associate with the ionic calcite crystal flocs, providing colloidal stability.

The projection and interaction of the nonpolar hydrocarbon dispersant tails via van der Waals forces result in a stable, completely wetted-out gelled structure. When incorporated into solventborne coatings, overbased calcium sulfonates impart a recoverable shear-thinning structure that assists in pigment suspension and antisag properties.

These products are incorporated at the pigment-dispersion stage of the manufacturing process. They do not require heat activation or polar activators. Minimum viscosity increase occurs in the "package feel" shear rate area; therefore, overbased calcium sulfonates are highly desired for use in high-solids formulations. The high temperatures encountered in curing solventborne-baking systems do not affect these products. Since they are pre-gelled, overbased calcium sulfonates do not affect the gloss of coating systems.

Mixed Mineral Thixotropes (MMTs)

MMTs are a combination of two different morphologies: one being a plate and the other being a rod. They are off-white proprietary powders that are organically modified and have a specific gravity of about 1.6. For very thin film applications, micronized versions are available. MMTs thicken systems similar to the way in which organoclays work, using hydrogen bonding to form a three-dimensional network. However the MMT networks use different spacing than do traditional organoclays due to the different particle shapes.

MMTs tend to build less package viscosity while providing more sag resistance than organoclays. Their morphology seems to provide ease of incorporation without using high levels of quaternary amine. Another advantage to coatings manufacturers is the ability to make high-solids premixes at pourable viscosities. When compared to fumed silica the big difference is in bulk density. MMTs have a low bulk density compared to traditional organoclays, but it is much higher than fumed silica which has an extremely low bulk density. MMTs are often easier

to incorporate compared to polyamides and castor derivatives and do not have their temperature and dwell time limitations.

Organic Thixotropes

Organic thixotropes include the category of cellulosics and acrylics described above under non-associative thickeners that interact with the water phase. There are other organic thixotropes as well that consist of products of various types of chemical modifications of castor oil and carboxylic acid and amines.

Castor oil derivatives are produced by modifying the castor oil by processes such as sulfonation, hydrogenation and esterification with polyols. The structure resulting from the use of castor oil derivatives is an artifact of polar bonding (hydrogen bonding).

These attractive forces exist between the pendant hydroxyl groups on the castor oil derivative and the similarly polar species on resins, pigments with bound water, other additives and solvents in the coating system. It is typically recommended that these products be incorporated by various processing techniques such as heat activation and the use of pregels to enhance the dispersibility of the products into the coating system.

Castor oil derivatives have been shown to be ineffective in coating systems cured by oven baking due to the required heat activation. If overheated during paint manufacture, these same products can form seeds that are very difficult if not impossible to re-incorporate by normal process equipment. Castor oil derivatives can cause gloss reduction in solventborne coatings due to their ability to isolate vehicles and solvents.

Polyamides are produced by raw materials and reaction conditions that produce high-molecular-weight, waxy solids with minimal terminal amide (reactive) functionality. This configuration results in a structure that usually exhibits a low amine value and good stability in formulated coating systems.

Polyamides create a structure by swelling in the solvents used in the coating systems. This increases molecular volume and chain entanglement, substantially increasing viscosity. These structures are weakly associated, and the attractive forces are disrupted under applied stress during mixing, spraying and other similar forces found in high-stress environments. This results in reduced viscosity.

Polyamides require high shear incorporation, and some products require heat activation. Studies of the surface chemistry of primers containing polyamides have shown that the migration of these products to the surface of a coating is responsible for sporadic intercoat adhesion failures of topcoats subsequently applied to polyamide containing primers.

There is a new polyamide additive (SLT) on the market for adhesives and sealants, which allows formulators to use a cold manufacturing process. This polyamide is a biobased, 100% solids additive and VOC free. This additive provides higher viscosity and good shear thinning compared to earlier polyamides.

Other Types of Thickeners

Organo titanates, such as triethanolamine titanate, are also sometimes used at very low levels to achieve even higher levels of structure than obtainable with cellulosic colloids alone. The level has to be determined dependent on the cellulosic/surfactant system used.

Metallic soaps such as aluminum stearates, octoates and calcium linoleate pulps have been used as thickeners for solventborne coatings. They develop a gel structure with the solvent.

A hydroxypropyl guar, which is a propylene oxide-modified polysaccharide, can be used as a thickener for waterborne systems. Chemically the polysaccharide is guar gum, which is a molecular chain comprised of beta-1,4-linked anhydromannose units with single galactose units linked alpha-1,6 to every other mannan unit in the main chain.

Xanthan gum is a naturally occurring polysaccharide that is a very good thickening and stabilizing additive for low-solvent, aqueous-based coatings and related products. In this environment, xanthan gum solutions exhibit pseudoplastic flow and have very good suspension characteristics. [Note: pseudoplastic systems have shear thinning char-

acteristics and exhibit high viscosity at low shear rates and low viscosity at high shear rates.] It also aids in preventing skinning and in preventing paint 'streaking' or slumping when applied. Xanthan gum, a polysaccharide that is rendered soluble through pyruvate and acetate substituted trisaccharide side chains, is produced by fermentation of the bacterium *Xanthomonas campestris*. The bacterium that forms xanthan gum is found in particular green vegetables. In these vegetables, it protects the bacterial colony from arid conditions and resulting dryness. The polymer has a stiff rod-like structure rather than a random coil in solution associated with most natural polysaccharides, a characteristic that gives it its unusual rheological properties. Xanthan gum is used in color-pigment dispersions, exterior fence paints, low-solvent emulsion paints, silicate paints, stucco coatings, and thickened chloride/water paint strippers. It is used at relatively low levels of about 0.05% to about 1% with the higher percentage used in thick coatings, such as are involved in stucco coatings, to prevent sag.

THIXOTROPES (BODYING AGENTS)

See *Thickeners*

These are additives used to impart thixotropy to a coating. A thixotropic system is one that exhibits a time-dependent decreasing viscosity or shear stress at a constant shear rate. When the shearing force is eliminated, the viscosity returns over a period of time to its original 'at-rest' value. Fumed silica is often the additive of choice to control and increase viscosity and thixotropy because it is very efficient.

Some of the surface silicon atoms in fumed silica bear hydroxyl groups that are capable of forming hydrogen bonds between other fumed silica aggregates. This forms a network of silica when a sufficient concentration of fumed silica is dispersed in most liquid systems. The rheological control of fumed silica in liquids depends on the tendency of its aggregates to hydrogen bond.

It is this network that then in turn increases the viscosity of the system and produces thixotropic behavior or the time-dependent recovery of viscosity after shearing. This behavior occurs because the shear forces from mixing are able to break the inter-aggregate hydrogen bonding and cause the viscosity of the system to decrease. Then once the shear force is removed the hydrogen bonding will reform and the viscosity build increase.

In dry powders the use of fumed silica imparts free flow and anti-caking properties. The submicron particle size of the fumed silica allows it to move easily between materials. It may in fact form a layer on the surface of larger particles and behave as tiny ball bearings.

TOUGHENING AGENTS

Fusion-bonded-epoxy (FBE) powder coatings are used worldwide where long-term corrosion protection is critical such as on oil, gas and water pipelines. These coatings must survive pipe manufacture and process demands as well as field performance at various temperatures. Increasing the toughness of these coatings can improve corrosion protection.

Many approaches have been used to toughen epoxy systems, often in composite applications, where toughening agents act through various mechanisms to dissipate an applied load. Liquid rubbers, core-shell particles, glass beads, and thermoplastic-modified epoxies, and various combinations of these, are among the toughening agents used.

Complications with these products may include significantly increasing the viscosity of formulations containing them, a dependence of the morphology on cure kinetics, the necessity of vigorous mixing to disperse the modifiers or the addition of further additives to prevent particle agglomeration.

Other toughening methods involve the use of completely immiscible or pre-formed modifiers, such as thermoplastics or core-shell rubbers. These can be difficult to evenly disperse in epoxy formulations or can cause significant increases in the viscosity of a formulation. However, they typically do not decrease the Tg of the cured product.

Block copolymers are used to enhance the performance of FBE powder coatings in terms of improved flexibility and impact resistance



while still maintaining the ability to provide corrosion protection. Block copolymers function by creating second phase morphologies and not by acting as compatibilizers for various components in the FBE.

An important attribute of any coating powder is its ability to flow before its gels. Most thermoplastics or core-shell particles used as toughening agents increase the melt viscosity of the epoxy resin, and hence the flowability of the coating powder is reduced causing adhesion problems due to the poor surface coverage.

Block copolymer toughening technology can be used to dramatically enhance the flexibility and impact resistance of FBE coatings without compromising other key properties such as T_g, flowability and corrosion protection. In doing so, this novel technology has broken the conventional Viscosity-T_g-Toughness paradigm, in which toughenability often comes at a large penalty to viscosity and T_g of the cured product.

TRIBO-CHARGING ADDITIVE

There are two techniques to apply powder onto a substrate. The major one in North America is the corona process, where the sprayed powder particles are forced through an electrical field to become negatively charged. The charged particles are attracted and deposited on the grounded object to be painted, which is generally a metallic substrate. The second application is the tribo-static process where the particles are forced through a Teflon tube and are charged positively by friction with the tube walls. The tribo charging process provides more uniform and thinner layers and less overspray. Depending on their composition tribo-static powders require additives to improve their chargeability. Certain hindered amine light stabilizers (HALS) improve tribo-charging in addition to their radiation stabilization properties. Even very low concentrations of HALS, especially in hybrid systems, can significantly increase the tribo-value of various powder systems.

UV ABSORBERS AND LIGHT STABILIZERS

See Hindered Amine Light Stabilizers, Nanotechnology

Materials that preferentially absorb UV radiation in a coating and transform the UV energy into longer wavelength energy. Chemical compositions that protect the coating film, transparent or semi-transparent films, and the substrate from photo-degradation.

The ultraviolet region of the electromagnetic spectrum extends from about 100 to 400 nanometers. It contains the following regions:

- Ultraviolet A: 320 to 400 nanometers (used for photocuring);
- Ultraviolet B: 280 to 320 nanometers (used for photocuring and causes 'sunburn');
- Ultraviolet C: ~15 to 280 nanometers (usually used for sterilization purposes).

Many radiation sources emit ultraviolet wavelengths to some degree. The sun emits very strongly throughout the ultraviolet region, and even though it is only a portion of the total energy reaching the earth, it is the radiation that is particularly harmful to exterior coatings. Ultraviolet radiation is sufficiently energetic to break covalent bonds in polymer structures that hold a coating film together. This energy decreases as wavelength increases and is about 140 kilocalories at 200 nanometers and 70 kilocalories at 400 nanometers.

Coatings are not only protective or functional; they also provide decorative effects that are aesthetically pleasing. In either case they must withstand environmental influences and possible subsequent damage. This means that coatings have to be able to withstand deterioration and/or failure of any sort. Ultraviolet radiation is often responsible for polymer degradation in a coating. This radiation, coupled with moisture and various other air pollutants such as acid rain, can quickly cause the degradation of an organic film if it is not adequately protected.

The polymeric binder in the coating film is subject to attack by ultraviolet radiation because of its organic nature. When a polymer readily absorbs ultraviolet radiation, and this is the usual case, regions in the polymer are activated to a higher energy state and free radicals can be formed. When these radicals are formed, the degradation process has begun.

Certain polymers have chromophores as a part of their chemical structure. Chromophores readily absorb radiation. However, even the binder polymers that do not contain chromophores as a part of their polymer structure end up being formulated and cured in a system that contains crosslinking agents, pigments, fillers, extenders, catalysts, flow-control agents, biocides and other ingredients that will absorb radiation and thus can lead to degradation. Merely because chromophores exist in the molecular structure and ultraviolet radiation is absorbed, it does not mean that bond breakage and degradation will occur. It only means that the potential for degradation exists.

Sunlight, oxygen and water all work together to cause polymer degradation of the coating. In the process, free radicals are formed that react with atmospheric oxygen to generate peroxy radicals. These very quickly form hydroperoxides, which in turn generate a radical on the polymer backbone itself. The weak hydroperoxide will cleave easily in the presence of heat and sunlight and produce more radicals. As this process occurs, the polymer's mechanical and chemical structure is slowly degraded and broken down. We usually see this in the form of peeling, flaking, chalking and fading.

Absorption and degradation are very complicated processes. For purposes of simplicity here we can look at the process as follows:

Polymer-R absorbs ultraviolet radiation to generate a photoexcited state: Polymer-R*

Excited Polymer-R* → Polymer-R• free radical

Free Radical Polymer-R• + O₂ → Polymer-ROO• a peroxy radical

The peroxy radical then abstracts a hydrogen from a molecule, R-H, in the system that has an available hydrogen to form Polymer-ROOH and R•, a new free radical. Then the process continues.

All of the commercial UV absorbers (UVAs) and stabilizers that we use as additives act on one of the above processes. The UV absorbers prevent the excitation state by absorbing the UV radiation that would produce it. Absorbers today have good thermal stability and some have the capability of being crosslinked to the coating polymer. UV absorbers are designed such that they preferentially absorb UV radiation, dissipate the absorbed energy and do not cause degradation of the polymeric film.

UV absorbers are incorporated into organic films that are subjected to exterior exposures. Their function is to absorb incoming UV radiation and dissipate the energy before it can be absorbed by the polymer in the coating. This action has to continue to occur over the lifetime of the coating. The most important UV absorbers are: 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxyphenyltriazines, 2-hydroxybenzophenones, cyanoacrylates, salicylates, and oxanilides. The benzotriazoles and triazines have excellent spectral coverage, high extinction coefficients, and excellent photo-permanence. Recent UVA developments have focused on increasing molecular weight and/or adding functionality, which minimizes migration out of the coating, improvements on increasing extinction coefficients and photo-permanence and designing encapsulation techniques which facilitate waterborne systems without the need for solvents or pre-emulsification.

UV absorbers compete for the incoming UV radiation with the polymer itself. The more effective the use of UV absorbers in an exterior coating, the less prone the coating will be to the visual effects of UV degradation such as chalking, loss of gloss etc. UV absorbers depend on the thickness of the coating to be effective. The thinner the coating, the less effective they are. UV absorbers are even more effective when used in combination with Hindered Amine Light Stabilizers. (*See HALS for more information on these additives.*)

For coatings used in exterior environments the combination of UV absorbers and hindered amine light stabilizers (HALS) is effective in reducing the damaging effects of ultraviolet radiation.

The development of new reactive HALS and UVAs can meet needs for improved compatibility in polar coatings as well as reduced migration. In

addition, work continues on development of high-purity powder forms that are also ideal for use in the powder coatings.

These systems are compatible with highly polar, highly crosslinked systems such as polyester (or acrylic) urethanes and melamines. A non-reactive HALS – or NOR-HALS – possesses a reactive hydroxy functionality enabling it to co-condense with melamine and isocyanate crosslinkers. As a result, it exhibits improved compatibility and migration resistance in many coatings systems. These may be combined with other HALS that contain reactive hydroxy functionality to achieve non-migrating systems. Potential applications include coatings-over-plastic substrates (particularly polyurethanes), acid-catalyzed clearcoats, clearcoats over acid-catalyzed basecoats and powder coatings.

The reactable HALS and UVAs react quickly, are noninteracting and exhibit outstanding solubility, thermal permanence and radiation stabilizing effectiveness. Their migration resistance makes them attractive for use in wet-on-wet applications. There are also reactables with low melting ranges for use in powder coating applications and UV/powder hybrid applications.

In powder coatings, the purpose of UV absorbers is to reduce the rate of polymer degradation due to the environmental exposure of UV radiation. The chemistry is usually based on benzotriazole but can also be benzophenone based. These materials absorb harmful UV radiation and convert it into low levels of heat energy. The levels are usually 1.0-5.0% and they are normally used in combination with a hindered amine light stabilizer.

Inorganic UV Absorbers

Titanium Dioxide

Titanium dioxide white pigments are designed by their particle size for optimum light scattering in the visible region. For high light refraction, a maximum refractive index is a prerequisite. However, this is not sufficient – the particle size has to be fine-tuned as well. Unlike standard-sized titanium dioxide pigments, ultra-fine titanium dioxides, which were initially developed for transparent UV protection, ideally do not scatter visible light. However, standard-size and ultra-fine titanium dioxides have the same refractive index, so it is the finest particle size that is responsible for the transparency of the coating. The finer the dispersed particles the more transparent the coating. Thus, for transparent UV absorption the finest grades in optimum dispersion are applied. It has to be noted as well, that certain ultra-fine titanium dioxides grades with selected 'intermediate' primary particle size do scatter blue light. This is why these nanosized TiO₂ particles are used in metallic coatings and other pigmented systems in which sophisticated color effects are desired.

Titanium dioxide absorbs UV radiation and serves as a photo-semiconductor. This property is practically independent from the particle size. Energy absorption leads to the transfer of an electron from the valence band to the conduction band. This process creates two mobile charged particles: the negatively charged electron in the conduction band, and the positive charge (hole) in the valence band. UV radiation is absorbed and transformed into thermal energy. However, unlike organic substances, the chemically inert titanium dioxide does not decompose, so that the long-term stability of the entire system is increased.

In order to tame the UV radiation and prevent it from causing damage by forming radicals, foreign ions such as trivalent aluminum (Al³⁺) are incorporated into the inner crystal lattice of TiO₂. In addition, the surface of the pigment may be encapsulated with an inorganic coating consisting of aluminum oxide (Al₂O₃) and/or silica (SiO₂). This stabilizing technology is generally used for photo-resistant and weather-resistant white pigments and inorganic UV absorbers. Typical white pigments have a crystallite size of 200 to 350 nm. They are available as anatase or rutile pigments. The inorganic TiO₂-based UV absorbers have a primary particle size of 10 to 50 nm and are usually offered as rutiles with a high-surface coating.

These surface coatings make it possible to modify not only the photoactivity but also the optical and colloidal properties of the white

pigment. It is also a must to achieve good dispersibility of the ultra-fine titanium dioxides. For this reason, the pigments are treated with an additional organic substance.

There are two types of ultra-fine titanium dioxides in the rutile modification (both containing >99% rutile) that differ mainly in their primary crystal size and doping. The type that was specially developed for transparent wood coatings has a primary crystal size of ~10 nm and a specific surface of ~110 m²/g (Mikrorutile 10 nm). The second product has a primary crystal size of 15 nm and accordingly a smaller specific surface area of ~70 m²/g (Mikrorutile 15 nm).

Nano zinc oxide is also used as a UV absorber and adds to the improvement of other coating properties.

Cerium Oxide Nanoparticles

Cerium oxide is largely used in the catalysis field (mainly for diesel engines), and in chemical and mechanical polishing (CMP). However, cerium oxide is also well known for its optical properties and ability to filter UV rays. Stable sols of cerium oxide nanoparticles with diameters of 10 nm are available. These sols appear as a clear liquid, since the particles are small enough to be totally transparent.

Despite their small size, cerium oxide nanoparticles are very effective in terms of UV filtration. According to theory, cerium oxide shows a UV cut-off threshold at around 370 nm, similar to that of nano titanium oxide. Cerium oxide and titanium oxide are both semi-conductors (with a band gap around 3.0 - 3.2 eV) and present the same classical UV absorption mechanism: under UV-light illumination, the absorption of a photon with a higher energy than the band gap creates an electron-hole pair.

In the case of titanium oxide, these holes and electrons migrate to the surface of the particles (rather than recombining together inside the particles). When holes and electrons are at the surface, they can react with oxygen, water or hydroxyls to form free radicals. These free radicals are oxidant entities, and can cause the degradation of organic molecules, in particular polymers, which is an important issue for protective coatings.

In contrast, cerium oxide absorbs UV without being photoactive. Indeed, cerium oxide has a localized electron (4f orbital), while titanium oxide has less localized electrons than cerium oxide (3d orbital). So the cerium-oxygen bonding is more ionic than the titanium-oxygen bonding and, logically, the charge carriers (holes and electrons centers) creation is lower than in the case of titanium oxide. Moreover, cerium oxide shows a very fast recombination of charge carriers before they can migrate to the surface (because of crystal defects, oxido-reduction reaction) so there is no further creation of free radicals. Due to the combination of these two phenomena, cerium oxide does not show any photocatalytic effect.

Cerium oxide nanoparticles, properly dispersed in coating formulations, combine the advantages of organic ultraviolet (UV) absorbers with those of mineral additives. The cerium oxide nanoparticles ensure the durability of the UV absorption function while improving the hardness and strengthening the organic binders currently used in wood coating technology. Since the nanoparticles do not scatter light, the coating remains transparent.

Transparency (i.e., no coloration, no whitening) is an important requirement for the wood coating industry; since wood is a natural material, the coating must be as neutral as possible. When the durability is targeted, colored pigments are often added to help, but this negatively impacts the aesthetics of the end product. Organic UV absorbers are also efficient but their actions are limited because of progressive destruction of active molecules (migration, leaching, photochemical activity).

The surface mechanical properties (hardness and scratch resistance) of a coating are clearly improved by cerium oxide nanoparticles. The bulk characteristics of the organic host matrix are also strongly modified in the presence of cerium oxide nanoparticles: tensile strength, elongation-at-break or yield stress are significantly improved. The homogeneous distribution of cerium oxide nanoparticles throughout the matrix



does not support the hypothesis of the formation of an inorganic surface network to explain the reinforcement of the polymer film surface. Therefore, it is probable that a modification of the structural organization of the polymer chains around the particles occurs during the drying.

From a practical point of view, the improvement in mechanical properties combined with the UV filter protection delays the occurrence of cracks, and allows the coating to better follow the dimensional variations of the wood piece due to moisture pick-up and swelling. Improved scratch resistance contributes to better appearance and durability (e.g., the inhibition of weaknesses and micro cracks due to handling).

The introduction of cerium oxide nanoparticles into the organic matrix results in a significant modification of hydrophilic properties of the coating, leading to an improvement in water resistance. The contact angle of a water droplet characterizes the water resistance of a surface. This important parameter is significantly increased upon addition of cerium oxide nanoparticles.

Organic UV Absorbers

The most common UV absorbers for coatings are 2-hydroxyphenylbenzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyltriazines, and oxalanilides. Salicylates, formamidines and cyanoacrylates may also be used on an individual basis.

The photoprotection mechanism resides in the ability to form reversible intramolecular hydrogen bonds between an o-hydroxyl group and a heteroatom such as nitrogen. Upon absorption of UV-light, an electron is promoted to an excited singlet state and, via intersystem crossing, to an excited triplet state. This is followed by an excited state intramolecular proton transfer, or enolization, with proton transfer taking place along the intramolecular hydrogen bond. The quinonoid intermediate tautomerizes through a rapid non-radiative relaxation process (heat) and return proton transfer, thus regenerating the original ketone. This process, called the keto-enol tautomerism mechanism, is nothing but a continuously repetitive proton transfer.

Due to the bathochromic shift of the absorption maximum toward the long-wavelength spectrum, halogenated benzotriazoles are particularly suited for the protection of photo-sensitive wood. The halogen substituent modifies the electron density and expands the delocalized electron system. As a result, less energy is required to bring the electrons into the excited state and the absorption of radiation is shifted towards lower frequencies. In this case the absorption maximum reaches the areas of the visible sunlight, thus more efficiently protecting the substrate from the damaging effect of this type of radiation.

In the late 1970s, oxalanilide UV absorbers were already almost entirely replaced by various hydroxyphenylbenzotriazoles (BTZ), which became the dominant UV absorber class during the 1980s and continue to be so for a variety of traditional applications. These materials were already characterized by much broader spectral coverage and much better photo stability. In spite of the dominant position of the hydroxyphenylbenzotriazoles, there are still requirements that cannot be satisfactorily met with these products due to certain technical limitations of their chemistry. These include limited absorption at shorter wavelengths, interaction issues with certain metal (e.g. Al-based) catalysts, leading to significant yellowing, as well as inadequate protection of the substrate at reduced film build. Development efforts in the 1990s resulted in the introduction of the first generation of hydroxyphenyltriazine (HPT) UV absorbers.

Generally speaking, hydroxyphenyltriazines exhibit much less tendency to interact with certain metal catalysts and even better photo stability than hydroxyphenylbenzotriazoles, as well as high absorption at shorter wavelengths. These features make this UV absorber class highly versatile in terms of both traditional and advanced applications such as UV curing. Furthermore, combinations with BTZ allow broader spectral coverage than HPT alone, along with superior protection at short wavelengths versus BTZ alone.

Conventional BTZ and HPT UV absorbers exhibit fairly similar extinction, except in the 300 nm range. Adequate UV protection at

low film builds can therefore only be achieved through significantly higher dose levels, which in turn may compromise the secondary properties of the paint film.

The more recent development of advanced chromophores based on hydroxy-phenyl-triazine chemistry has allowed up to 3.5 times higher extinction than the state of the art. This extremely high extinction allows the application of thin films along with superior UV protection at comparatively low dose levels. The position of the absorption maximum in the 320-330 nm range also makes these chromophores interesting candidates for the protection of substrates sensitive at this wavelength range, e.g. polycarbonate.

The efficacy of a UV absorber depends both on its absorption characteristics and on its secondary properties, such as photo stability, which needs to be very high. This is particularly important in thin film applications, where the product's inherent stability rather than the internal filter effect (i.e., UV absorber molecules protecting each other) plays the dominant role. Advanced hydroxyphenyltriazine technology allows superior protection at low film builds, whereas delamination is observed in the presence of conventional UV absorbers.

The spectral coverage as such as well as the position of the absorption maximum are determining factors in UV stabilization of substrates sensitive at wavelengths that are not or not sufficiently covered either by conventional or advanced chromophores. These wavelengths extend from the ≥ 360 nm range to the visible and slightly above.

A shift of the absorption spectrum of the UV absorber can be achieved to a significant extent through specific substitution patterns; however, there are obviously limitations both in terms of chemistry and color. The more the spectrum is shifted towards the visible, the higher the risk of bringing in too much color. This in turn means that a proper balance needs to be achieved between the spectral coverage and the product's inherent color.

Both UV and visible light lead to decomposition of the lignin structure of wood, resulting in discoloration/darkening of pale woods in particular. In order to filter out the UV light component as far as possible, broader spectral coverage is needed than can be achieved with conventional UV absorbers.

Cutting out the UV light either by cut-off filters (which allow a certain wavelength range to be selectively cut out, e.g., a filter labeled GG 320 excludes all wavelengths below 320 nm, a filter labeled GG 385 excludes all wavelengths below 385 nm, etc.) or by the red-shifted trisresorcinol-triazine (TRITA) UV absorber in lieu of a filter can greatly reduce the formation of colored chromophores. Since such species, however, are also being formed in the visible range, sufficient protection can scarcely be achieved by the UV absorber alone. In order to fully prevent their formation, spectral coverage as far out as >450 nm would be needed, which, in turn, would result in a major color impact by the UV absorber.

Therefore, a modified concept involving specific co-stabilization was developed. Such co-stabilizers, which are chemically based on free nitroxyl radical chemistry, are typically used for pretreatment purposes. Such materials can trap the radicals formed on the wood surface by the visible light, thereby preventing photo-oxidation of lignin.

The range of UV absorbers available today includes both conventional and advanced UV absorber technology. In traditional applications conventional hydroxyphenylbenzotriazoles as well as hydroxyphenyltriazines will certainly continue to play an important role. These products, however, do not meet the requirements for thin film applications or for applications requiring enhanced or specific protection at certain wavelengths. Development work has led to an extension of the available product range beyond conventional technologies, thereby allowing applications previously considered difficult or even impossible. Advanced hydroxyphenyltriazines are closing the gap for thin film applications or applications where enhanced protection at shorter wavelengths is necessary. Superior protection of wood substrates can be achieved by a specific concept, i.e., the combined use of red-shifted triazine-based UV absorbers and lignin stabilizers. Protection of systems or composites based on aromatic epoxies can be considered the biggest

challenge in terms of the UV absorber properties needed. Today this can be realized through novel red-shifted UV absorber technology, which combines comparatively low color with broad spectral coverage reaching into the near visible.

Furthermore, the application of the various products as such, or combinations thereof, allow paint companies to adjust the protection to the level needed. In water-based coatings – although not further discussed here – this is achieved through specific water-compatible product forms.

New mini-emulsion polymerization techniques have developed aqueous preparations of hydrophobic UV absorbers, which enables easy incorporation and effective use in waterborne coatings. The products can be added as supplied by simple stir-into the formulations without any cosolvent at any stage of the manufacturing process and are ideal for post addition. These products also allow dispersion of hydrophobic substances into aqueous systems without separation problems upon storage. The dispersed additive does not influence the optical properties of clear coatings such as gloss and transparency. These products also show high water leaching resistance and excellent long-term protection.

VISCOSITY MODIFIER

A material which, when added to a coating, has a measurable effect on the rheological properties.

WATER-REMOVAL AGENTS/SCAVENGERS

See Moisture Scavenger

PTSI (p-toluenesulfonyl isocyanate) is a low-viscosity reactive additive useful as a water scavenger in the formulation of specialty urethane products such as coatings, adhesives and sealants. The reaction of PTSI with water generates carbon dioxide and the corresponding toluene-sulfonamide, which is generally inert to further reaction with alkyl and aryl isocyanates. The sulfonamide is usually soluble in common coating solvents and presents no significant toxicity hazards. The reaction of PTSI with water introduced from pigments and solvents in the paint formulation generates carbon dioxide and soluble inert chemical products. Experience has demonstrated that 13 grams of PTSI effectively scavenges 1 gram of water, however compatibility with the binder should always be tested.

PTSI provides the formulator of specialty urethane products with an expedient and efficient alternative to physical methods of dehydration in common use. It is also recommended for the storage stabilization of purified diisocyanates against deterioration or discoloration. It can be used for: moisture-curing prepolymers, catalyzed prepolymers, prepolymer and polyol systems, urethane alkyd production, and urethane lacquer production.

Both one- and two-part systems can be formulated with PTSI as a scavenger for water introduced with solvents, pigments and fillers. The reactivity of PTSI toward active hydrogen atoms makes it useful as a scavenger for water and other isocyanate reactive groups such as free acid in powdered aluminum alkanoates and active hydrogen present in carbon black pigments, which cause polyurethane coatings to thicken during storage.

Molecular sieves are also used as water scavengers. They are composed of crystalline aluminosilicates that have cavities that are interconnected by common openings or windows. Their function of water scavenging is independent of temperature.

WATER REPELLENTS

Organosilicon compounds (silanes) are long-established water repellents. They feature excellent water repellency and will not significantly impair the water-vapor permeability of concrete. On concrete, they form extremely stable covalent bonds with the silicate matrix of the pores and capillary walls. The colorless, non-film-forming silane impregnating agent fabric prevents water and dissolved aggressive substances, such as salts, from gaining ingress into the building material via the capillaries. Silanes possess excellent durability and are extremely resistant

to external influences, such as UV radiation, thermal stress, aggressive substances and microbes.

WAXES

See Slip Aids; Surface Modifiers

The term 'wax' encompasses a large range of naturally occurring and synthetic material made from high-fatty-acid esters (typically C36 – C50) or from polymeric compounds (700 < molecular weight < 10,000) that differ from fats in being harder and less greasy. It is, however, important to realize that the chemical composition alone does not determine a wax. The term wax is basically a generic term for materials that have the following physical characteristics:

- solid at 20 °C, varying in consistency from soft and plastic to brittle and hard;
- a melting point of at least 40 °C without decomposing, which distinguishes waxes from oils and natural resins; and
- a relatively low viscosity at temperature slightly above the melting point; non-stringing but producing droplets. Droplet formation will exclude most low molecular weight polymers.

Naturally Occurring Waxes			Synthetic
Animal	Vegetable	Mineral*	
Bee wax	Carnauba	Montan	HDPE (high-density polyethylene), LDPE (low-density polyethylene), and PP (polypropylene)
Lanolin	Candellila	Paraffin	Fischer-Tropsch (polymethylene)
Lanocerin™	Jjoba oil	Microcrystalline	Fatty acid amide
Shellac	Ouricouri	Intermediate	PTFE (polytetrafluoroethylene)
	Esparto (Ozocerite)	Ozokerite	Polyamide

*Also called semi-synthetic waxes.

There are a large variety of waxes available on the market, often classified according to their origin. PP and PTFE although not being real waxes, are very often associated with this class of surface-conditioner additives because of the similar effects and performances they can provide.

To have a significant impact on coating or ink properties, the wax must migrate to the surface and be present in sufficient quantity to impart the desired properties. Two of the migration mechanisms that are generally proposed are noted here.

- **Blooming mechanism** – Molten wax particles float (or bloom) to the surface. When the coating cools down and recrystallization of wax particles takes place, a thin, continuous, wax-enriched surface layer is formed. Usually, the softer (low-melting) the wax, the more predominant is the blooming mechanism. Incompatibility or immiscibility between wax and coatings can enhance the migration phenomenon.
- **Ball Bearing mechanism** – In this case, solid wax particles individually migrate to the surface. Here they act as a physical spacer by pro-



truding above the coating surface, preventing another surface from coming into close intimate contact. Hard and high-melting-point waxes (HDPE, PTFE) function through this mechanism under certain conditions. Both the particle hardness and the extent of protrusion influence the importance of this effect.

With the wax layer or wax particles at the surface of the coating, the coefficient of friction has been altered (decreased) and the desired slip effect has been imparted to the film. This explains why waxes are often classified as 'surface conditioner additives.'

Waxes are usually less expensive, more reliable and less often associated with side effects (i.e., recoatability) than some other surface conditioner additives. In most cases, a decrease in intercoat adhesion is related to the usage of extremely non-polar waxes like paraffins and the surface effects tend to last longer because wax particles migrate very slowly to the surface.

Typical Wax Effects

Wax Type	Effects
Carnauba	Slip and lubricity, anti-blocking, abrasion resistance
Parafin	Anti-blocking, water repellency
Amides	Sandability, slip and lubricity, soft-feel
HDPE, LDPE	Slip, abrasion (scratch and mar) resistance, anti-blocking
PP	Anti-slip, anti-blocking, abrasion resistance
PTFE	Excellent slip and lubricity, anti-blocking, abrasion resistance.

Wax emulsions are extensively used in aqueous coating formulations. Ready-to-use emulsions can be incorporated by simple mixing. Their very fine particle size ensures an intimate and homogeneous incorporation. Wax emulsions can be stabilized by either a steric mechanism (using nonionic emulsifiers) or by an electrostatic mechanism (using ionic emulsifiers, mostly anionics). Combining anionic and nonionic emulsifiers gives the emulsion an optimum stability.

Wax properties that have the greatest impact on formulation performance include the chemical composition, molecular weight, melting point, hardness and, in the case of emulsions or dispersions, the particle size. When selecting a wax it is important to consider the melting point, particle size and particle size distribution, pH, type of surfactant and order of component addition.

Most of the emulsions available are characterized by a monomodal particle size distribution of either a unique wax or wax combination. There are bimodal-function-distribution (BFD) emulsions available that result in a much higher packing density of wax particles at the coating surface. This is achieved because the small particles will insert into the interstices created by the larger particles. Thus, a layer with a much higher wax density is formed, and this results in enhanced performance.

Wax additives that are water-based can penetrate wood surfaces and produces excellent water beading and anti-swell properties. They can improve swell resistance by as much as 80%, and extend the life and beauty of exterior wood. They dry completely clear and are typically used for outdoor wood decking and fence applications. The water protection also helps control cracking, splintering, color fading, and mold and mildew.

WET EDGE EXTENDERS

These additives keep a film open or wet during a painting operation. They allow lapping from an adjoining section or panel to newly painted substrate. This is accomplished by controlling water evaporation rate through the use of glycols, glycol ethers, polyoxyethylene glycols and certain thickeners. Some extender pigments that have a high water demand are also useful in this area though mainly by augmenting other compounds deliberately added for this purpose. *See also Retention Aids.*

WETTING AGENT

See Surfactant

Wetting agents are additives comprised of amphiphilic molecules that improve the dispersion and/or adhesion process. Basically they are surfactants. Wetting agents are used to lower the surface tension.

The polarity and cohesive hydrogen bonding between water molecules lead to very high surface tension in water-based systems. High surface tension makes it very difficult for paint to properly wet the surface of substrates with uneven and/or porous surfaces and proper wetting is necessary for an even and adherent coating. Poor wetting can cause cratering and an increase in film defects. This problem is magnified if dirt particles and other contaminants are present. When paint is applied to very low surface energy materials, such as plastics, air entrapment, crawling, framing and poor adhesion often result.

To address these issues, formulators have turned to additives designed to increase substrate wettability and lower surface tension of the coating. In order to achieve complete wetting, coatings must have lower surface tension than the substrate.

Substrate wetting is defined as the replacement of adherent air at the substrate surface by a liquid coating. A surface is said to be wetted if a liquid spreads over the surface evenly without the formation of droplets. When the liquid is water and it spreads over the surface without the formation of droplets, the surface is said to be hydrophilic. In terms of energetics, this implies that the forces associated with the interaction of water with the surface are greater than the cohesive forces associated with bulk liquid water. Water droplets form on hydrophobic surfaces, implying that cohesive forces associated with bulk water are greater than the forces associated with the interaction of water with the surface.

Practically, hydrophobicity and hydrophilicity are relative terms. A simple quantitative method for defining the relative degree of interaction of a liquid with a solid surface is the contact angle of a liquid droplet on a solid substrate. If the contact angle of water is less than 30°, the surface is designated hydrophilic since the forces of interaction between water and the surface nearly equal the cohesive forces of bulk water, and water does not cleanly drain from the surface. If water spreads over a surface and the contact angle at the spreading front edge of the water is less than 10°, the surface is often designated as superhydrophilic, provided that the surface is not absorbing the water, dissolving in the water or reacting with the water. On a hydrophobic surface, water forms distinct droplets. As the hydrophobicity increases, the contact angle of the droplets with the surface increases. Surfaces with contact angles greater than 90° are designated as hydrophobic. The theoretical maximum contact angle for water on a smooth surface is 120°.

Micro-textured or micro-patterned surfaces with hydrophobic asperities can exhibit apparent contact angles exceeding 150° and are associated with superhydrophobicity and the "lotus effect."

While the contact angle of water on a substrate is a good indicator of the relative hydrophobicity or hydrophilicity of a substrate, it is not a good indicator for the wettability of the substrate by other liquids. Critical surface tension is associated with the wettability or release properties of a solid. It serves as a better predictor of the behavior of a solid with a range of liquids.

Liquids with a surface tension below the critical surface tension of a substrate will wet the surface, i.e., show a contact angle of zero. The critical surface tension is unique for any solid and is determined by plotting the cosine of the contact angles of liquids of different surface tensions and extrapolating to 1. The contact angle is given by Young's equation.

Hydrophilic behavior is generally observed by surfaces with critical surface tensions greater than 45 dynes/cm. As the critical surface increases, the expected decrease in contact angle is accompanied with stronger adsorptive behavior and with increased exotherms associated with the adsorption.

Hydrophobic behavior is generally observed by surfaces with critical surface tensions less than 35 dynes/cm. At first, the decrease in critical surface tension is associated with oleophilic behavior, i.e., the wetting

of the surfaces by hydrocarbon oils. As the critical surface tensions decrease below 20 dynes/cm, the surfaces resist wetting by hydrocarbon oils and are considered oleophobic as well as hydrophobic.

Wetting is especially difficult on low-energy surfaces, i.e., substrates with low surface energy or substrates contaminated by dirty particles or liquid contaminants such as grease. If that occurs, wetting defects such as crazing, crawling or poor adhesion may occur. When the surface energy of the substrate is relatively high, wetting may become a critical factor if highly dynamic application processes, such as a roller-coating application, are involved.

Wetting may be improved by raising the surface energy of the substrate through cleaning or by lowering the surface tension of the coating by using additives designed for this purpose. For aqueous systems, a substrate-wetting additive is a molecule having both a hydrophilic and a hydrophobic part. The additive's molecular structure determines that the orientation will drastically lower the surface tension of the liquid. The non-polar area of the molecule rests airward and the polar section of the molecule resets in the aqueous phase. Most polar molecular parts contain either ionic substances or polyether segments. The hydrophobic part is usually a specially selected polyhydrocarbon. Using fluorinated groups or polysiloxane chains gives special properties.

Low-molecular-weight silicone surfactants such as tri- penta- or hexasiloxanes lower the static surface tension of waterborne coatings better than hydrocarbon-based surfactants, and they are more effective than higher molecular weight silicone-based surfactants. These low-molecular-weight surfactants combine the strong reduction of static surface tension with excellent spreading ability. They are ideal substrate-wetting additives for coatings on difficult-to-wet substrates like plastics and metals. They are outstanding at wetting the pores of wood substrates.

In general, high-molecular-weight silicone surfactants provide good static surface tension reduction, poor spreading ability and acceptable dynamic surface tension reduction and foaming properties. Low-molecular-weight silicone surfactants provide very good static surface tension reduction, very good spreading ability and good dynamic surface tension reduction and foaming properties. The non-ionic fluoropolymer surfactants provide outstanding static surface tension reduction, acceptable spreading ability, but poor dynamic surface tension reduction and foaming properties. Organic surfactants provide good static surface tension reduction, acceptable spreading ability and outstanding dynamic surface tension reduction and foaming properties. These considerations are important in formulation.

Surface tension and interfacial tension once the coating is applied, are determined by all components of the coating. Surface tension of resins can vary from 57.6 dynes/cm for melamine resins to below 40 dynes/cm for acrylics and alkyds. Solvents vary from 72.7 dynes/cm for water to 22 dynes/cm for VM&P naphtha. It is important to realize that surface tension differences as low as 1-2 dynes/cm can give rise to defects such as craters.

Changes in surface tension as a coating dries, as well as differences across the substrate, can cause the coating to flow from areas of low surface tension to high surface tension. It is this flow that is the cause of most coating defects. Many of these defects can often be eliminated by removal of contaminants such as cutting oils, fingerprints or dirt from the substrate.

There are two main approaches to counteract this surface tension driven flow. The first is to reduce the overall surface tension and thus the differences between high and low. (Note that the surface tension of a coating increases as the solvents evaporate.) The second is to resist the flow by changing the rheology – most commonly achieved by increasing the viscosity. This approach has to be balanced with flow and leveling characteristics.

Defects that reduce the smoothness of a film, such as craters, pin holes, orange peel, fish eyes, picture framing and crawling, are all caused by flow due to surface tension differences. Many of these problems can be solved by including a combination of additives to reduce the surface

tension of the coating. For example, several well-known companies provide organically modified polysiloxanes with a wide range of surface tensions and compatibilities. Often referred to as surface additives or wetting aids, these materials can provide benefits at levels as low as 0.01%. It is important to note that high levels of polysiloxanes can cause intercoat adhesion problems, but with the proper guidance from the suppliers such issues can be avoided.

There are multipurpose silicone polyether additives designed specifically for all types of water-based coatings, including wood coatings, UV-cured systems, etc. This type of silicone additive lowers the surface tension of waterborne coating formulations and significantly enhances wetting properties, but does not have a negative effect on other important properties such as recoatability.

The organo-modified silicone additives each contain a different polyether portion that enhances incorporation of the additive into the coating. The silicone within the additive migrates to the surface of the coating where, because of its structure at the air-coating interface, it imparts beneficial properties to the coating. The specific properties enabled by the silicone additive i.e., increased wet-ability and improved slip and mar resistance without reduction in clarity or recoatability, are a function of the length of the silicone portion of the molecule.

A distinct advantage of the silicone polyether additive is its ability to wet problem surfaces such as PVC and other plastics without the need to add other solvents. This feature increases the ability of the formulator to meet strict VOC regulations while providing expected appearance and adhesion properties. Because it creates a very low dynamic surface tension, this type of additive spreads quickly and evenly. Ease of use is also important and addition is possible at the grind or let down stages of production, or even after all other steps are completed (post-added).

There are new superwetters on the market that are 100% silicone polyether co-polymers, consisting of a hydrophobic, methylated, short-chain silicone backbone with pendant hydrophilic ethylene oxide chains. The ethylene oxide chains are end-capped with hydrophilic organic groups such as hydroxy, methoxy or acetoxy.

These new superwetters are low-viscosity and low-molecular-weight materials and are easy to incorporate into coatings and inks. They migrate quickly to, and pack efficiently at, the coating surface, giving rise to low surface tension required to achieve good wetting performance. The superwetters provide excellent static surface reduction. While the ethylene oxide content (HLB) doesn't influence the surface tension directly in water, this can affect the solubility and therefore performance of the surfactant in a coating or ink formulation. Therefore, having a range of HLB values allows the formulator to choose the right product for a given formulation.

There are also new multi-functional, silicon-free wetting additives that promote strong dynamic surface tension reduction in aqueous systems, resulting in excellent wetting and application characteristics. This type of additive can benefit manufacturers who apply formulated products using roller, curtain, flow, disc, or spray methods as it promotes foam reduction and elimination of surface defects, such as cratering, crawling and fish eyes.

XANTHAN GUM

See *Thickeners*

Xanthan Gum is a naturally occurring polysaccharide that is a very good thickening and stabilizing additive for low-solvent, aqueous-based coatings and related products. In this environment, xanthan gum solutions exhibit pseudoplastic flow and have very good suspension characteristics. [Note: pseudoplastic systems have shear thinning characteristics and exhibit high viscosity at low shear rates and low viscosity at high shear rates.] It also aids in preventing skinning and in preventing paint "streaking" or slumping when applied. Xanthan gum, a polysaccharide that is rendered soluble through pyruvate and acetate substituted trisaccharide side chains, is produced by fermen-



ADDITIVES REFERENCE GUIDE

tation of the bacterium *Xanthomonas campestris*. The bacterium that forms xanthan gum is found in particular green vegetables. In these vegetables, it protects the bacterial colony from arid conditions and resulting dryness. The polymer has a stiff rod-like structure rather than a random coil in solution associated with most natural polysaccharides, a characteristic that gives it its unusual rheological properties. Xanthan gum is used in color-pigment dispersions, exterior fence paints, low-solvent emulsion paints, silicate paints, stucco coatings, and thickened chloride/water paint strippers. It is used at relatively low levels of about 0.05% to about 1% with the higher percentage used in thick coatings, such as are involved in stucco coatings, to prevent sag.

ZEOLITES

See *Molecular Sieves*

Zeolites are naturally occurring aluminosilicates.

References

1. Bieleman, J., Ed., *Additives for Coatings*; Wiley-VCH: Germany, 2000.
2. Biller, K. *Powder Coatings – Foundation for the Novice Formulator*; BNP Media: Troy, MI, 2004.
3. Calbo, L.J., Ed., *Handbook of Coatings Additives*; Marcel Dekker: New York, 1992.
4. Hare, C.H., *Protective Coatings*; Technical Publishing Company; Pittsburgh, PA 1994, SSPC 94-17
5. Koleske, J.V., Ed., *Paint and Coating Testing Manual*, 14th Edition of the Gardner-Sward Handbook, ASTM Philadelphia, 1995.
6. Koleske, J.V., Ed., *Paint and Coating Testing Manual*, 15th Edition of the Gardner-Sward Handbook, ASTM Philadelphia, 2012.
7. LeSota, S., Ed., *Coatings Encyclopedic Dictionary*; Federation of Societies for Coatings Technology: Blue Bell, PA, 1995.
8. Orr, E.W. *Performance Enhancement in Coatings*; Hanser/Gardner Publications, Inc.: Cincinnati, 1998.
9. Schick, M.J., Ed., *Nonionic Surfactants*, Physical Chemistry, Vol. 23 of Surfactant Science Series; Marcel Dekker: New York, 1987.
10. Schick, M.J., Ed., *Nonionic Surfactants*, Vol. 1 of Surfactant Science Series; Marcel Dekker: New York, 1966.
11. SciQuest CD, Vol. 1. Created by Consolidated Research and ITE Consultants.
12. Wicks, Z.W., Jr.; Jones, F. N.; Pappas, P.S. *Organic Coatings Science and Technology*, 2nd Edition; John Wiley & Sons: New York, 1999.
13. Zorll, U., Ed., *European Coatings Handbook*; Vincentz Verlag: Germany, 2000.
14. Commission International de l'Eclairage, "International Lighting Vocabulary," CIE, Paris, 1970.
15. <http://news.thomasnet.com>

In addition, raw material supplier literature was used, as well as material taken directly from feature articles published in PCI.

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