Waterborne UV Curable Resins for Industrial Wood Applications

Coatings Trends and Technologies
Rosemont, IL
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Laurie Morris
Senior Chemist
Alberdingk Boley, Inc.
Interior Industrial Wood Coatings
Types of Solvent-based (SB) Coatings used in Interior Industrial Wood Applications
Advantages/Disadvantages of SB Coatings
Water-based (WB) Coatings used in Interior Industrial Wood Applications
Experimental – WB UV for Interior Wood
Conclusions

Exterior Industrial Wood Coatings
Traditional Exterior Wood Coatings
Experimental – WB UV for Exterior Wood Phase 1
Experimental – WB UV for Exterior Wood Phase 2
Conclusions
Types of Solvent-based Coatings Used in Industrial Wood Applications

**Lacquer –**
Nitrocellulose, oil base alkyd or vegetable oils
Applications: Residential furniture

**Pre-catalyzed lacquer –**
Nitrocellulose, oils or oil-based alkyd, plasticizer, and urea-formaldehyde
Uses weak acid catalyst – butyl acid phosphate
4 month pot life
Applications: Office, institutional and residential furniture

**Conversion Varnish –**
Oil-based alkyd, urea-formaldehyde, and melamine
Uses strong acid catalyst, PTSA
24 – 48 hour pot life
Highest performance
Applications: KCMA, office and institutional furniture
Advantages

- Fast drying
- Good wood warmth
- Cost effective
- Easily repaired
- Tolerate climate differences well
- Good chemical resistance
- Good wear resistance

Disadvantages

- High volatile organic compounds (VOC)
- Extreme flammability
- Poor indoor air quality due to odor and formaldehyde emissions
- Pot life (conversion varnish)
Water-based (WB) Alternatives to SB Coatings

**WB Acrylics**
Self-crosslinking, multiphase, 1K or 2K
Applications: Residential and Institutional Furniture, KCMA

**WB Polyurethane Dispersions**
Polyester or Polycarbonate, 1K or 2K
Applications: Office furniture

**WB Acrylic/Polyurethane Blends**
Copolymers or Cold Blends, 1K or 2K
Applications: Residential, Institutional or Office furniture, KCMA

**WB UV Curable Dispersions**
UV PUDs and Acrylic Hybrids
Applications: Office Furniture, KCMA
Kitchen Cabinet Manufacturers Association (KCMA)

Purpose:
To establish a nationally recognized performance standard for kitchen and vanity cabinets.

Finish requirements:
- Shrinkage and Heat Resistance
- Hot And Cold Check Resistance
- Chemical Resistance
- Detergent and Water Resistance
**Architectural Woodwork Standards**

Purpose:
To provide design professionals with logical and simple means to comprehensively specify elements of architectural woodwork.

Finish requirements:
- Chemical Resistance
- Wear Index
- Cold Check
- Adhesion
Industrial Wood Specifications

Individual Office Furniture Manufacturer’s Specifications

- Chemical/Stain Resistance
- Green Print Resistance
- Toughness/Adhesion
- Plasticizer Resistance
- Hot print Resistance
- Hot/Cold Check Resistance
- Ballpoint Pen Indentation
- Resistance to Discoloration from Office Equipment “Feet”
- Boiling Water Resistance
- Steam Resistance
- Impact Resistance
- Resistance to fading or chalking
- Resistance to yellowing

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PUD Chemistry

OCN-R-NCO + OH-P-OH + HOCH₂-CH₂OH
(Polyisocyanate) Polyol

\[ \text{Catalyst} \]
\[ \text{NMP} \]
\[ \text{Acetone or MEK} \]
\[ \text{Reactive diluent} \]

\[ \text{OCN}-\text{R}-\text{NH}-\text{C}-\text{O}-\text{P}-\text{O}-\text{C}-\text{NH}-\text{R}-\text{NH}-\text{C}-\text{O} + \text{O}-\text{C}-\text{NH}-\text{R}-\text{NCO} \]
\[ \text{CH}_3 \]

\[ \text{NR}_3 \]

\[ \text{OCN}-\text{R}-\text{NH}-\text{C}-\text{O}-\text{P}-\text{O}-\text{C}-\text{HN}-\text{R}-\text{NH}-\text{C}-\text{O} + \text{O}-\text{C}-\text{NH}-\text{R}-\text{NCO} \]
\[ \text{CH}_3 \]

\[ \text{Water/polyamine} \]

Polyurea/urethane Dispersion

COO⁻ NR₄⁺

\[ 50-500 \text{ nm} \]
UV curing polyurethane dispersions: polymer structure
WB UV PUDs

- High molecular weight dispersions
- Low shrinkage
- Adhesion to multiple substrates
- Excellent chemical resistance
- Excellent mechanical properties
- Multiple polymer design options
- Low MFFT -- Solvent free formulations; no reactive diluent
- Dual cure options
Steps in the Curing Process of WB UV Coatings

Coalescence

Radical polymerization
Coalescence

**Stage 1** – Water evaporation, particles arrange, dense cubic packing

**Stage 2** – Deformation of polymer particles

**Stage 3** – Interface of individual particles dissipates

**Stage 4** – Interdiffusion of polymer chains, formation of mechanically stable polymer film
Polymerization Reaction

Photo-initiation

PI initiator \[ \xrightarrow{UV \text{ Light}} \] R* radicals

Start

R* + M \[ \rightarrow \] R-M*
radical resin intermediate

Growth

R-M* + M \[ \rightarrow \] R-M-M*

Termination

R-M* + *M-R \[ \rightarrow \] R-M-M-R
Waterborne UV

**Benefits**
- Excellent appearance
- Provides excellent wood protection
- Very low VOC
- Eco-friendly
- Water clean up
- High hardness & flexibility
- Excellent adhesion
- Resoluble / reclaim
- Immediate property development

**Challenges**
- Some grain raising
- Drying ovens required
- Humidity dependence
- Finish defects (incomplete dry)
A study has been conducted to compare the properties of three WB UV coatings with commercially available solvent-based conversion varnish, water-based conversion varnish and water-based pre-catalyzed lacquer. The project plan was to develop high performance WB UV resins and investigate their performance for industrial wood applications.
Solvent based Conversion Varnish
Chemistry: Oil based alkyd/melamine/PTSA catalyst
Weight Solids: 50%
Volume Solids: 41%
VOC: <500 g/l
10 parts Conversion Varnish + 1 part catalyst + 3 parts Reducer
Pot Life = 12 hours

Water based Conversion Varnish
Chemistry: Urethane/Acrylic blend/WB Isocyanate
Weight Solids: 28%
VOC <200 g/l
10 parts Urethane/Acrylic blend + 1 part WB Isocyanate
Pot Life = 6 – 8 hours

Water based Precatalyzed Lacquer
Chemistry: Self-crosslinking Acrylic
Weight Solids: 25%
VOC <185 g/l
Water-based UV Products Evaluated

**WB UV 1**
Chemistry: UV PUD (polyester)/Acrylic Hybrid
Weight Solids: 48%
VOC: <15 g/l
MFFT: 0°C

**WB UV 2**
Chemistry: UV PUD (polyester)
Weight Solids: 40%
VOC: <40 g/l
MFFT: 0°C

**WB UV 3**
Chemistry: UV PUD (polyester)/Acrylic Hybrid
Weight Solids: 42%
VOC: <25 g/l
MFFT: 0°C
## WB UV Formulations

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<td>&lt;50</td>
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**Application:** Spray approximately 3 wet mils of coatings over 18X18 inch stained birch plywood panel. Air dry for 10 minutes. Force dry for 10 minutes at 50°C. Cure with mercury bulb at 500 mJ/cm². Sand with 3M Superfine Sanding Sponge. Apply a second coat and repeat dry time and curing. Wait 7 days before testing unless otherwise indicated in the test method. For Door Edge Soak – same as above except use a 4X4 inch oak panel and coat all sides.

**Test for:**
- Chemical resistance
- Plasticizer resistance
- Print resistance
- Boiling water resistance
- Scrape adhesion
- Ball Point Pen Indentation
- Door Edge Soak
- Hot and Cold Check
Measure machine power output

Power Puck
Chemical/Stain Resistance

Test method:

Apply enough chemical/stain to create a \(\frac{1}{4} - \frac{1}{2}\) inch diameter spot on the test panel.

Cover with a watch glass.

Allow chemical/stain to dwell according to specification.

Remove chemical/stain and wash the surface of the panel with water.

Rate each chemical/stain on a scale of 0 to 5 with 0 being complete destruction of the film and 5 being no effect on the film.
Chemical Resistance – KCMA – 24 hour dwell (except mustard 1 hour dwell)
Chemical Resistance – Furniture Specifications – 16 hour dwell

- Lysol
- Windex
- Acetone
- Betadine
- Nivea
- Red Wine
Boiling Water Resistance:

Apply 10 ml boiling water to the test panel. Place a ceramic cup full of boiling water on top of the 10 ml of water. Wait 1 hour. Remove the cup and wipe with a paper towel. Wait 24 hours. Evaluate for whitening.
Scrape Adhesion – Cut a 4X7 inch piece from each test panel. Test adhesion with 5000 grams of weight using the loop stylus. Rate on a scale of 0 to 5.

Ball Point Pen Indentation – Cut a 4X7 inch piece from each test panel. Test with the small pen attachment (#5785) and 300 grams of weight. Rate on a scale of 0 to 5.
Print and Plasticizer Resistance

**Green Print Resistance** - After curing test panel wait 1 hour the apply a 2 inch square piece of #10 cotton duck cloth to the finish. Apply a force of 2 lb/square inch directly to the duck cloth. Wait 24 hours then remove the cotton duck cloth. Evaluate for printing.

**Hot Print Resistance** - After curing the panel wait 14 days then apply a 2 inch square piece of cotton duck cloth to the finish. Apply a force of 1 lb/square inch directly to the duck cloth. Place the specimen in the oven at 60C for 24 hours. Allow the specimen to cool to room temperature and then remove the duck cloth. Evaluate for printing.

**Plasticizer Resistance** - Apply a 2 inch square piece of red vinyl to the test panel. Apply a force of ½ lb/square inch. Place the specimen in the oven at 50C for 72 hours. After cooling at room temperature for 1 hour, remove the vinyl square. Evaluate for softening and blistering.
Other KCMA requirements

**Edge Soak**: Place a cellulose sponge in a plastic container. Level container and fill with detergent solution (1% Dawn® dish soap by weight in water) to one half inch below top level of sponge. Place panel on sponge, cut side down. Permit to stand for 24 hours.

**Hot and Cold Check Resistance**: Cut a 4”X4” piece from each panel. Cycle as follows: Place panel in humidity cabinet at 50C and 70% humidity for one hour. Remove for 30 minutes and allow to reach original room temperature and humidity. Place in freezer at -10C for one hour. Remove and allow to reach original room temperature and humidity. Repeat for five cycles.
Conclusions

All the WB UV coatings have excellent chemical resistance. WB conversion varnish and SB conversion varnish have very good chemical resistance. WB Pre-Cat Lacquer has adequate chemical resistance for KCMA coatings.

WB UV 2, WB conversion varnish and SB conversion varnish have the best scrape adhesion.

All the coatings have excellent ball point pen indentation, plasticizer resistance, hot print and green print resistance, hot and cold check resistance and edge soak.

All the WB UV coatings have superior boiling water resistance.

WB UV coatings have excellent properties for interior industrial wood applications.
Environmentally friendly exterior wood coatings are traditionally made from WB acrylic dispersions and PUDs.

Both 1K and 2K coatings are used.

WB acrylics provide excellent UV stability.

PUDs provide excellent flexibility, a necessity because wood is dimensionally unstable.

Blends of acrylic dispersions and PUDs are typically used for optimal performance.
Identify the best combination of UV resin and exterior grade acrylic modifying resin.

Evaluate hardness development, block resistance, water resistance, cure response and QUV resistance.

Evaluate each coating with 2 different photoinitiator packages to determine optimal cost performance package.
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<th>Modification Type</th>
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<td>UV 7</td>
<td>UV PUD</td>
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- Self X-linking acrylic resin 1
- Self X-linking acrylic resin 2
- No modification
# Formulations – Phase 1

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In Phase 1 all coatings were cured at 800 mJ/cm$^2$.

The coatings with only alpha hydroxy ketone photoinitiator were cured using a mercury lamp.

Coatings with both alpha hydroxy ketone and acyl phosphine oxide photoinitiator were cured using both a mercury lamp and a gallium lamp.
2 peaks (810 cm$^{-1}$ and 1730 cm$^{-1}$) were investigated. The peak at 810 is a C=C which reacts during UV exposure. The peak at 1730 is a C=O and will not react during UV exposure.

\[
\text{Relative concentration of UV cured group (±)} = \frac{[A]_{810}^{UV}/[A]_{1730}^{UV}}{[A]_{810}^{0}/[A]_{1730}^{0}} \times 100, \quad (2)
\]

where \([A]_{810}^{0}\) is the IR absorbance at 810 cm$^{-1}$ before UV irradiation, \([A]_{1730}^{0}\) the IR absorbance at 1730 cm$^{-1}$ before UV irradiation, \([A]_{810}^{UV}\) the IR absorbance at 810 cm$^{-1}$ after UV irradiation and \([A]_{1730}^{UV}\) the IR absorbance at 1730 cm$^{-1}$ after UV irradiation.
Infrared Spectroscopy

- **C = O**
  - 1730 cm\(^{-1}\)

- **C = C**
  - 810 cm\(^{-1}\)
Measure % Cure by IR

- Peak differences at 810 nm
Cure Response - % Cure

- a-hydroxy ketone
- a-hydroxy ketone + acyl phosphine oxide

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Koenig Hardness Development

![Bar chart showing comparison between a-hydroxy ketone and a-hydroxy ketone + acyl phosphine oxide for UV 1 to UV 7.]
Make a drawdown on a 3B-H Leneta chart using a 3 mil bird bar. Air dry for 10 minutes then force dry for 10 minutes at 50C. Cure. Cut off a 1” X 8.5” strip from the card perpendicular to the draw down direction. Cut this strip in half to give two 1”x 4.25” strips. Put the two pieces together with each coated surface touching (face to face). Make a duplicate. Place the samples on a glass plate and put a 1000 gram weight on top of the samples. Place in a 50C oven for one hour. Remove from the oven and rate the block resistance.
Water Resistance
QUV – Gloss Retention

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Delta E after 4000 hours

- a-hydroxy ketone
- a-hydroxy ketone + acyl phosphine oxide
Discussion – Phase 1

All samples showed excellent QUV results with minimal gloss and color changes after 4000 hours of exposure.

The addition of acyl phosphine oxide photoinitiator did not impact the properties of the coatings. In Phase 2 testing, only alpha hydroxy ketone photoinitiator will be used.

UV 3 was eliminated from the study due to production difficulty.

UV 4, UV 5 and UV 6 were eliminated from the study due to low cure response and hardness development.

UV 1, UV 2 and UV 7 continued to Phase 2 testing.
In Phase 2 coatings were evaluated according to the specifications outlined in the American Architectural Manufacturers Association AAMA 653-14 Voluntary Performance Requirements and Test Procedures for Organic Coatings on Wood and Cellulose Composite Substrates.

This specification covers factory applied coatings intended for service in exterior environments.

QUV resistance was repeated on poplar substrate.

Coatings were formulated using traditional defoamers, surface tension modifiers, wax emulsion and rheology modifiers.

The solids of the coatings was controlled with water.
The American Architectural Manufacturers Association (AAMA) is made up of window, door, skylight, curtain wall and store front manufacturers, suppliers and test labs. These large and small companies represent both residential and commercial applications.

AAMA members develop and update the standards that are referenced in many national and state building codes.

AAMA offers a third party product certification program to provide manufacturers with the means to independently demonstrate product performance to their customers via the AAMA Certification Label.

http://www.aamanet.org/
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Panel Preparation

Unless otherwise stated in the AAMA 653-14 specification, all panels were prepared by:

Spray approximately 4 wet mils of coating over a 4 X 6 inch unstained southern yellow pine panel.

Air dry for 10 minutes.

Force dry for 10 minutes at 50C.

Cure with a mercury lamp at 800 mJ/cm².

Sand with a 3M Superfine Sanding Sponge.

Repeat steps 1 – 4.

All panels had the cut edges sealed with a 2K 100% solid urethane sealer. All sides of the panels were coated. All panels were aged for 7 days before testing was performed.
Data

- Wet Adhesion
- Dry Adhesion
- Impact Resistance
- Muriatic Acid Resistance
- Mortar Resistance
- Detergent Resistance
- Humidity Resistance

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Data

Cold Crack Cycles Passed

Q O P Q

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QUV Panels after 1700 hours

Cyclic - 4 hours UVA340 @ 60C; 4 hours condensation @ 50C

Panels for QUV testing were prepared in the same way as the AAMA panels except the substrate was 2 X 4 inch poplar panels.
QUV – Color Retention – Delta E after 1700 hours
All coatings passed the AAMA 653-14 tests.

Gloss retention is excellent on all coatings.

Controls performed poorly in QUV color retention. These products are typically used as a topcoat over a stain or pigmented basecoat. The stain/basecoat provides UV protection for the wood.

This study examined clear self-sealing topcoats over a very light colored wood.

The experimental samples all had good QUV color retention.
Coatings made from WB UV resins are excellent candidates for industrial wood coatings for both interior and exterior applications. They have very good chemical resistance and mechanical properties. They can be formulated at low VOCs and have low toxicity. They are viable alternatives to solvent-based chemistries.
Questions?

Laurie Morris
Senior Chemist
Alberdingk Boley, Inc.
Phone: (336) 821-5531
lmorris@alberdingkusa.com