High Molecular Weight Silicone Emulsions: Preparation, Properties, and Applications

CHT USA – Brian Mulhern –Senior Research and Development Chemist

Sink or Swim 2023

OVERVIEW

- Chemistry and properties of silicone polymers
- Silicone emulsions and stability
- High molecular weight silicones and gums
- Applications and emulsification of silicone gums
- New advancements in silicone gum emulsions

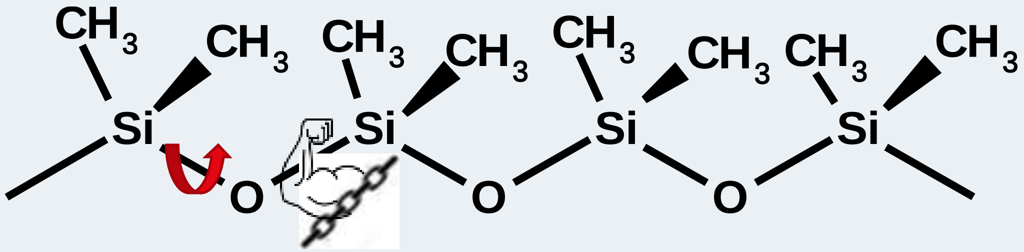
CHT
SMART CHEMISTRY
WITH CHARACTER.

Brief Description of Silicone Material Classes

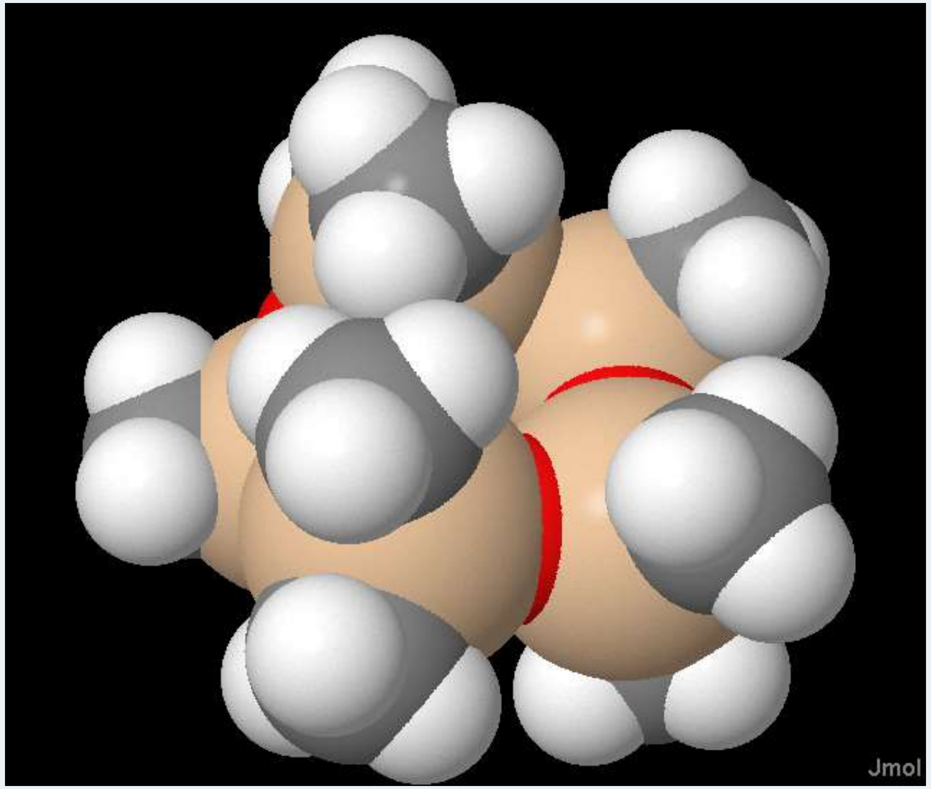
- **Linear silicone (volatile to non-volatile) polydimethylsiloxane (PDMS)** – 0.65 – 1,000,000 cSt
- **Ultrahigh MW PMDS (gum) -** ~20MM cSt – ‘dimethiconol’
- **Silicone resins** – network ceramic/dimethyl solids – trimethylated silica
- **Organic -modified silicones** –Silicone glycols – alkane modified silicone; amine modified silicones
- **Silica-silicone compounds** – food and cosmetic grade antifoams – ‘simethicone’
- **Silicone quats** – charged quaternary amines on silicone backbone
- **Silicone Crosspolymers** – dispersion of crosslinked silicone in a carrier

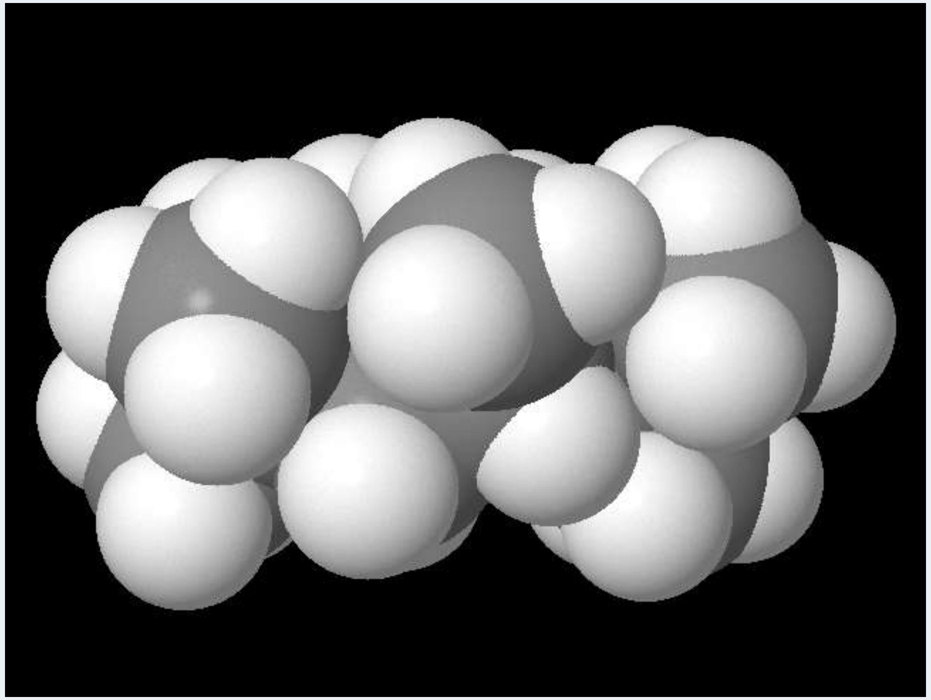
CHT
SMART CHEMISTRY
WITH CHARACTER.

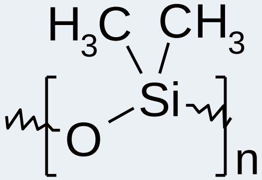
SILICONE UNIQUENESS



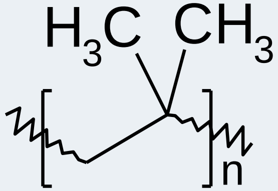
Long, Strong Intramolecular Bonds...Weak Intermolecular Bonds







polydimethylsiloxane



polyisobutylene

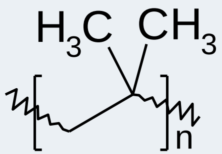
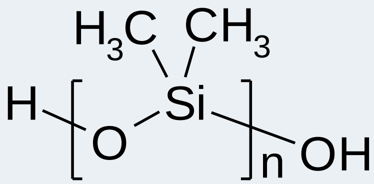
Brian Mulhern

CHT
SMART CHEMISTRY WITH CHARACTER.

Impact of Free Space, Easy Rotation and Weak Attraction on Useful Properties

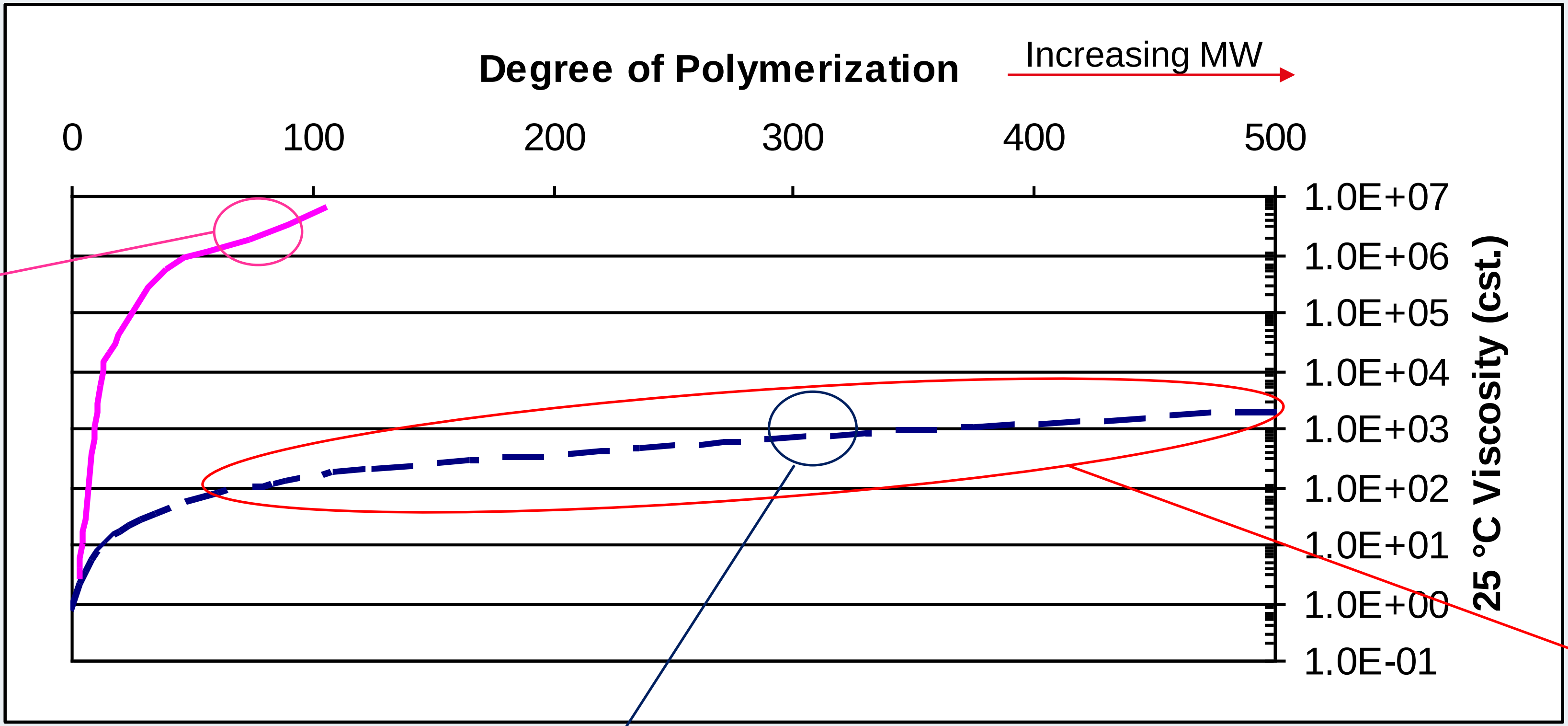
- Highest oxygen permeability of any polymer
- Combined with bio-inertness permits – high safety and compliance –food grade possible
- Low rotational energy gives low energy conformations on surfaces –excellent surface modification flow properties
- Low surface tension (easy spreading) – little goes a long way in surface coverage
- Smooth, ultra low friction modifying
- Hydrophobic
- Thermal Stability

Silicone vs Organic Polymers

Property		
Form	**Amorphous**	**Amorphous**
T_g (ºC)	**-70**	**-123**
Density (g/cc)	**0.92**	**0.97**
Fractional Free Volume	**0.026**	**0.071**
Permeability to O_2 (cm^3 cm/(cm^2 s cm Hg))	**0.081**	**60**
Critical Surface Tension (mN/m)	**33**	**22**
Viscosity (n~10) (cSt)	570	6.5
Viscosity (n~100) (cSt)	5,000,000	140

Impact of Increasing Chain Length in PDMS and PIB

Less than 100 repeat units
is a non-flowing paste/solid



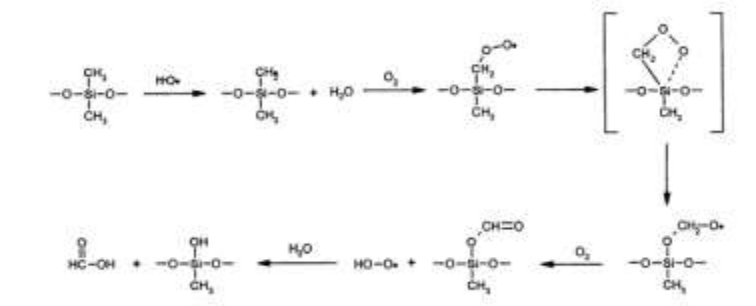
PDMS has useful visc
across the entire MW range

More than 300 repeat units
has a viscosity of less than honey

CHT
SMART CHEMISTRY
WITH CHARACTER.

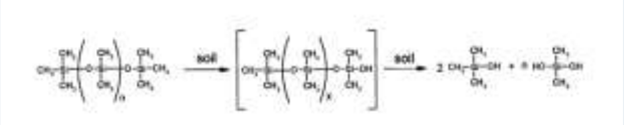
WHAT HAPPENS TO SILICONE IN THE ENVIRONMENT?

Quartz Sand



Evaporation and degradation in the atmosphere

Typical degradation time: <30 days

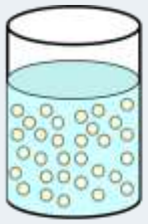


Journal of Polymers and the Environment, Vol. 11, No. 4, October 2003 (© 2003) 129 1566-2543/03/1000-0129/0 © 2003 Plenum Publishing Corporation A Review of the Fate and Effects of Silicones in the Environment

Emulsion Basics

Emulsion: A dispersion of one immiscible liquid in another, usually stabilized by a **surf**ace **act**ive **a**g**ent.**

Surfactant: A substance which tends to reduce the surface tension of a liquid in which it is dissolved.



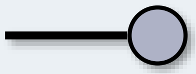
Oil in Water Emulsion (O/W)

Surfactants are amphipathic, act as barriers

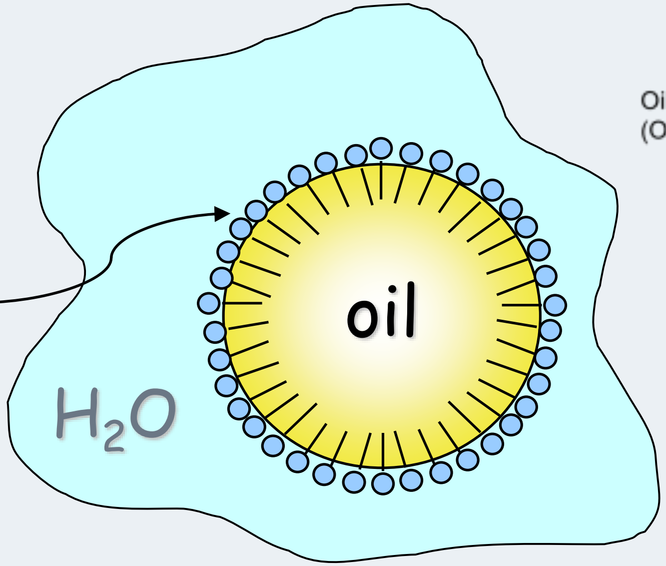
Three main types of surfactants: Nonionic, Cationic, and Anionic

Hydrophilic head

Hydrophobic tail (Lipophile)



surfactant molecule

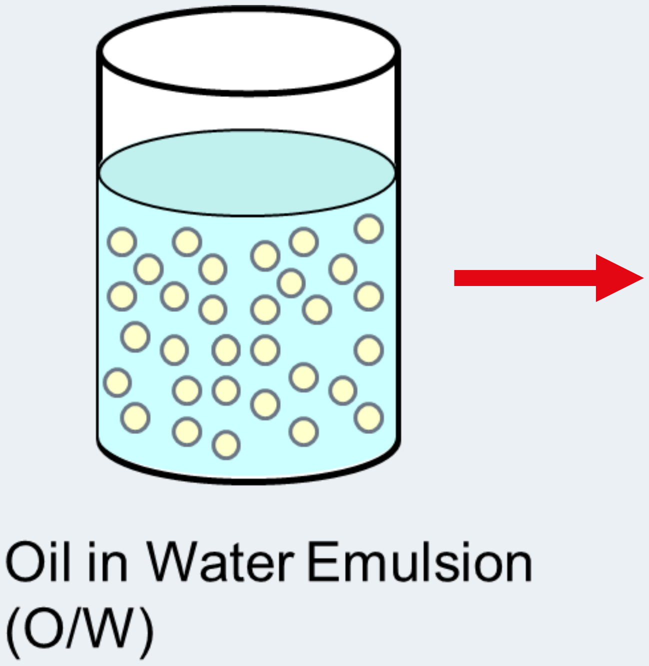


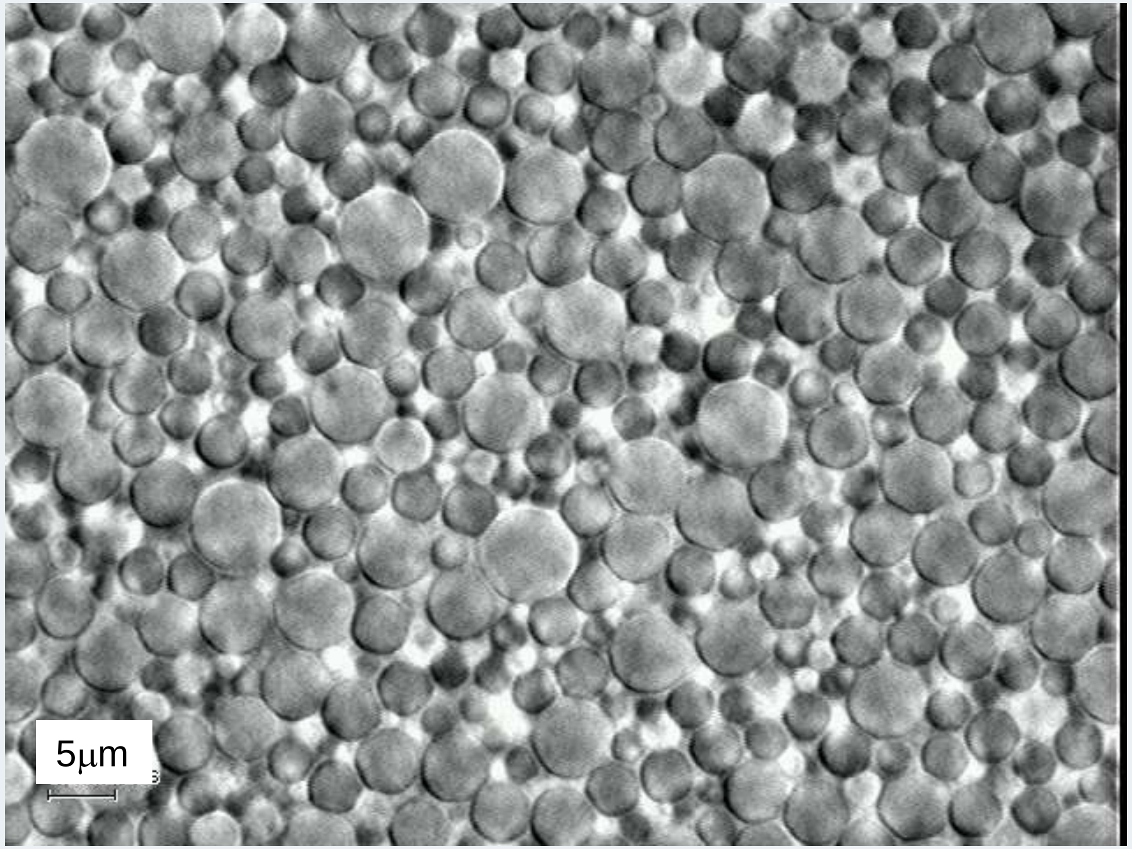
Oil-in-Water Emulsion (O/W)

Type of surfactant used imparts certain properties to the emulsion.

In case of multiple surfactant types, the emulsion takes its type from the "**more critical**" surfactant used (i.e., nonionic + anionic = anionic emulsion.)

Oil in Water Emulsion





Optical micrograph by Jennifer Stasser

CHT
SMART CHEMISTRY WITH CHARACTER.

How Various Types of Emulsions are Made

High Shear Processing aka "Mechanical Emulsions"

Mix oil, H_2O, surfactant; subject mixture to high shear.

Mechanical emulsions is a broad term which captures various methods of high shear processing.

Emulsion Polymerization (EP):

Subject polymerizable monomer, H_2O, & surfactant to high shear; carry out polymerization of monomer. Useful with hydrophobic polymerizable monomers.

Think of each particle in this emulsion of being a micro-reactor

Microemulsion:

Emulsions < 100nm; spontaneously formed emulsions. Don't require shear forces. Thermodynamically stable.

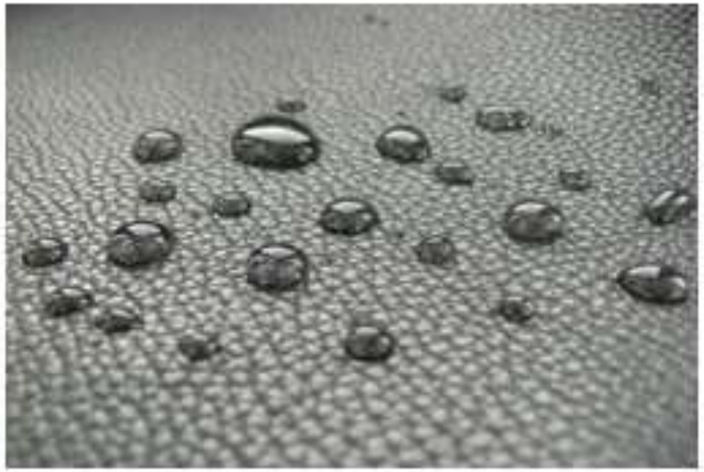
CHT SMART CHEMISTRY WITH CHARACTER.

Controlling Emulsion Stability

Most emulsions are thermodynamically unstable. They will eventually separate.

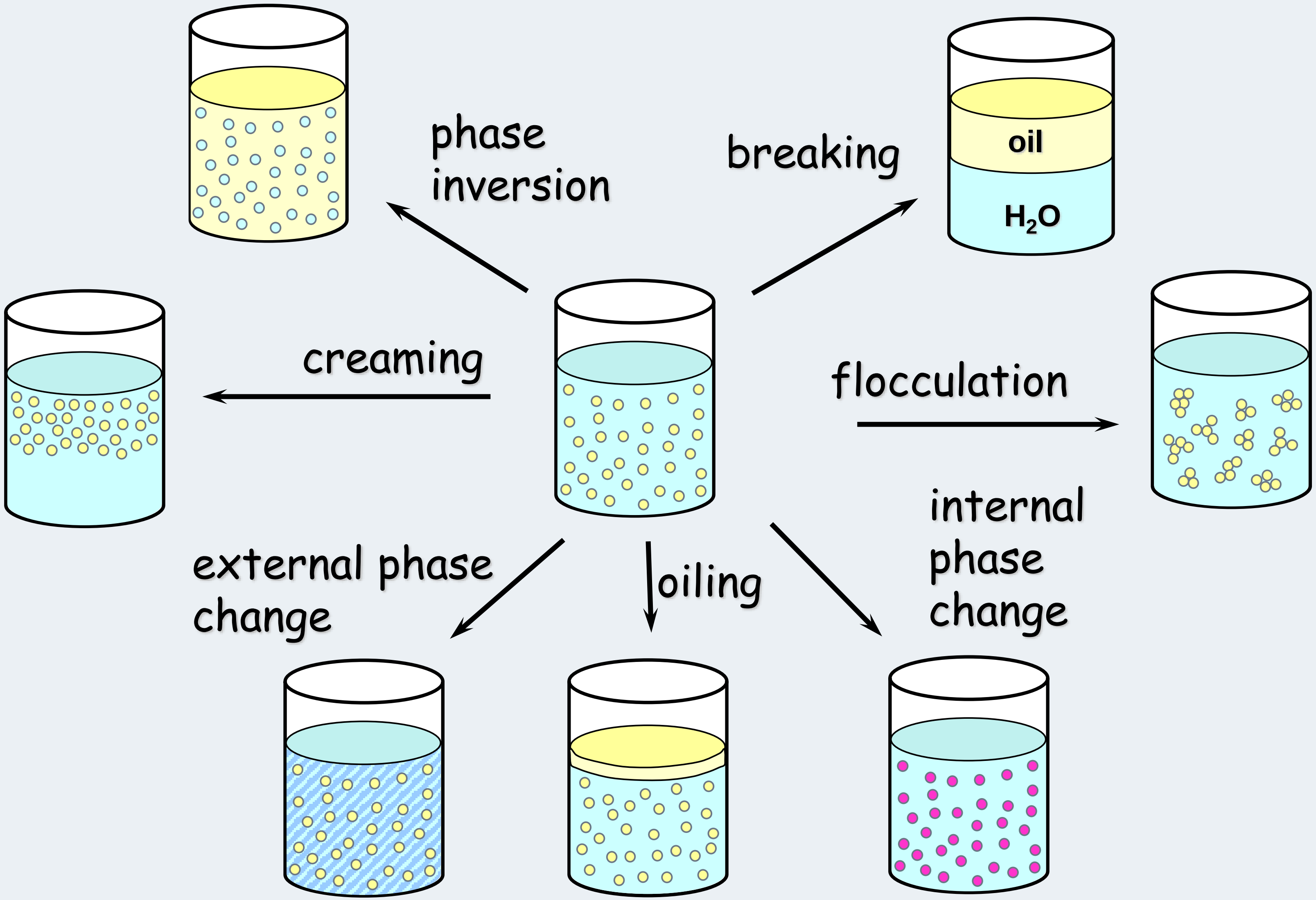
<u>Factors which influence emulsion stability</u>

- Type and level of emulsifier/surfactant/dispersant
- Particle size and distribution
- External destabilizing conditions (shear, freeze/thaw, temp.)
- Density difference and interfacial tension between the two phases
- Viscosity of external phase



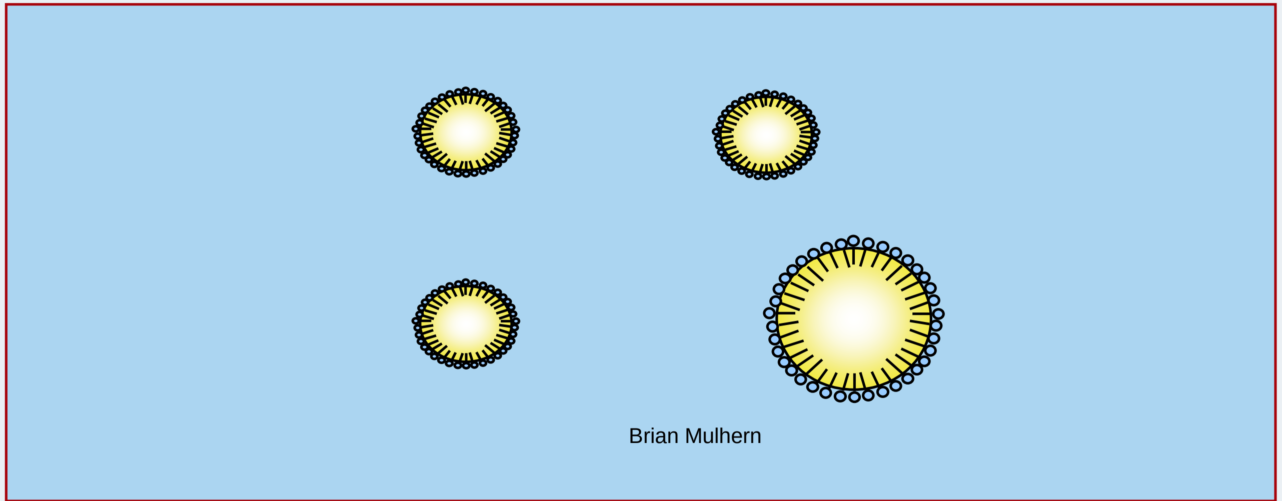
CHT
SMART CHEMISTRY
WITH CHARACTER.

The Many Faces of Instability



Particle Size Affects Emulsion Stability

- Emulsion particles are in constant motion thanks to Brownian Motion! These particles carry energy and constantly collide with one another.
- Each particle has a barrier, in the form of surfactant (ionic stabilization and steric stabilization), to prevent particles from coalescing as they collide.
- Larger particles carry more energy (momentum) than smaller particles. If sufficient momentum is achieved, it can penetrate the particles “barrier” thus beginning the process of flocculation/coalescence.
- Gravitational force also affects emulsions as the particles tend to segregate in emulsions this can be observed by creaming or settling.



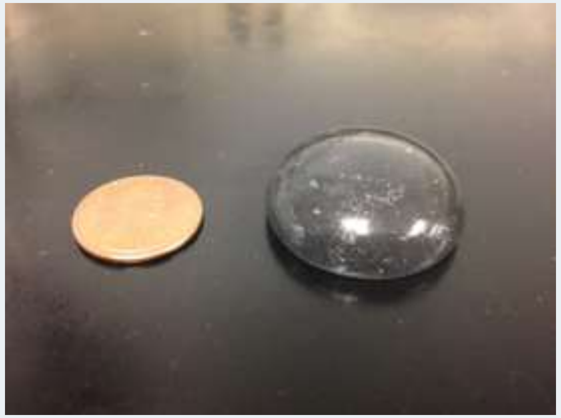
SMART CHEMISTRY WITH CHARACTER.

Particle Size Affects Rheology Properties

- Viscosity of dispersed phase has no influence of emulsion viscosity.
- Emulsion rheology depends upon how particles interact with each other.
- Higher solids content leads to higher viscosity emulsions. More particles are interacting with each other.
- Smaller particle sizes lead to higher viscosity emulsions. Higher surface area, lower volume
- Not only does the particle size dictate the rheology profile, but the particle size distribution also plays a large role.

SILICONE GUM

initial



1 hour

24 hours

- Silicone gum - High MW linear polydimethylsiloxane (PDMS) having a
  - Viscosity on the order of 20M cP (20K Pa-sec)
  - DP of about 3,500 and higher
  - Mn ~260,000
- Usually SiOH terminated, also Me3SiO- (methyl) and H2C=CH- (vinyl) groups
- Silicone gum emulsions for slip additives usually are made of SiOH terminated polymer.

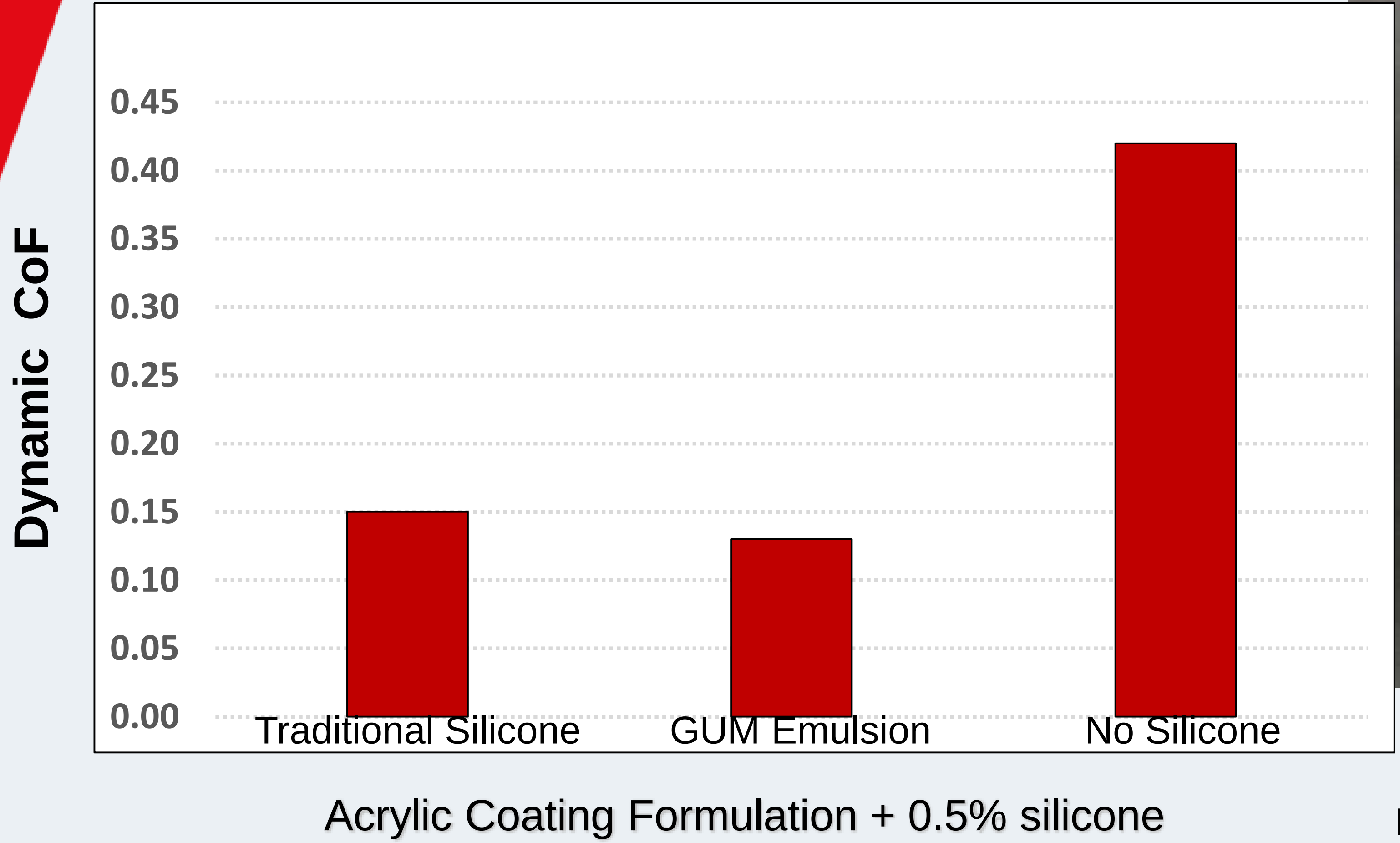
Brian Mulhern.

SILICONE GUM EMULSIONS

- Silicone gum emulsions find great utility as slip additives in coatings.
- Very high MW PDMS (eg- silicone gum) has become preferred slip additive in numerous coating applications.
  - Leather coatings – Also used to modify haptic properties including the hand (feel) of leather surfaces.
  - Printing Inks and overprint varnishes
  - Solvent resistance
  - Provide gloss
- Silicone gum emulsions provide block resistance to many coatings, including leather coatings, inks and overprint varnishes.
- Silicone gum emulsions are also used in specialized release applications.

CHT
SMART CHEMISTRY WITH CHARACTER.

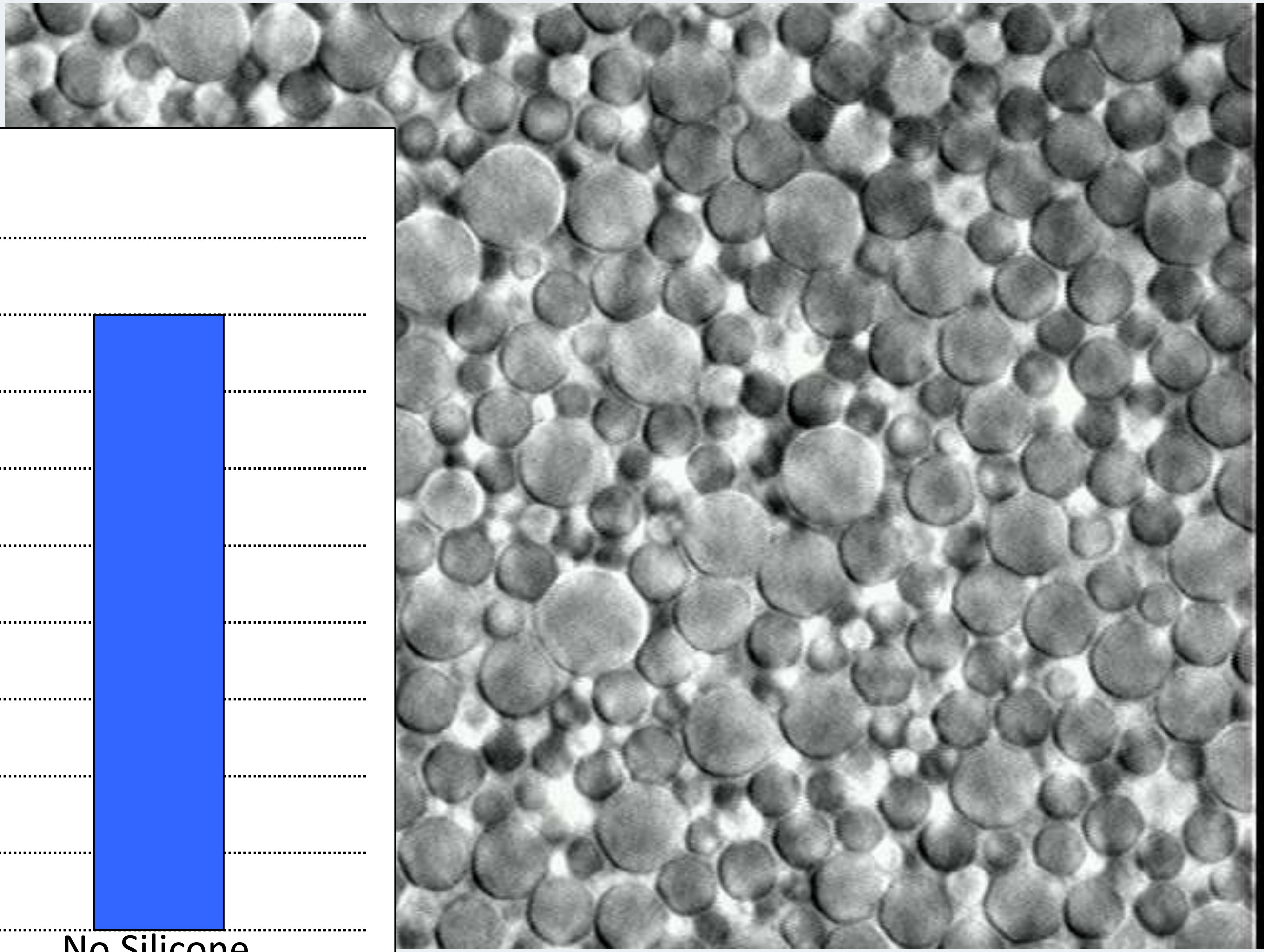
GUM EMULSION PERFORMANCE TESTING:
ACRYLIC COATING COEFFICIENT OF FRICTION

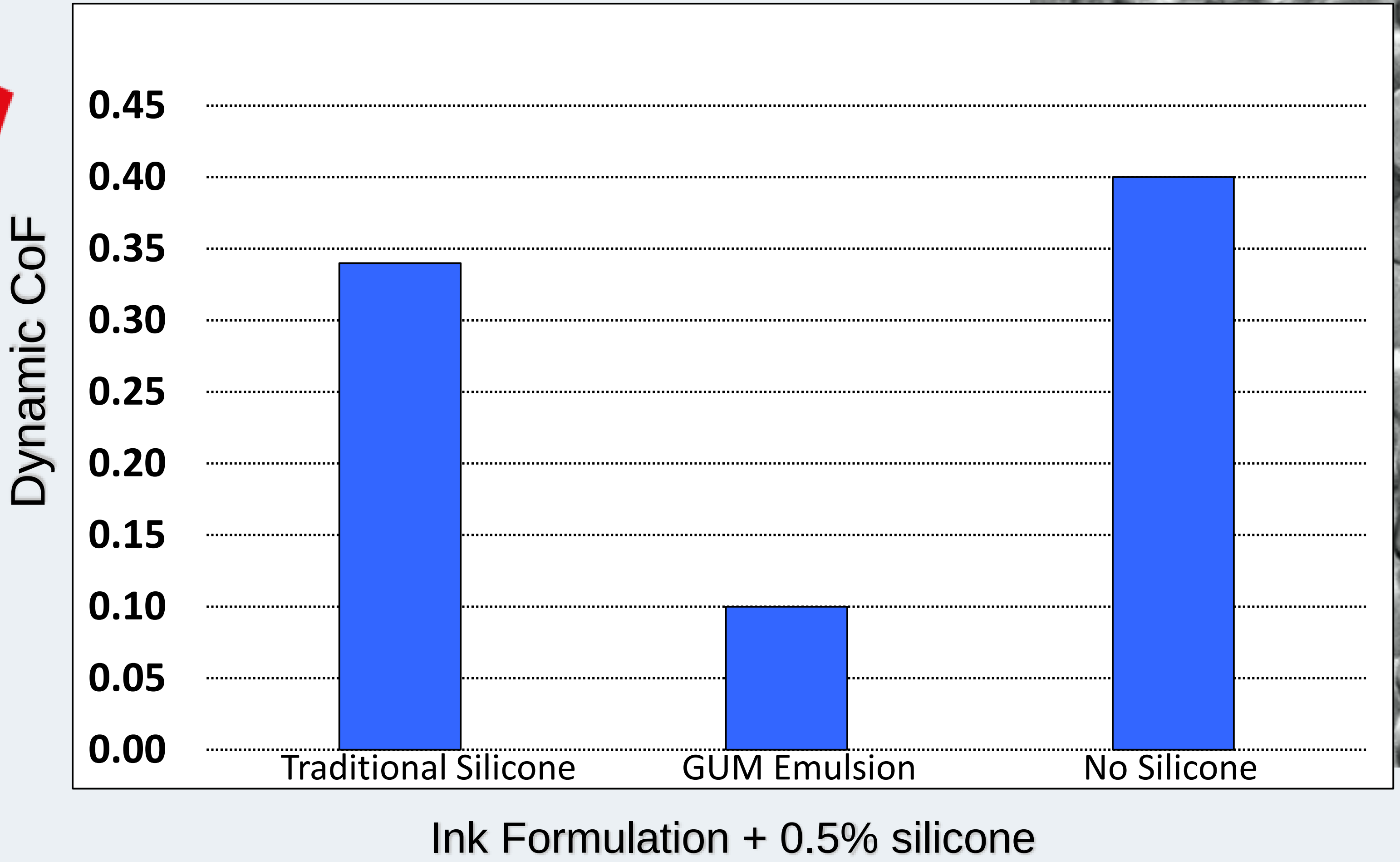


From US 8,877,293

CHT
SMART CHEMISTRY WITH CHARACTER.

GUM EMULSION PERFORMANCE TESTING: PRINTING INK COEFFICIENT OF FRICTION (COF)





From US 8,877,293

CHT
SMART CHEMISTRY WITH CHARACTER.

Brian Mulhern

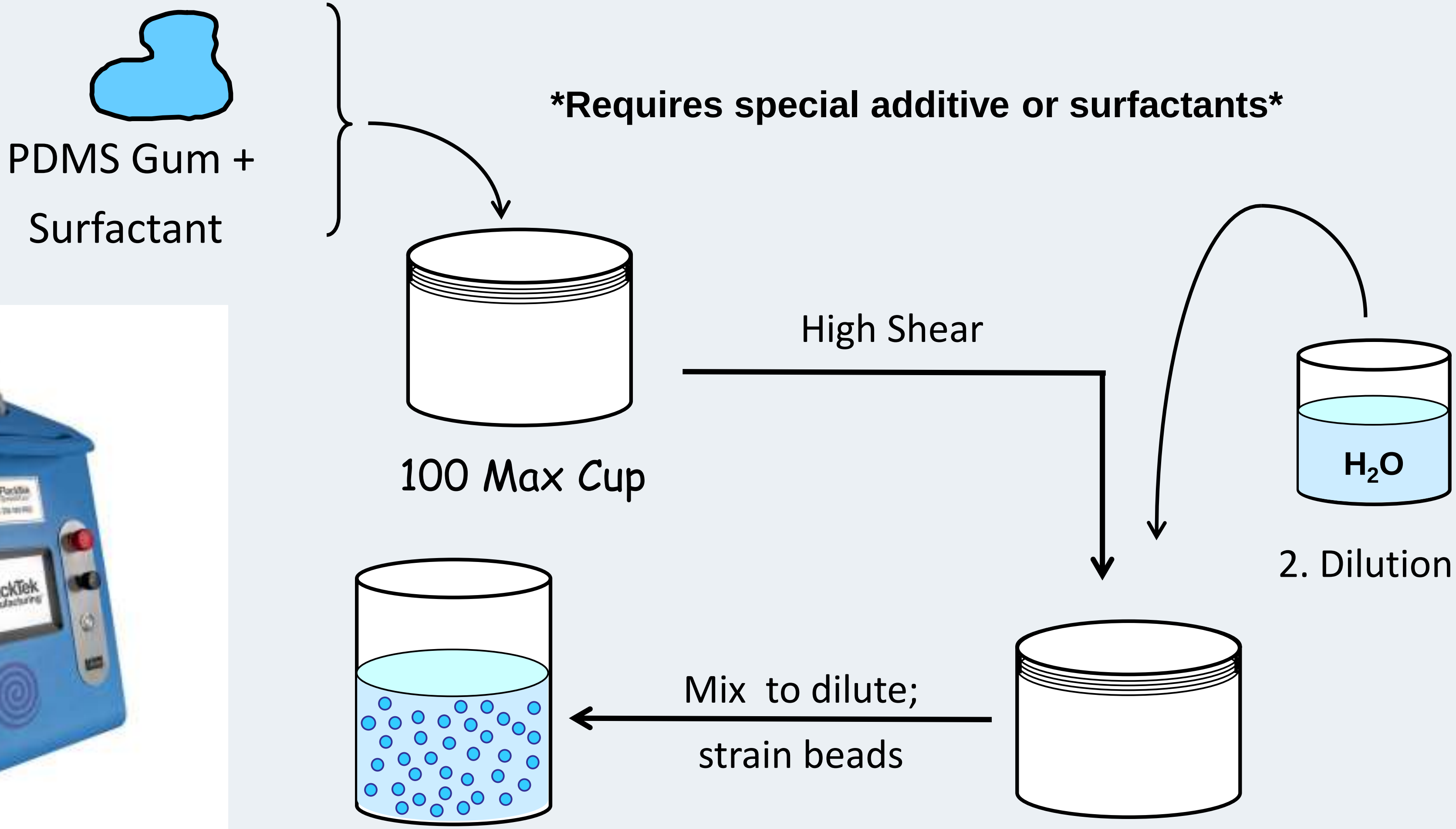
SILICONE GUM EMULSIONS

- Silicone gum is inherently difficult to emulsify due to the very high viscosity
- Silicone gum emulsification possible using specialized surfactants including certain SPE (silicone polyethers)
- Commercially available silicone gums emulsions typically contain cyclic silicones or organic solvents (can be bad for HS&E)
- Silicone gum preparation using EO/PO-based polymeric surfactants patented

CHT
SMART CHEMISTRY WITH CHARACTER.

GUM EMULSIONS HIGH SHEAR PROCESSING

From US 8,877,293



o/w emulsion: 50% gum,
~2-3µm particle size

Brian Mulhern

GUM EMULSION STABILITY

- Emulsion Stability - Important criterion for using a gum emulsion slip additive in a coating or ink.

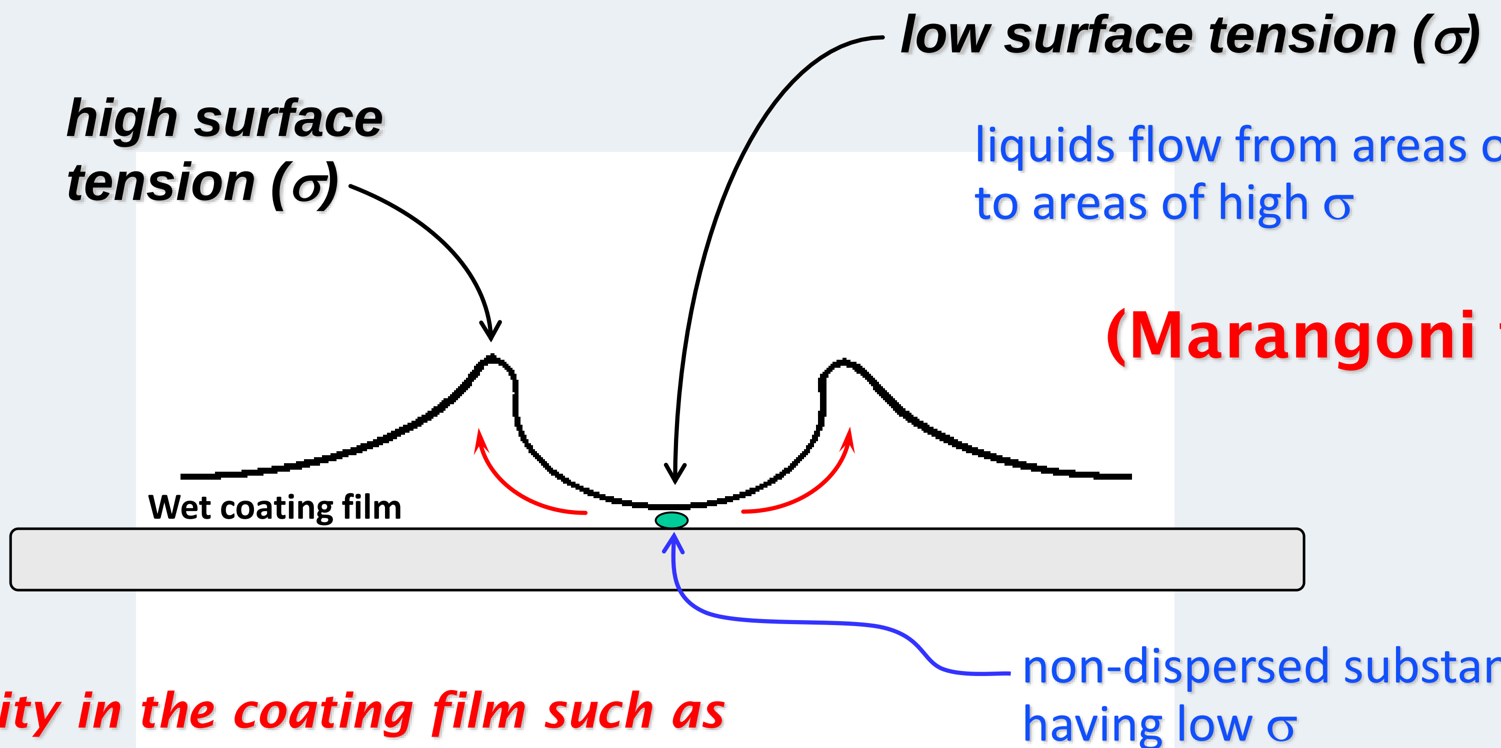
- Insufficient silicone gum emulsion stability causes:
  - Precipitation
  - Coagulation
  - Separation
  - Creaming
  - Sedimentation
  - Craters in their cured, dried coatings.

- Craters - Almost always caused by gum emulsion instability in the organic coating

- Emulsion stability is critical when incorporated into water-based organic formulas – often need additional hydrophilic process aid - may contain residual aromatic solvent (bad for HS&E)

CHT
SMART CHEMISTRY
WITH CHARACTER.

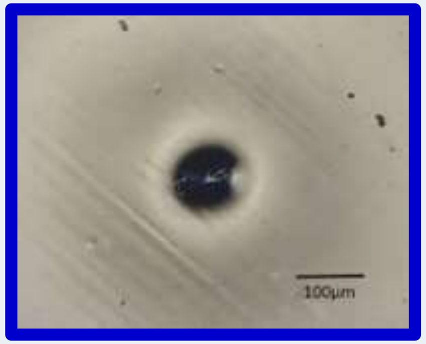
COATING DEFECTS: CRATERS



liquids flow from areas of low σ to areas of high σ

(Marangoni flow)

A low σ impurity in the coating film such as undispersed PDMS can cause a crater…



CHT
SMART CHEMISTRY WITH CHARACTER.

INDUSTRIAL ROUTES TO SILICONE GUM EMULSIONS

Methods for preparing silicone gum emulsions include the following:

1) **Mechanical emulsion of gum or gum dispersion**
    1) Produces emulsions that provide slip properties to coatings
    2) Requires a combination of decreasing gum viscosity, highly specialized additives, and highly specialized equipment
    3) Performance is generally lower than that of neat gum emulsions due to diluents/additives
    4) Solvents not good for HS&E
2) **In-situ emulsion polymerization** of reactive siloxanes
    1) Produces emulsions of polymers having viscosities comparable to silicone gum emulsions
    2) Excellent slip properties (low CoF, abrasion resistance, anti mar, anti blocking)

CHT patented mechanical emulsification method for using an aminofunctional siloxane as a process aid:

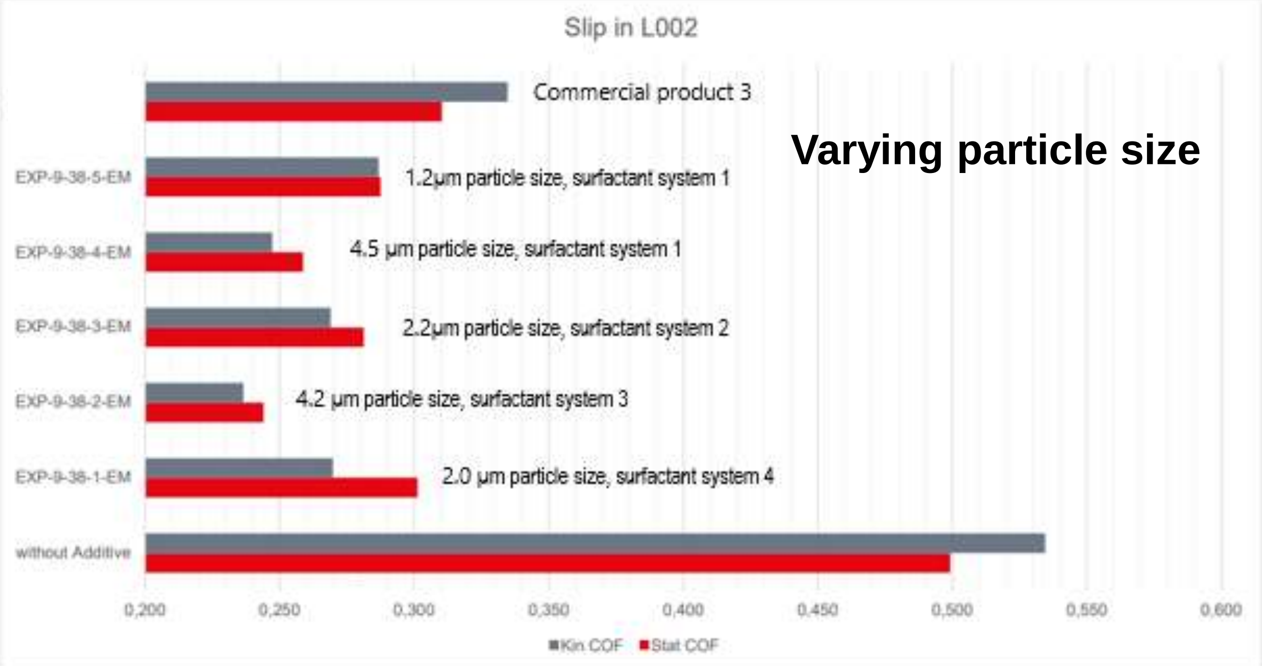
Reduced cyclic silicone content

No residual aromatic solvent

Surfactants non-hazardous

GUM EMULSIONS – SLIP TESTING

Results

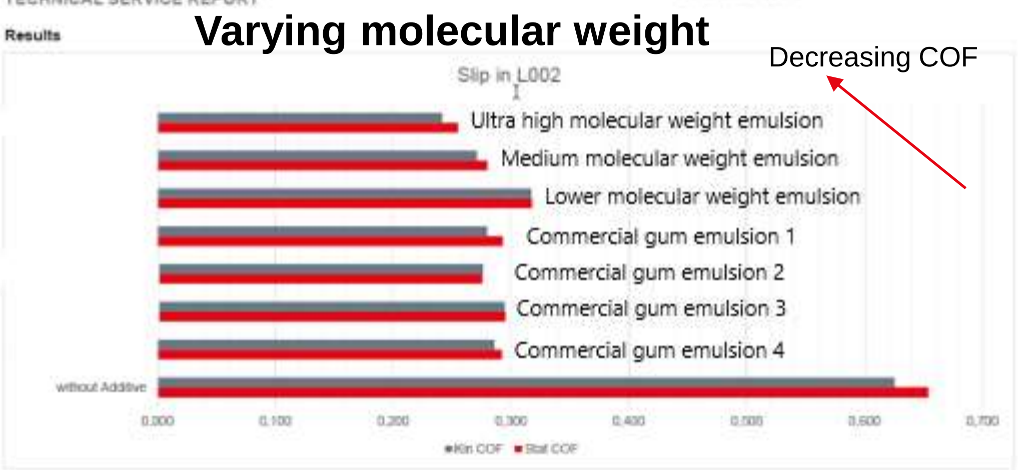


As shown above all of the tested samples improved the slip. EXP-9-38-2-EM and EXP-9-38-4-EM showed the best results.

S-2201259
TECHNICAL SERVICE REPORT

BF Construction & Assembly
BU Graphic Arts

Results



As shown above all of the tested samples are very similar in their performace and were able to reduce the slip by half, but EXP-8-25-1-EM had a slightly higher result and EXP-8-25-3-EM had a slightly lower result than the rest of the tested samples.
The overall comparability is very good.

Slip is dependent on:

- **Molecular weight**
- **Particle size**
- **Surfactant system**

CHT
SMART CHEMISTRY
WITH CHARACTER.

SUMMARY

- Silicone gum and silicone gum emulsions provide slip, block resistance, haptic properties and release advantages in coatings and inks.
- Silicone gum emulsion stability is critical for desired coating performance and appearance
- New technology provides a pathway to make food compliant silicone gum emulsion coating additives
- Gum emulsions can be tailored for the application through surfactant selection, particle size, and moleculare weight of the polymer
- In-situ polymerization – low cyclic content, no diluents or organic solvents, can be FDA compliant
- Amino functional silicone processing aid – emulsion stability, no residual solvents, can be FDA compliant

Water-Borne
Food Compliant
High Performance
Coatings & Inks

Thanks!

Acknowledgement / Scientists

Dr. Robert Graff

Donald T. Liles

Dr. Alice Hirt

Dr. Pete LeBaron

Dr. Bruce Berglund

Brian Mulhern
Senior Research and Development Chemist - Cassopolis
Research & Development

P +1(269) 445-0847 ex 265
E brian.mulhern@cht.com

CHT USA Inc. | USA
805 Wolfe Avenue | Cassopolis, MI 49031
www.cht.com | www.cht-silicones.com