# Super Dispersible Pigment Treatment for Applications in Multimedia

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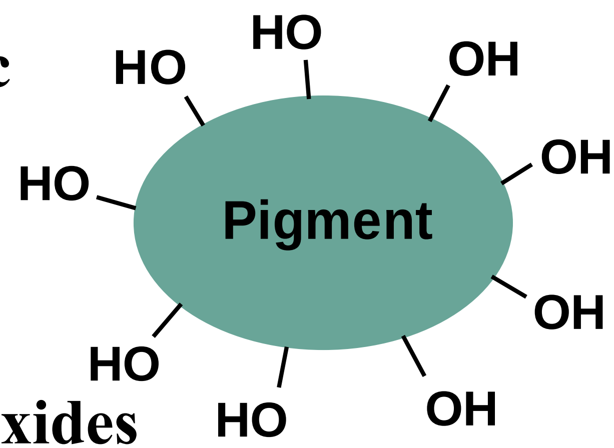
# Outline

1. Common surface treatments and their properties
2. Design and formation of superdisperible surface treatment
3. Evaluation of stability of surface treatment
4. Evaluation of dispersibility
5. Conclusions

# 1. Surface Treatment

- **Modifies pigment surface to hydrophobic and/or lipophilic**
- **Improve the skin feel**
- **Improve the chemical stability of metal oxides**
- **Improves pigment wetting and size reduction during dispersion process**
- **Improved dispersion stability and formula stability**

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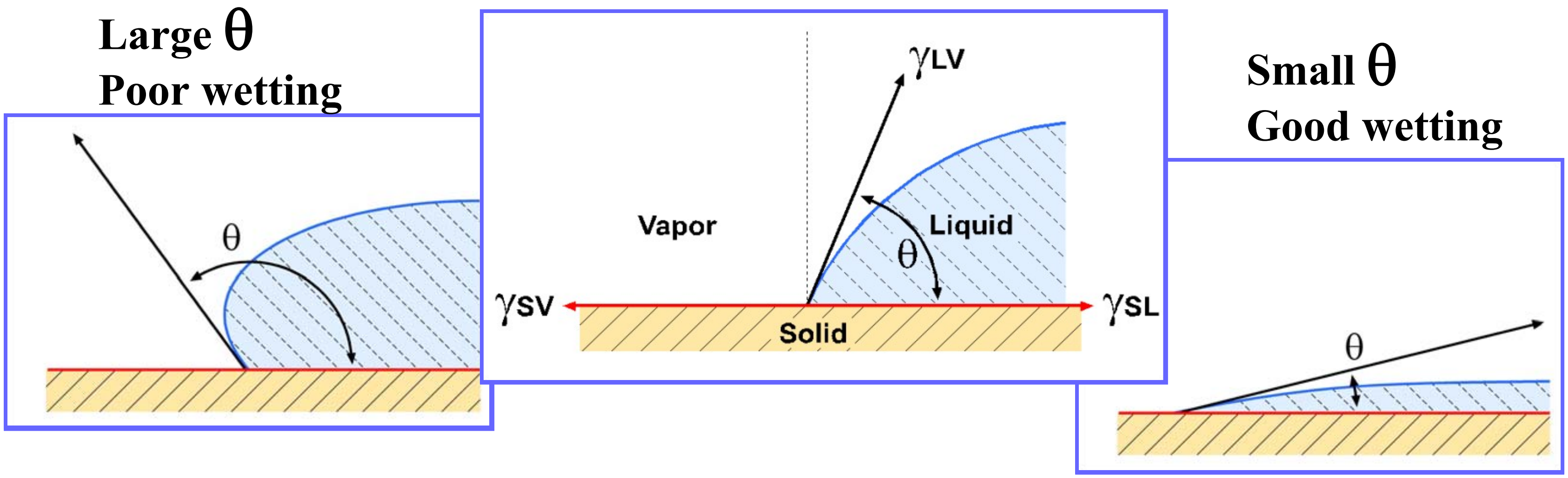
# Popular Treatments & Their Drawbacks

| | Coating | Pros | Cons |
|---|---|---|---|
| Hydrophobic | Methicone | Hydrophobic | $H_2$ potential<br>Disperses poorly in esters |
| | Dimethicone | Nice feel<br>No $H_2$ potential | Not as stable at low pH<br>Disperses poorly in esters |
| | Alkoxysilane | No $H_2$ potential<br>Hydrophobic | Reacts too slowly<br>Dispersibility in esters is fair |
| | ITT / Metal soap | Lipophilic<br>Easy to react with pigments | Not very hydrophobic,<br>especially at low pH |
| | Perfluorinated compounds | Repel both water and oil | Difficult to wet |
| Hydrophilic | Polysaccharide | Natural product | No chemical bonding |
| | Synthetic surfactant | Highly dispersible | No chemical bonding |

# Wetting & Penetration




## Wetting

Young-Dupre Equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta$$

γ: interfacial tension
θ: Contact angle

## Penetration

The driving force for the capillary action

$$\text{Force} = 2\pi r \gamma_{LV}\cos\theta$$

r = radius of the crack opening

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# Wetting & Penetration

## Theory :

- Surface tension is a result of difference in surface energy
- Liquid of lower surface energy can wet surface of higher energy and show a smaller contact angle
- Smaller contact angle generates a higher driving force for penetration

## Practice:

- Increase the surface energy of coating without loss of hydrophobicity

# Surface Energy of Common Coatings & Liquids

| Coatings | Surface Energy (dyne/cm$^2$) |
|---|---|
| Perfluorinated compounds | 18 – 20 |
| Dimethicone | 20 –24 |
| Methicone | - |
| Alkoxysilane | - |
| Wax (polyethylene) | 30 - 31 |
| Metal Soap/Organic Titanate | 30 - 35 |

| Liquids | Surface Energy (dyne/cm$^2$) |
|---|---|
| Water | 72.8 |
| Castor oil | 39 |
| Olive oil | 35.8 |
| Liquid petrolatum | 33.1 |
| Capric caprylic triglyceride | 30 |
| Mineral oil | 30 - 35 |
| Dimethicone | 20 –24 |
| Perfluorinated liquid | 16 – 20 |
| Cyclomethicone | 17.8 ( @25°C) |

(All measured @ 20 $^{o}$C)

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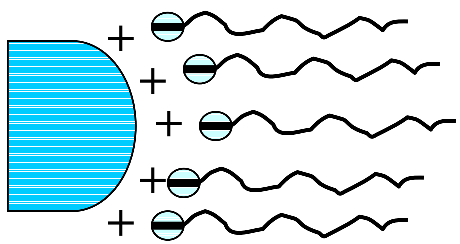
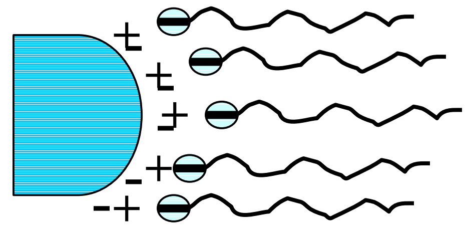
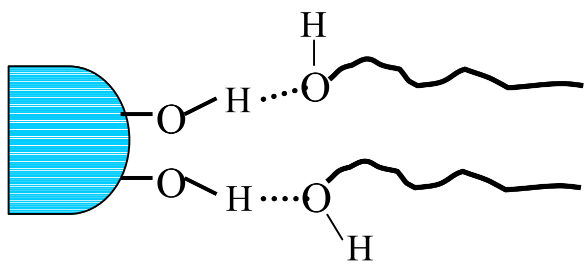
# Act of Dispersants

## *Anchoring Through Ionic or Acidic/Basic Groups.*

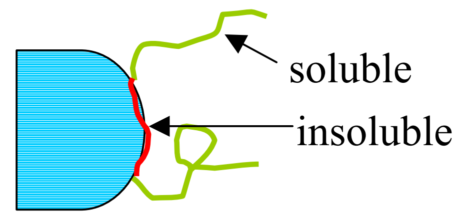




### *Anchoring Through Hydrogen-Bonding Groups.*




### **Anchoring Through Solvent-Insoluble Polymer Blocks.**




**Result: reduced inter-particulate attraction for aggregation**

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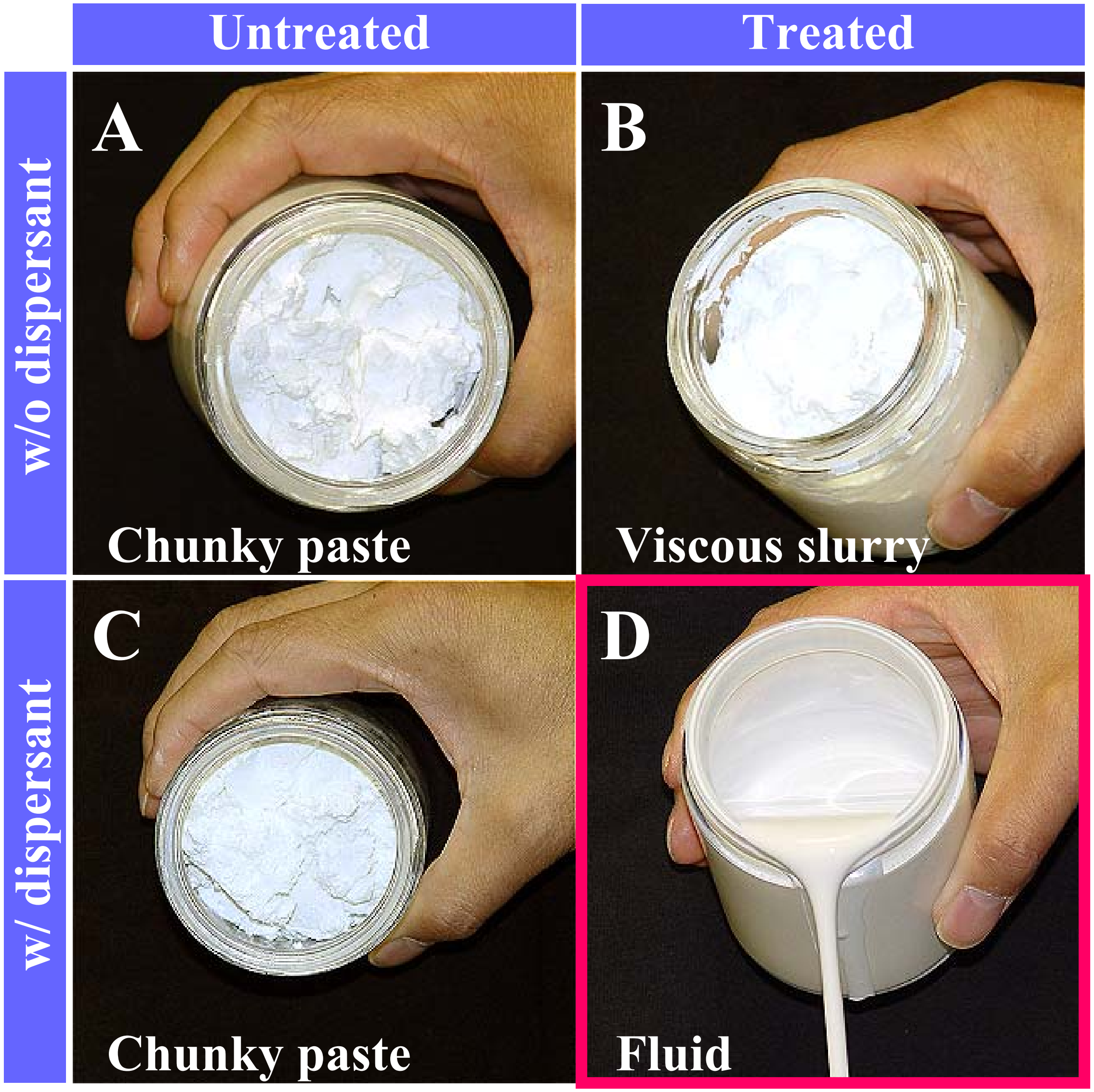
# Pigment Dispersion Examples




15nm $TiO_2$ : 45% *
Treatment : Methicone (B & D)
Vehicle : Cyclopentasiloxane
Dispersant : 10 % KF-6017 (C & D)

* note : in mix A, only 33% $TiO_2$ was used (maximum amount possible)

**Easy handling**
**Better dispersion**

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# Design of Superdispersible Surface Treatment

## 1. Modify surface energy

Isopropyl titanium triisostearate (ITT) + { **Alkoxysilane**, **Methicone**, **Dimethicone** } → **Crosslinked coating on pigment**

**** US Provisional patent application No. 60/472,527***

## 2. Minimize the interaction among particulates

**Coating + Dispersant as secondary coating**

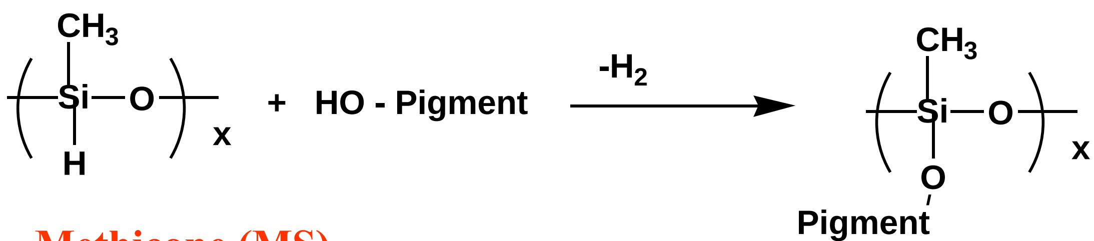
# Chemical Reactions During Surface Treatment

$$(C_{17}H_{35}OCO)_3\text{-Ti-}OC_3H_7 + HO\text{ - Pigment} \xrightarrow{-\ C_3H_7OH} C_{17}H_{35}OCO\text{-Ti-O - Pigment}$$

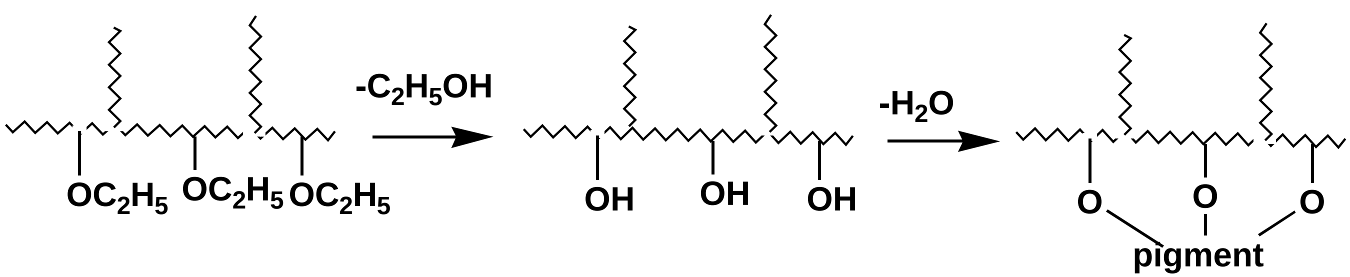
**ITT**

$$C_8H_{17}\text{- Si }(OC_2H_5)_3 \xrightarrow{-\ C_2H_5OH} C_8H_{17}\text{-Si-}(OH)_3 + HO\text{ - Pigment} \xrightarrow{-H_2O} (C_8H_{17}\text{-Si-}O_3)x\text{ - Pigment}$$

**Triethoxy caprylylsilane (TCS)**




**Methicone (MS)**




**Triethoxysilylethyl polydimethylsiloxyethyl dimethicone (TPDM)**

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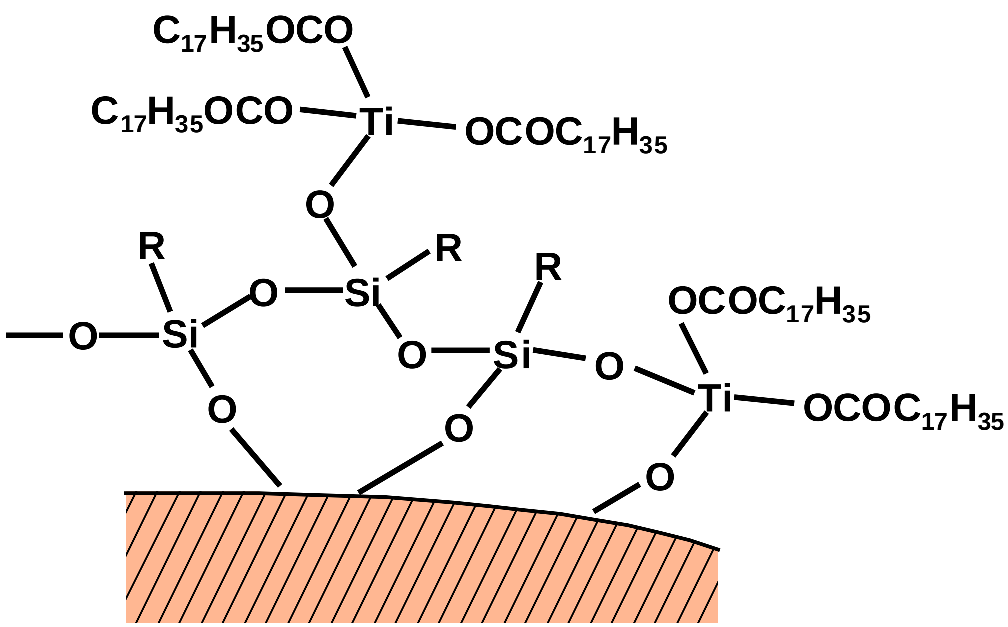
# Crosspolymer Treatment - Structure




*ITT/TCS Crosspolymer: R = $C_8H_{17}$*

*ITT/Methicone Copolymer: R = $CH_3$*

**Crosslinked, 3-dimensional web-like structure**

R = $C_8H_{15}$, ITT/TCS (TTS)

R = $CH_3$, ITT/Methicone (TTM)

R = [ $Si(CH_3)_2O$]x, ITT/TPDM (TTDM)

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# Catalytic Effect of Titanate on Silicone Reactions

**Hydrophobicity of treated 10 nm $TiO_2$**


7% 7% 3.5% of each

***2 g of Treated Pigment in 50 mL Water***
***Shaken 10 times - Picture taken after 10 minutes***

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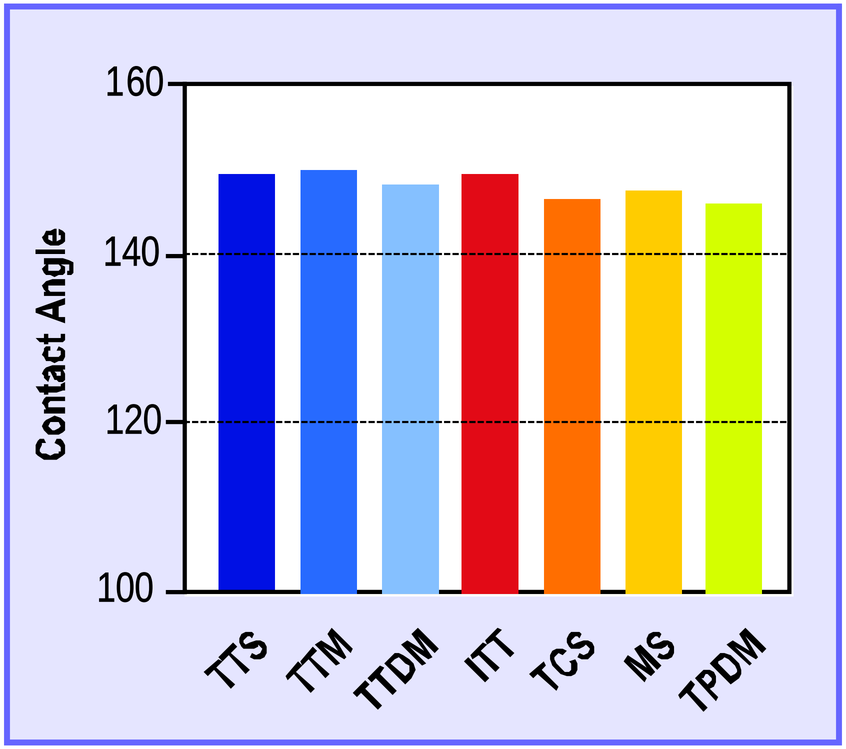
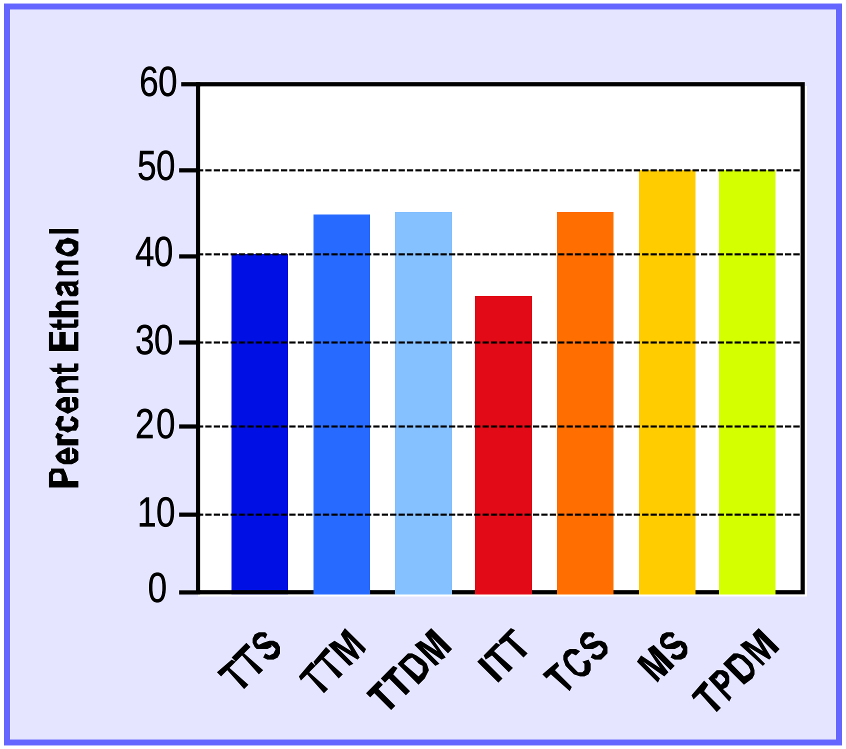
# Hydrophobicity of Crosspolymer Treatment

## Contact angle of Various Surface Treatments




## Hydrophobicity of Various Surface Treatments

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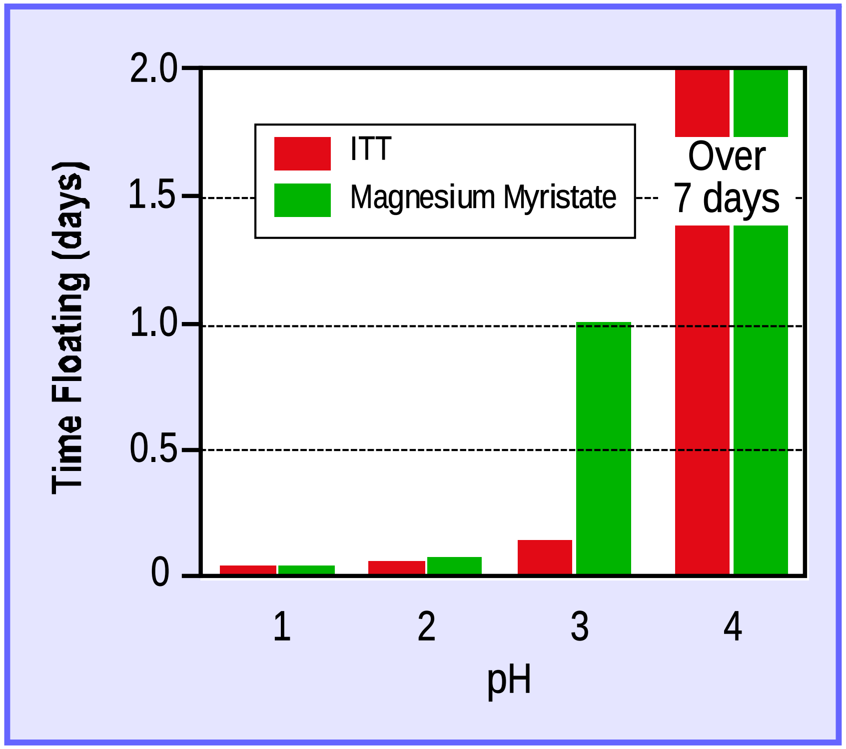
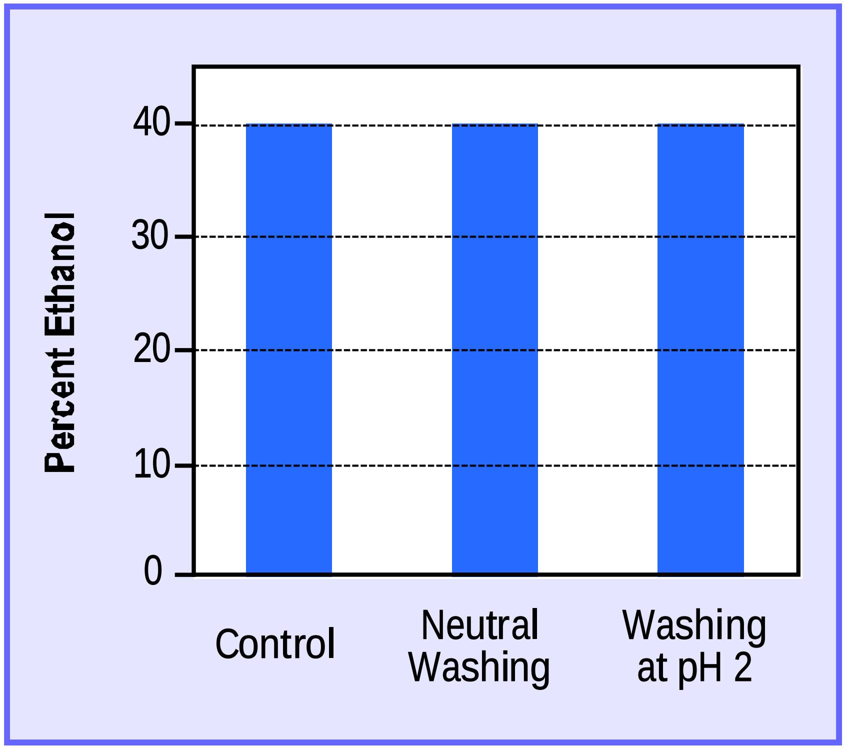
# Stability of TTS Treatment Toward Acid

## Hydrophobicity by Floating Test

### Metal Soap / ITT




### TTS Crosspolymer




**TTS coated pigment floats almost indefinitely at pH 2**

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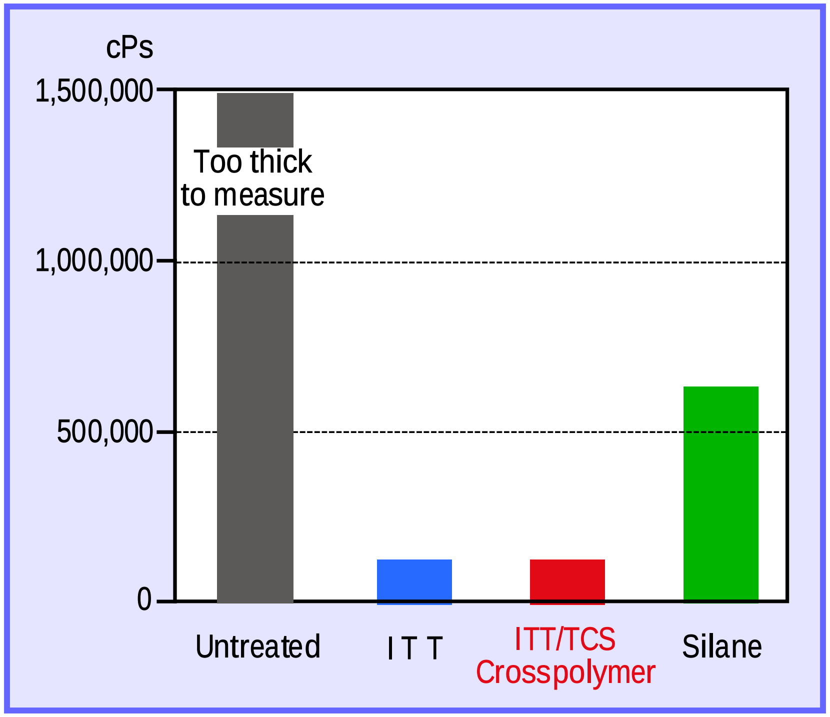
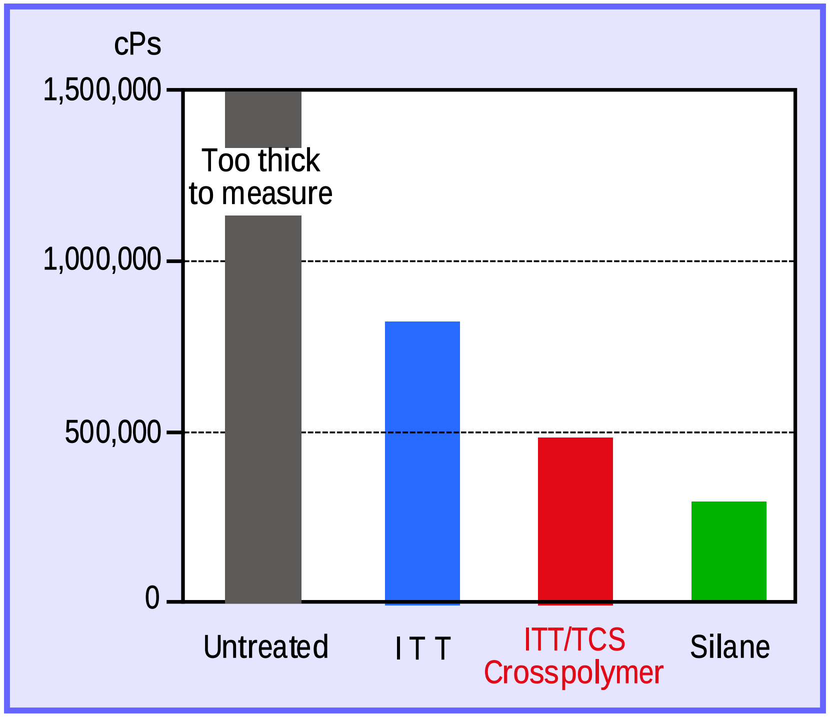
# ITT/TCS (TTS) Crosspolymer Treatment

## Viscosity of Iron Oxide Dispersions

### 75% in Mineral Oil




### 73% in Cyclopentasiloxane

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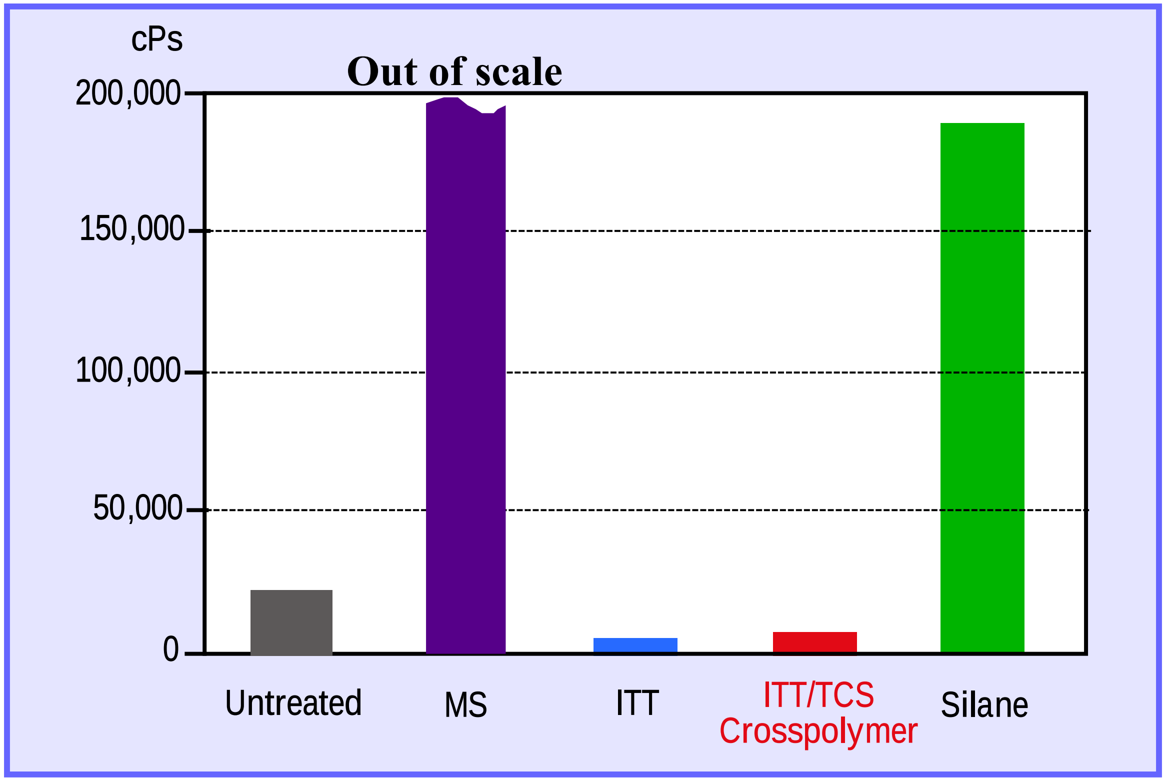
# TTS Crosspolymer in C12-15 Alkyl Benzoate

## Viscosity of 75% Rutile $TiO_2$ Dispersions




*** Dispersant: 1.5 %of polyhydroxystearic acid**

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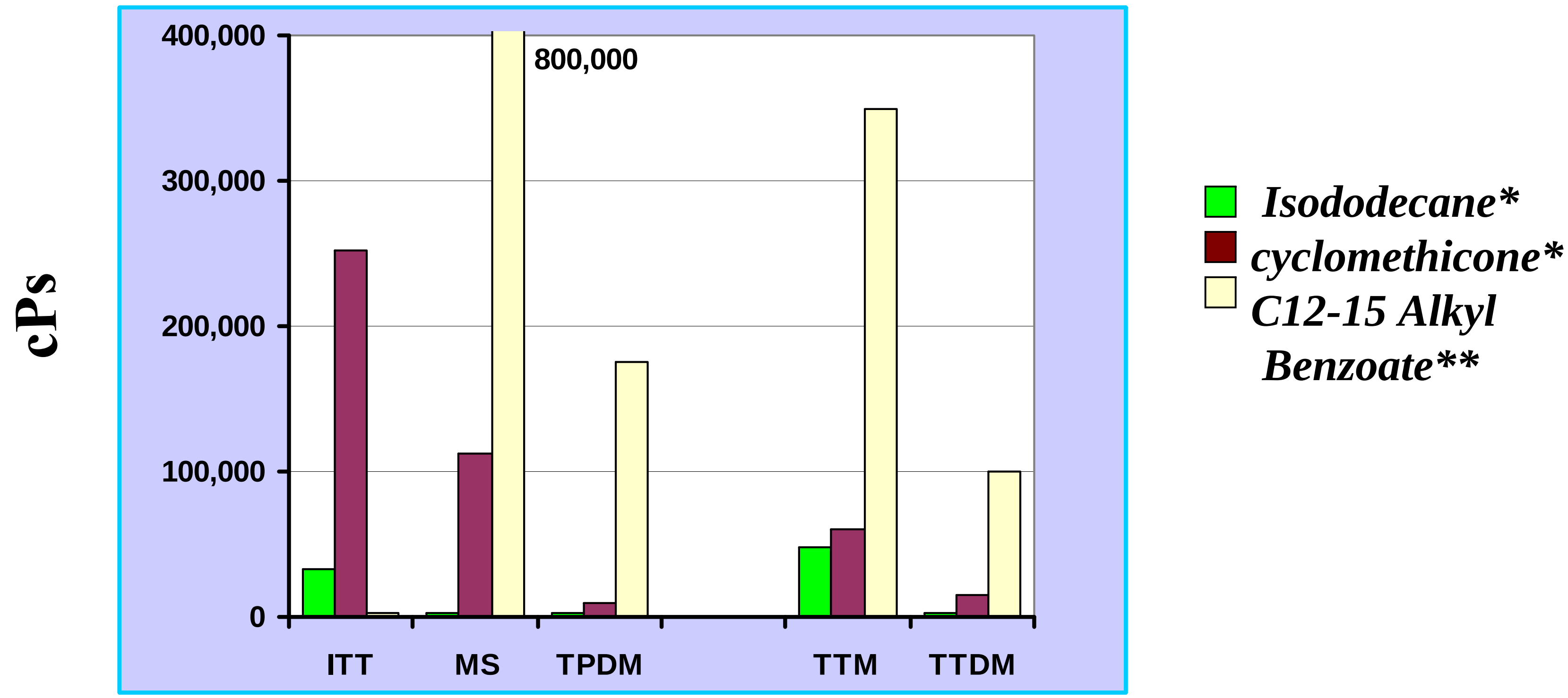
# TTM & TTDM Crosspolymer Treatments

## Viscosity of 75% Anatase $TiO_2$ Dispersions




**   w/ 2.5% of PEG/PPG-20/15 dimethicone*
*** w/ 1.5% of polyhydroxystearic acid*

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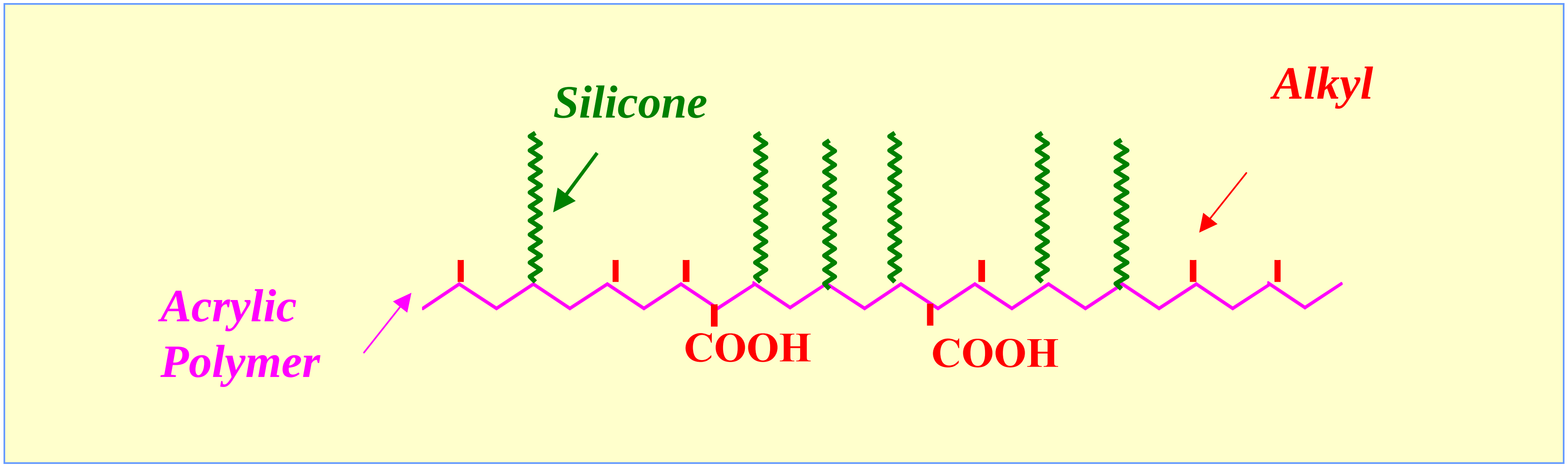
# Use of Dispersant as Auxiliary Coating




• INCI: Acrylates/Ethylhexyl Acrylate/Dimethicone Methylacrylate Copolymer

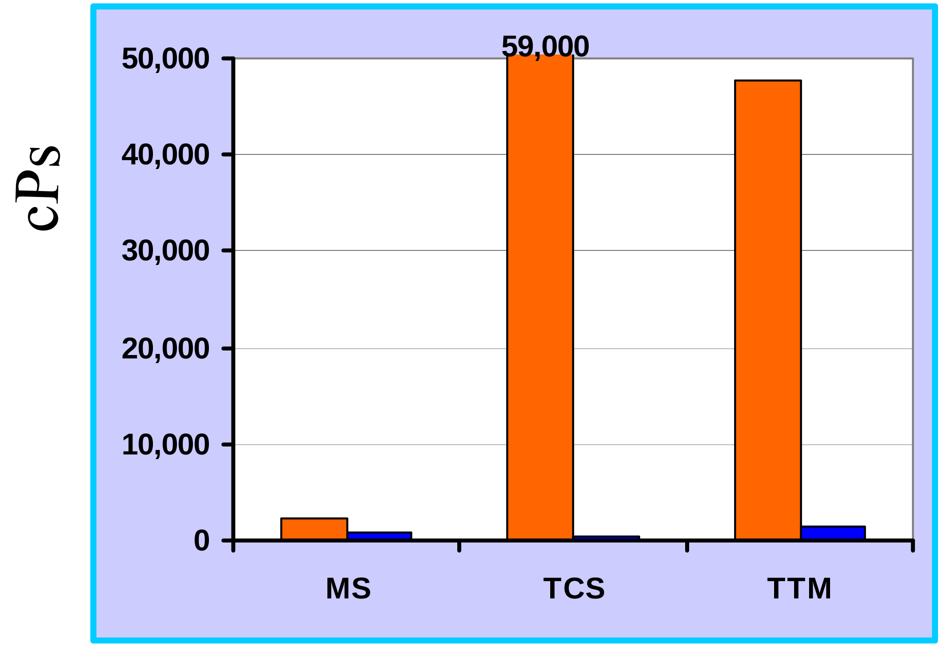
• Designed for dispersing pigment primarily in cyclomethicones

# Effect of Acrylate/Silicone Copolymer on Dispersibility

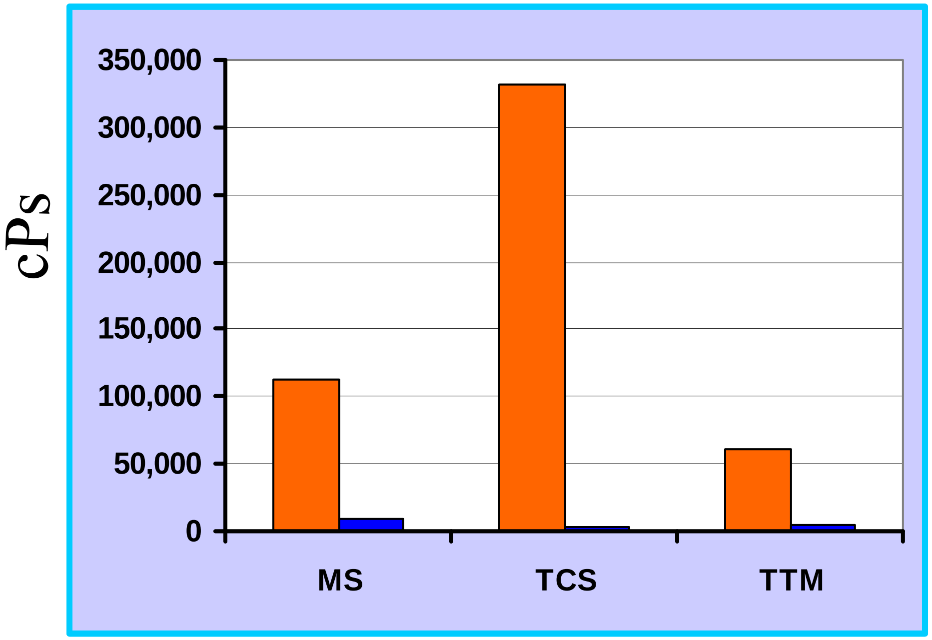
Viscosity of 75% $TiO_2$ Dispersion

***( 2.5% of PEG/PPG-20/15 Dimethicone)***

in Isododecane




in Cyclopentasiloxane




**0 %** **3% of Acrylate/Silicone Copolymer**

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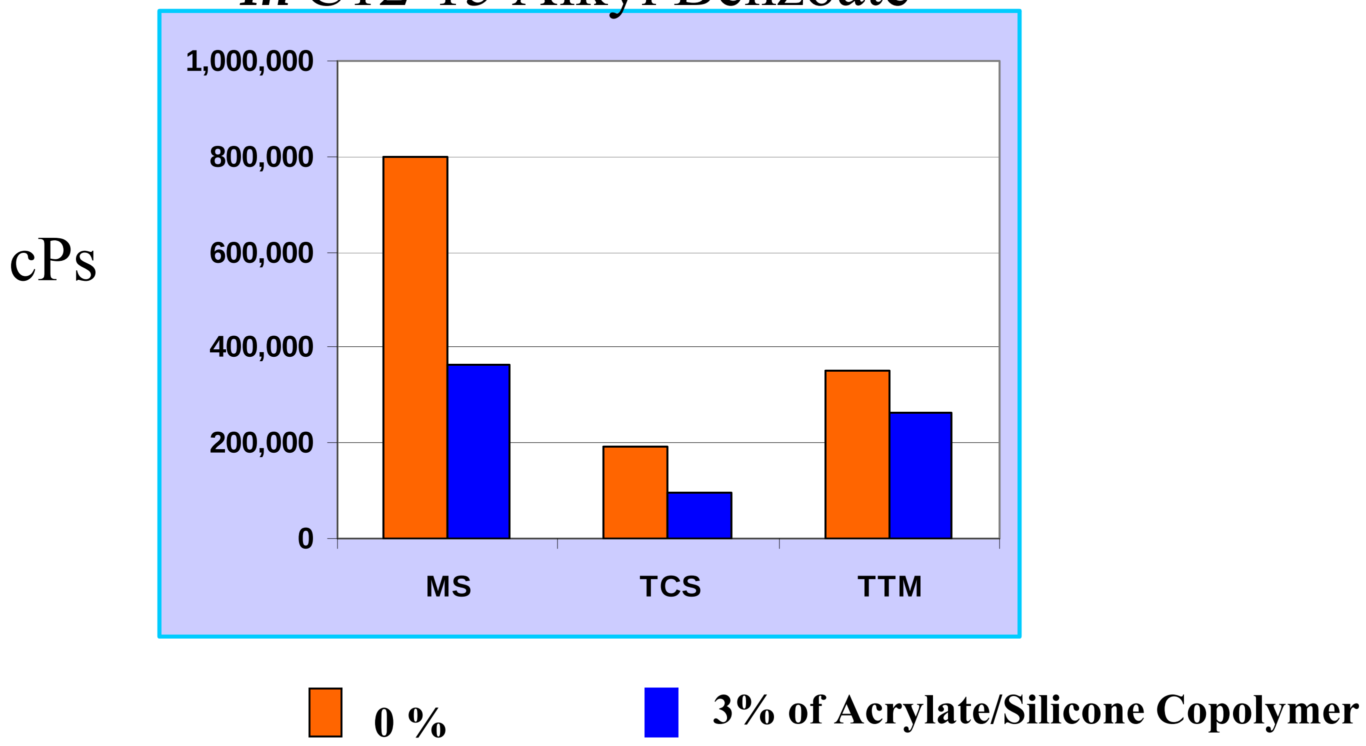
# Effect of Acrylate/Silicone Copolymer on Dispersibility

Viscosity of 75% $TiO_2$ Dispersion
***(With 1.5% of polyhydroxystearic acid)***

***In*** C12-15 Alkyl Benzoate

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# Conclusions

- **The use of hybrid or composite materials to treat pigments can enhance their chemical stability and wetting by multimedia.**
- **Organo titanates and dimethicone crosspolymer treatment was found to be super dispersible in hydrocarbon, cyclomethicone and ester.**
- **When used as auxiliary coating, proper dispersant can greatly improve the dispersibility of treated pigments. Acrylate / Silicone copolymer was found to be very effective for dispersing pigments in hydrocarbon and cyclomethicone.**
- **Hybrid compounds offer more benefits and will be the future for pigment surface modification.**

# Acknowledgements


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