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SURFACE TREATMENTS TO IMPROVE PIGMENT DISPERSION IN AQUEOUS MEDIA

Jane Hollenberg, Yun mi Kim, Ph.D., Youlin Pan, Ph.D., and Barry Arkles, Ph.D.

Gelest, Inc., Morrisville, PA

OBJECTIVE

Study of hydrophilic silanes as a means to improve pigment wetting and dispersion in water based color cosmetics. Correlation of methodology to measure performance.

MATERIALS AND METHODS

Silanes: Triethoxysilanes having the following hydrophilic "R" groups: $PEG_{6\text{-}9}$, carboxyl, aminopropyl, and acetyl hydroxyprolyl were synthesized.

Pigments treated : Titanium Dioxide (anatase), Red Iron Oxide, Yellow Iron Oxide, Black Iron Oxide

Tests performed:

Aqueous dispersion (visual): 0.3 grams of pigment was added to 15 ml deionized water. Behavior was observed without stirring.

Sedimentation: Ultrasound used to disperse treated pigments in water. 10 ml aliquots were introduced into graduated cylinders, sealed and allowed to stand for one month. Sediment density (mg/ml was measured)

Dispersion viscosity (Butylene Glycol): Dispersions of the pigments were prepared by wetting in butylene glycol with stirring for one hour, followed by three passes over a three roll mill. Viscosity was measured using a Brookfield viscometer, standard spindles @ 20 RPM.

Formulation: Anionic oil in water emulsion concealer containing 20% pigment: Parameters observed were: ease of pigment wetting, presence or absence of color flotation during processing and in final product, pigment dispersion.

RESULTS

Visual Evaluation

	Yellow Iron Oxide	Red Iron Oxide	Black Iron Oxide	Titanium Dioxide
control (untreated)	wets, falls to bottom	wets, falls to bottom	wets, falls to bottom	wets, falls to bottom
$PEG_{6\text{-}9}$ Silane	self disperses	self disperses	dispersion, settles	self disperses
Aminopropyl Silane	wets slowly, disperses	disperses 50%	sl dispersion; settles	wets slowly; sl dispersion
Na Carboxyethylsilanetriol	self disperses	self disperses	dispersion; settles	self disperses
Acetyl Hydroxyprolyl Silane	self disperses	self disperses	sl dispersion; settles	self disperses

.All of the pigments with hydrophilic modification deagglomerate and disperse without stirring to some extent. $PEG_{6\text{-}9}$ Silane and Sodium Carboxyethylsilanetriol treated pigments dispersed completely, some particles remaining in suspension for over one month.

Sedimentation

Sedimentation study is another means to compare multiple surface treatments in a vehicle. Sediment volume is affected by dielectric/wetting characteristics of the vehicle and the presence or absence of surface treatment . Relative changes in performance among surface treatments and levels of treatment can be quantified. Higher sediment volume is due to flocculation, indicating poor wetting and dispersion, whereas low sediment volume is the result of deflocculation in a system having good particle wetting.

Sediment Density (g/ml)

	Pigment			
Treatment	Yellow Iron Oxide	Red Iron Oxide	Black Iron Oxide	Titanium Dioxide
control (untreated)	0.11	0.42	0.38	1.00
$PEG_{6\text{-}9}$ Silane	dense, incomplete	dense, incomplete	0.63	0.45
Aminopropyl Silane	0.21	0.83	0.40	0.37
Na Carboxyethylsilanetriol	1.25	2.00	0.83	1.25
Acetyl Hydroxyprolyl Silane	0.33	1.00	0.56	0.48

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All of the hydrophilic treatments deflocculate the iron oxides. Once dispersed by ultrasound, the untreated titanium dioxide wets well. Only Sodium Carboxyethylsilanetriol treatment further reduces the sediment volume.

Dispersion Viscosity

Multiple surface treatments can be evaluated on a given pigment substrate by preparing pigment grinds. Lower viscosity at equal concentration and degree of dispersion (particle size) indicates better wetting.

Dispersion Viscosity (cps)

	Pigment , % in Butylene Glycol			
Treatment	Yellow Iron Oxide 45%	Red Iron Oxide 50%	Black Iron Oxide 50%	Titanium Dioxide 50%
control (untreated)	73,400 cps (spindle #7)	24,500 cps (spindle #6)	10,950 cps (spindle #6)	11,150 cps (spindle #6)
$PEG_{6\text{-}9}$ Silane	1,610 cps (spindle #3)	2,100 cps (spindle #4)	3,970 cps (spindle #4)	12,150 cps (spindle #6)
Aminopropyl Silane	675 cps (spindle #3)	4,100 cps (spindle #4)	9,000 cps (spindle #4,5)	4,700 cps (spindle #4)
Na Carboxyethyl-silanetriol	540 cps (spindle #3)	2,690 cps (spindle #4)	6,500 cps (spindle #4,5)	415 cps (spindle #3)
Acetyl Hydroxy-prolyl Silane	520 cps (spindle #3)	3,120 cps (spindle #4)	5,940 cps (spindle #4,5)	2,870 cps) (spindle #3)

All of the hydrophilic treatments pigments improved wetting and dispersion in butylene glycol, except, surprisingly, $PEG_{6\text{-}9}$ Silane on titanium dioxide. Comparison of the silane treatments showed the dispersions of carboxylated silane treated pigments have the smaller agglomerate size and higher degree of color development.

Formulation

o/w concealer

	Parameter			
Treatment	Dispersion	Color development (1 is lowest)	Wetting	Flotation
control (untreated)	undispersed pigment	1	slow	white
$PEG_{6\text{-}9}$ Silane	complete	4	rapid	white/yellow/black
Aminopropyl Silane	undispersed TiO_2	2	slow	white
Na Carboxyethylsilanetriol	complete	5	rapid	yellow > 60°C
Acetyl Hydroxyprolyl Silane	complete	3	intermediate	none

DISCUSSION

Deposition of the polar compounds alone on the pigment surfaces did not produce the instant dispersion effect that results from surface treatment with silanes having the polar compounds as a functional group. The dry treated pigments are deagglomerated to some extent due to the milling steps in the treatment process, but the effect on the tests was negated by particle size reduction steps of all samples used for dispersion testing. The greater surface area actually can appear to slow the wetting process, but the results of the viscosity and sedimentation tests show that wetting of the treated particles improved compared to that of the untreated pigments.

The dramatic dispersion of the hydrophilic treatments seen in visual evaluation is confirmed by the quantitative measurements:

The sedimentation test shows effect of the treatments on wetting of the particles. Of the silanes evaluated, $PEG_{6\text{-}9}$ Silane and Sodium Carboxyethylsilanetriol produced the densest sediments and the most uniform improvements over the untreated oxides. Whether complete deflocculation is desirable in a given formulation is a separate issue.

Dispersion viscosity measurements indicated that $PEG_{6\text{-}9}$ Silane and Sodium Carboxyethylsilanetriol treated iron oxides exhibited the best wetting. Sodium Carboxyethylsilanetriol treatment is the most effective treatment for titanium dioxide.

Interaction of the treated surfaces with other raw materials has an effect on performance in actual formulation. Surface activity of the PEG group of the $PEG_{6\text{-}9}$ Silane may affect the formation of the emulsion, causing excessive pigment flotation and appears to influence wetting of some thickening agents. The anionic nature of Sodium Carboxyethylsilanetriol does stabilize pigment dispersions, but the effect of the added electrolyte on other raw materials must be considered. Similarly, the amino group of aminopropyl silane reacts with formulation ingredients as would any other amine.