Surface Treatments

Enhancing the Performance of Your Products
Introduction

Surface treatment of pigments and fillers is used to improve performance in a variety of cosmetic formulations. Surface coatings improve skin feel by smoothing the rough pigment surfaces and reducing oil absorption. Treated pigments compress more easily, permitting formulation of pressed powders with lower binder content, further improving skin feel. In addition to the deagglomeration achieved by the coating process alone, surface characteristics can be modified to optimize wetting in a variety of vehicles. Surface treated pigments and fillers have permitted the development of new product forms, including cosmetically elegant water in oil foundations, cream to powder cosmetics, and powder to liquid formulations.

Surface treatments are applied by a variety of mechanisms:

**Chemical Reaction:** A permanent chemical bond is formed between the surface treatment molecule and the pigment surface, resulting in an insoluble, shear resistant coating. Chemically bonded treatments are recommended for use in aqueous and anhydrous dispersed systems.

**Precipitation:** The treating compound is either precipitated by the pigment surface or is precipitated by addition of a polyvalent metal ion, forming a continuous, hydrophobic coating. Precipitated coatings are tenacious but may be dissolved from the pigment surface during prolonged heating in oil.

**Adsorption:** Molecules can be adsorbed onto the surface of pigments or fillers, resulting in a shear resistant coating. **Electrostatic:** Under conditions of high shear, small particles are adhered to the surface of the larger pigment or fillers.
Reacted Treatments

Silicon chemistry is the basis for many reacted coatings due to the ease with which certain substituent groups bonded to a silicon atom may be hydrolyzed. Briefly, SiH, SiOR (R = methyl or ethyl), SiNH₂, or SiX (X = halogen) will react in the presence of water to form SiOH (silanol groups) which can self associate or condense with the hydroxyl groups found on metal oxide surfaces to form stable bonds, either Si-O-Si or Si-O-M (M = metal atom). Such compounds are also called coupling agents, because they are capable of modifying a surface in such a way that it can be "coupled" to a dissimilar vehicle. Because Si-C bonds are stable and not subject to hydrolysis, various functional "R" groups can be attached to a silicon atom having hydrolyzable groups and bound through the Si-O- linkage to a pigment or filler surface, altering the physical and chemical properties of that surface through the following reaction:

\[ R_{4-a}SiX_a + a(H_2O) = R_{4-a}Si(OH)_a + a(HX) \]

\( R = \text{alkyl, aryl, alkenyl} \) \( X = \text{H, OR, NH}_2, \text{halogen} \)

\[
\begin{array}{cccccc}
R & R & R & R & R & R \\
\mid & \mid & \mid & \mid & \mid & \mid \\
\text{HO} - \text{Si} - \text{O} - \text{OH} & - \text{Si} - \text{O} - \text{OH} & - \text{Si} - \text{OH} & \rightarrow & - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} & ~ + \text{XH}_2\text{O} \\
\mid & \mid & \mid & \mid & \mid & \mid \\
\text{OH} & \text{OH} & \text{OH} & \text{O} & \text{O} & \text{O} \\
\text{OH} & \text{OH} & \text{OH} & \mid & \mid & \mid \\
\mid & \mid & \mid & \mid & \mid & \mid \\
\end{array}
\]

Common cosmetic fillers, including talc, mica, and sericite, being silicates, possess surface hydroxyl groups suitable for reaction with silanols, as do the metal oxide pigments, titanium dioxide, zinc oxide, the iron oxides, chromium pigments, and the zeolitic ultramarines.
Reacted Treatments, continued

D/I-Methicone

\[
\begin{align*}
\text{CH}_3 \\
(CH_3)_2\text{SiO-(SiO)}_n\text{Si(CH}_3)_3 \\
\text{H}
\end{align*}
\]

The treating compound is a polymer, polymethylhydrogensiloxane, INCI name methicone. The pendant hydrogen substituents on the siloxane chain serve as the reactive groups.

In the presence of even trace amounts of water, the Si-H bonds convert to SiOH. The SiOH groups then hydrogen bond with pigment or filler surface hydroxyl groups, and upon curing, form covalent Si-O-pigment chemical bonds. The coating formed is highly hydrophobic and is not solubilized by common solvents. As are all compounds containing Si-O-bonds, the treatment is stable between pH 3-9.

Methicone treatment result in a cured film surface that significantly improves the characteristics of colors and minerals. Pigments and fillers treated with methicone are hydrophobic and wet well in oils, particularly silicone oils. In powder form, the primary benefits are: free flowing dry powders, anti-caking, high water repellency, improved slip, enhanced feel, better skin adhesion, and improved payoff. In anhydrous systems, Methicone treatment improves wetting, dispersion, and suspension characteristics.

The enhanced wetting in silicone and polar oils imparted by methicone treatment is used to advantage in water-in-silicone foundation formulation and in anhydrous cream powder systems. When incorporating methicone treated materials into systems containing water, care must be taken to utilize the “D/I”, "emulsion grade", of treatment to avoid hydrogen generation.
AS-Alkyl Silane

\[
\begin{align*}
R & & R = \text{Alkyl, i.e. Caprylyl} \\
\| & \quad \| \\
R'O-Si-OR' & & R' = \text{Alkoxy, i.e. Ethoxy} \\
\| & \quad \| \\
\text{Trialkoxy Alkyl Silane} & \\
\| &
\end{align*}
\]

Another approach to the deposition of coatings through the reaction of silanols with the substrate is the use of monomeric alkyl silanes as starting materials. Alkyl silanes consist of a silicon atom having at least one non-reactive, alkyl "R" group and at least one hydrolyzable "X" group, the total of the reactive and non-reactive groups being equal to four. In practice, many alkyl silanes utilized are ethoxy silanes, due to the relatively benign nature of their byproduct, ethanol. The chain length of the "R" groups can vary from C\textsubscript{1} to C\textsubscript{18}, with the majority of commercial materials being treated with C\textsubscript{8} alkyl silane.

Following hydrolysis of the Si-OR' groups to silanol (Si-OH) the alkyl silane can self associate or hydrogen bond to the pigment surface. As with methicone, following cure, stable bonds are formed between the pigment and the treating compound. A trialkoxy silane pictured above will tend to condense onto the pigment surface as a mixture of oligomers formed via reaction among the molecules of the silane. The end result is a siloxane coating which has pendant organic "R" groups which generally lend better compatibility with organic waxes and oils than do the methicone coatings.

Precise properties imparted by the alkyl silane coating vary according to the identity of the "R" group, the longer the "R" chain, the more organic character the coating will have. Pigments treated with C\textsubscript{8} silane are more hydrophobic than methicone treated pigments, wet better in commonly utilized cosmetic oils, and have a lower oil absorption. They are utilized in anhydrous systems and water-in-oil formulations, as are the methicone and dimethicone treated materials. They can be easily dispersed in oils or silicones and can be used in mascaras, foundations, wet/dry products and hot pours.
Alkyl Silane, continued

In anhydrous compact formulations, the excellent wetting imparted by alkyl silane treatment allows incorporation of high pigment loads to achieve a "powdery" sensation upon application to the skin while maintaining a low melt viscosity for hot filling. The improvement in compatibility between the dispersed solids and the vehicle is a benefit in formulation of stick products, including lipsticks, eyeshadows, and foundations, as the adverse effect of many inorganic pigments on stick structure is eliminated. Because byproducts of alkoxy alkyl silane treatment are the alcohols corresponding to the R' group, there is no concern over residual hydrogen evolution in emulsions. The formulator can determine which type of treatment is most appropriate in a given system first based on theoretical considerations and then actual experimental comparisons of performance.
Reacted Treatments, continued

**PFD-Trifluoropropyl Dimethicone**

Pigments treated with compounds having perfluoro substituent groups have the property of water repellency, in addition to that of hydrophobicity. Due to the resistance to wetting by oils, color cosmetics, particularly eye shadows and foundations, formulated with perfluoro compound treated pigments and fillers are less sensitive to sebum exudation, resulting in improved wear properties. The perfluoro compounds utilized by Color Techniques do not contain the environmental contaminate perfluorooctanoic acid. PFD treated pigments and fillers resist oil and water, yet can be incorporated into cosmetic formulations through the use of appropriate wetting agents, particularly silicone glycol copolymers. PFD treated pigments and fillers offer the additional advantages of excellent skin adhesion and exceptionally creamy feel.
Adsorption

**GA - Hydrophilic**

This surface treatment uses the highly branched polysaccharide product, Galactoarabinan, a naturally derived material from larch trees.

The galactoarabinan coating hydrates readily, causing pigments and fillers treated with the material wet out rapidly with little or no high shear agitation. Dispersions formed are so thoroughly deagglomerated that improved suspension is observed due to the smaller agglomerate size achieved. The galactoarabinan acts as a protective colloid, inhibiting destabilizing particle-particle attractions through steric effects, prolonging shelf life. As for all coatings, compatibility with other formula ingredients, particularly gums and thickeners, must be assured so as not to lose the beneficial effects of the surface treatment.

In water-based systems, GA treated pigments show better stability, as evidence by enhanced color value, when dispersed and compared to untreated pigments. It also reduces the viscosity of the system, which enables better wetting and higher loading capabilities of the pigment.
Electrostatic Attraction

LL - Lauroyl Lysine

Lauroyl Lysine is derived from the natural materials - L-Lysine and lauric acid. Treated materials do not irritate the skin or cause skin sensitization or photosensitization. They provide good lubricity and are smooth spreading, compatible with human skin, moderately anti-oxidative, act as a chelating agent and give excellent adhesiveness.
MM - Magnesium Myristate

\[(\text{CH}_3\text{CH}_2\text{COO}^-)_2\text{Mg}^{+2}\]

Magnesium Myristate is the magnesium salt of myristic acid. Magnesium Myristate coated pigments are an economical alternative to lecithin treated pigments.

Magnesium Myristate coatings lend a smooth, lubricious feel to pigments and fillers, improve compression of pressed powders, improve skin adhesion, and increase the wear time of color cosmetics. Just as magnesium myristate acts as a dry binders in pressed powders to achieve adequate compression of the cake and adhesion of the product to the skin, so are magnesium myristate coated pigments and fillers used. The thin homogenous layer of magnesium myristate which comprises the coating is more efficient than a powder dispersed in the product bulk, giving the desired benefits of compression and adhesion with a smoother, less draggy application, with less tendency toward glazing. Magnesium Myristate treated pigments exhibit good hydrophobicity but can be dissolved upon continuous heating in common cosmetic oils.

HSE - Herbal Skin Enhancers

To further enhance the qualities of our pigments and fillers, we are developing a series of surface treatments to give different herbal benefits. Acidic cetyl phosphate reacts with the surface hydroxyl groups on the pigments or fillers, forming a film capable of entrapping oil based herbal extracts. Already available is:

- **Green Tea** - with natural antioxidants to protect the skin against the damaging effects of free radicals
- **Mandarin Orange** - a natural antioxidant used to brighten complexions and soothe stressed skin
<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>COMPOSITION INCI Name(s)</th>
<th>COATING TYPE</th>
<th>CHARACTERISTICS</th>
<th>APPLICATIONS</th>
<th>REGULATORY STATUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Alkyl Silane</td>
<td>Triethoxycaprylylsilane</td>
<td>chemical bond</td>
<td>very hydrophobic; lipophilic; AS pigments wet easily into oil and silicones; no hydrogen potential; shear resistant</td>
<td>w/o, w/silicone foundation, wet/dry compacts, powdercream hot pours, stabilizes and aids wetting of inorganic sunscreens</td>
</tr>
<tr>
<td>D, D/I</td>
<td>Hydrophobics</td>
<td>Methicone</td>
<td>chemical bond</td>
<td>hydrophobic; D pigments wet easily in silicones; shear resistant</td>
<td>wet/dry compacts, powdercream hot pours</td>
</tr>
<tr>
<td>PFD</td>
<td>Trifluoropropyl Dimethicone</td>
<td>Trifluoropropyl Dimethicone</td>
<td>chemical bond</td>
<td>hydrophobic and lipophobic; resists wetting by common cosmetic oils and sebum; exceptional skin adhesion; improves wear</td>
<td>pressed powder foundation, blushers and eye shadows; water in silicone foundations</td>
</tr>
<tr>
<td>HSE</td>
<td>Herbal Skin Enhancer- Green Tea</td>
<td>Camellia Sinesis (Green Tea Leaf) Extract, Simmondsia Chinensis (jojoba) Seed Oil, Cetyl Phosphate, Ascorbyl Palmitate</td>
<td>mechanical, high shear, high temperature</td>
<td>increases substantivity, adds softness, lubricity, natural antioxidant protects against free radical damage, hydrophobic</td>
<td>pressed powders, foundations</td>
</tr>
<tr>
<td>HSE</td>
<td>Herbal Skin Enhancer- Mandarin Orange</td>
<td>Citrus Nobilis (Mandarin Orange), Simmondsia Chinensis (jojoba) Seed Oil, Cetyl Phosphate</td>
<td>Mechanical, high shear, high temperature</td>
<td>Increases substantivity, adds softness, lubricity, complexion brightener, natural antioxidant protects against free radical damage, hydrophobic</td>
<td>pressed powders, foundations</td>
</tr>
<tr>
<td>LL</td>
<td>Lauroyl Lysine</td>
<td>Lauroyl Lysine</td>
<td>mechanical, high shear added chemical bond</td>
<td>natural, pH of the skin, silky, smooth feel, adds hydrophobicity</td>
<td>pressed and loose powders, liquid foundation above plus w/o, w/silicone emulsions</td>
</tr>
<tr>
<td>MM</td>
<td>Magnesium Myristate</td>
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<td>precipitation</td>
<td>hydrophobic, shear resistant, MM treatment aids adhesion, compression</td>
<td>pressed powders</td>
</tr>
<tr>
<td>GA</td>
<td>Hydrophilics</td>
<td>Galactoarabinan</td>
<td>wet process, mechanical deposition</td>
<td>natural, GA treatment aids wetting, reduces viscosity in aqueous systems</td>
<td>o/w foundations, eyeliners, mascaras</td>
</tr>
</tbody>
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