Silicone Surfactants

Editors Note: This edition of **The Silicone Spectator®** will begin to address polymeric materials derived from silicone that have a at least two groups that in pure form are insoluble in each other. This type of molecule is amphilic, surface active and has important properties in formulations. We will start with molecules having silicone and water soluble portions.

Group Opposites

Everyone has heard the adage "oil and water don't mix". It is generally applied not to chemistry, but personalities. Nonetheless, it is quite true that oil, water and silicone do not mix! The introduction of silicone soluble groups into compounds that contain oil soluble and water soluble groups results in surface active agents with very interesting properties.

Molecules that contain water soluble, oil soluble and silicone soluble groups contain in one molecule three mutually insoluble groups. The concept of "hydrophilic and "hydrophobic" is related to water soluble, and in systems containing silicone needs to be expanded to include silicone compounds.

Hydrophilic (water loving)	**Hydrophobic (water hating)**
Oleophilic (oil loving)	**Oleophobic (oil hating)**
Siliphilic (silicone loving	**Siliphobic (silicone hating)**

Hydrophobic (water hating) materials can be either oleophilic or siliphilic.
Oleophobic (oil hating) materials may be either hydrophilic or siliphilic.
Siliphobic (silicone hating) materials may be either oleophilic or hydrophilic.

This means that when a fiber, like hair, is treated with either silicone or with hydrocarbon, very different hydrophobic coating results. If treated with silicone, the fiber will also be oleophobic. If treated with oil, the fiber will also be siliphobic. For application in waterproofing fibers, selection of the proper molecule is critical. Improper selection will result in unacceptable oil staining.

This also results in an expansion of the traditional well-accepted two-dimensional HLB system of Griffin[2] into to the 3D HLB system when oil soluble, water-soluble and silicone soluble portions are all in a molecule.

Amphilic Compounds

The presence of at least two groups that if pure compounds would be insoluble in each other in one molecule makes the molecule amphilic . Amphilic materials orient themselves at interfaces and are surface active (Surfactants). Amphilic silicone compounds offer advantages over amphilic materials based upon only oil and wa-

ter soluble groups. These include:

Improved surface tension reduction – 20 dynes/cm^2 rather than the 30+ dynes/cm^2
Wetting in water, and oil based systems.
Emulsification properties
Film forming properties
Irritation mitigation

The ability to properly choose a silicone surfactant can result in formulations with improved functionality.

Silicone Surfactants

A surfactant is a molecule with two portions that if pure would be insoluble in each other. In the case of surfactants it is an oil soluble and a water-soluble group. Such molecules are called amphilic. These molecules go to the interface where they lower surface tension. At a point called CMC (critical micelle concentration) micelles form. The surface tension of fatty surfactants are around 32 dynes/cm2. Micelles are aggregates of molecules.

Silicone surfactants are also amphilic materials, but the other group can be oil soluble or water-soluble. The silicone surfactant if composed of silicone and water-soluble groups will lower the surface tension of water to around 20 dynes/cm2. If the silicone surfactant has oil soluble and silicone soluble groups the surface tension of the oil will be lowered to 20 dynes/cm2

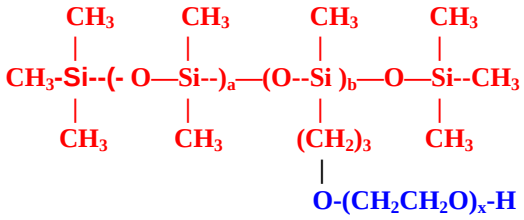
The lowering of surface tension is a necessary step toward wetting, detergency, spreading and emulsification. Most formulators are quite comfortable with water-based systems incorporating surfactants. The exact same properties can be observed in oil-based systems. It is perfectly legitimate to ask what is the critical micelle concentration of stearyl dimethicone in isopropyl myristate, or to use cetyl dimethicone to improve wettability of a pigment in oil.

Silicone surfactants are very important additives to a variety of formulations in which traditional surfactants simply cannot provide the needed surface tension reduction. The ability to reduce surface tension of a formulation is a critical first step in obtaining foam, emulsification, wetting and surface spreading. The optimization of these properties is achieved by proper selection of the silicone surfactant.

> **"The ability to reduce surface tension of a formulation is a critical first step in obtaining foam, emulsification, wetting and surface spreading. The optimization of these properties is achieved by proper selection of the silicone surfactant."**

Dimethicone Copolyols

Dimethicone copolyols (DMC) (also called PEG/PPG dimethicones, silicone glycols, silicone surfactants) are one class of amphilic materials having a water soluble and a silicone soluble portion in one molecule. They have been an important and growing class of raw materials used in the personal care market. They conform to the following structure:



The silicone soluble portion is shown in red, the water soluble portion is shown in blue. This class of amphilic polymers is sur-

face active. The activity is dependant upon the exact structure.

Structure Function Relationship

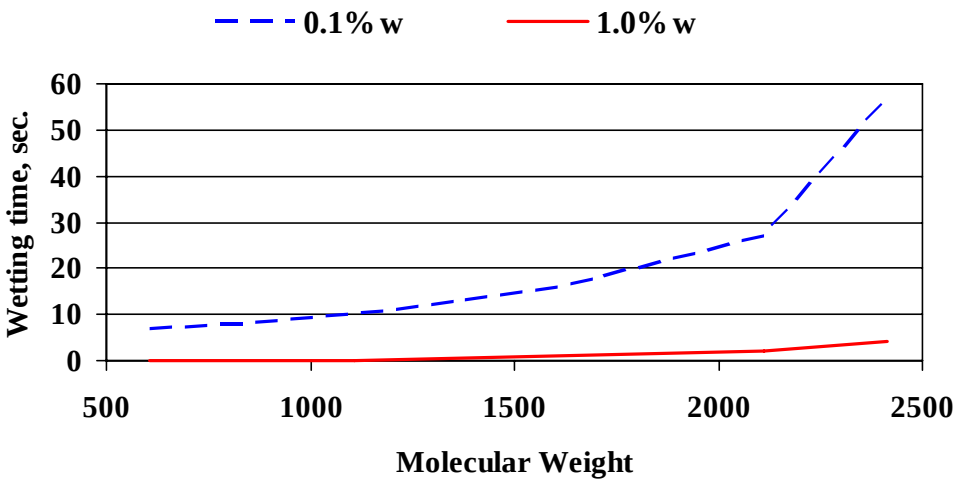
It is very helpful for the formulator to understand the structure function relationship for the various additives to a formulation. Wetting, conditioning and emulsification properties are directly effected by the structure of the DMC. Two important properties wetting and irritation to the eyes are considered here. We evaluated a number of products (Products A-F) for wetting and irritation.

"Dimethicone Copolyol Polymers are a class of amphilic polymers that are surface active. Their properties depend upon the exact structure".

Product Designation	Number of "a" units	Number of "b" units	Molecular Weight
A	0	1	607
B	0.9	1.3	808
C	2.3	1.8	1108
D	4.5	2.5	1610
E	6.8	3.0	2111
F	8.1	3.6	2412

Wetting Properties

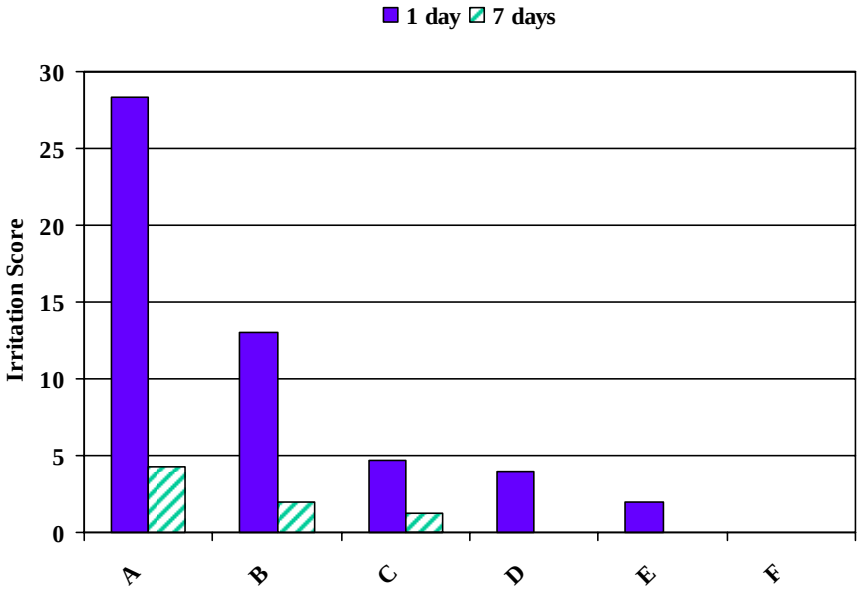
It is very desirable to have formulated products efficiently wet the substrate, including hair, skin and textile fibers to effectively deliver the desired result. Unfortunately, many DMC are poor wetting agents. This is due to the fact that most commercial products have a molecular weight in excess of 2500. The evaluation of the effect of molecular weight upon wetting demonstrated that products with desirable wetting speeds could be prepared over a relatively wide range of molecular weights.



Eye Irritation

It is critical that products used in personal care applications also be mild to the eye and skin. The products evaluated for wetting were likewise evaluated for eye irritation using the "Draize Primary Ocular Irritation Test"

Scale: Moderately Irritating	25.1 - 50,
Mildly Irritating	15.1 - 25,
Minimally Irritating	2.6 - 15
Practically Non- Irritating	0.6 - 2.5,
Non- Irritating	0 - 0.5.



The proper selection of a dimethicone copolyol can result in a product that has a desirable combination of properties in personal care formulations. Notwithstanding the fact that he lower molecular weight DMC have faster wetting times, products can be easily selected that provide both efficient wetting and low ocular irritation.

When is a Silicone Surfactant not a "Silicone Surfactant"?

This question actually has a very important answer, silicone surfactants are no longer "silicone surfactants*" when the amount of silicone in the molecule is too low to effect surface tension. At that point the molecules simply become fatty surfactants that have silicone attached. A molecule with a small percentage silicone in the molecule will not orientate at the interface with the silicone group orientated to the interface. The result will be a surface tension above 30 dynes/cm^2.

*** Since we have defined "silicone surfactants" as materials that lower surface tension below 30 dynes/ cm^2, it is important to note that not ALL surfactants with silicone in them function in this way. Function** is always dictated by structure!

Consider three different "PEG 8 Dimethicone" compounds. Should one expect the same surface tension at 0.5% by weight concentration?

INCI Name	MW	Surface Tension
PEG-8 Dimethicone	800	21.9 Dynes/cm^2
PEG-8 Dimethicone	6353	28.1 Dynes/cm^2
PEG-8 Dimethicone	12,500	31.0 Dynes/cm^2

Apparently not! One should not only expect different surface tensions, but also very different wetting times, foam properties, emulsification and conditioning properties. In fact the only commonality these materials have in a formulation is INCI name!

The fact that silicone surfactants possess both water soluble polyoxyalkylene groups and silicone groups allow these materials to have unique surface tension, emulsification, wetting and foaming, however not all silicone surfactant possess the same properties. Silicone molecules can have the properties of fatty surfactants or the properties of silicone compounds depending upon the orientation of the molecule at the interface. This variability in property results in what we call "**The Silicone Conundrum".** The term conundrum is defines as an intricate and difficult problem. The problem is how do I get the highly desirable properties of silicone in my formulation, when formulating with silicone can provide its owe set of problems? The Silicone spectator will address this problem in upcoming issues and present data on the structure / function relationship observed in silicone surfactants.

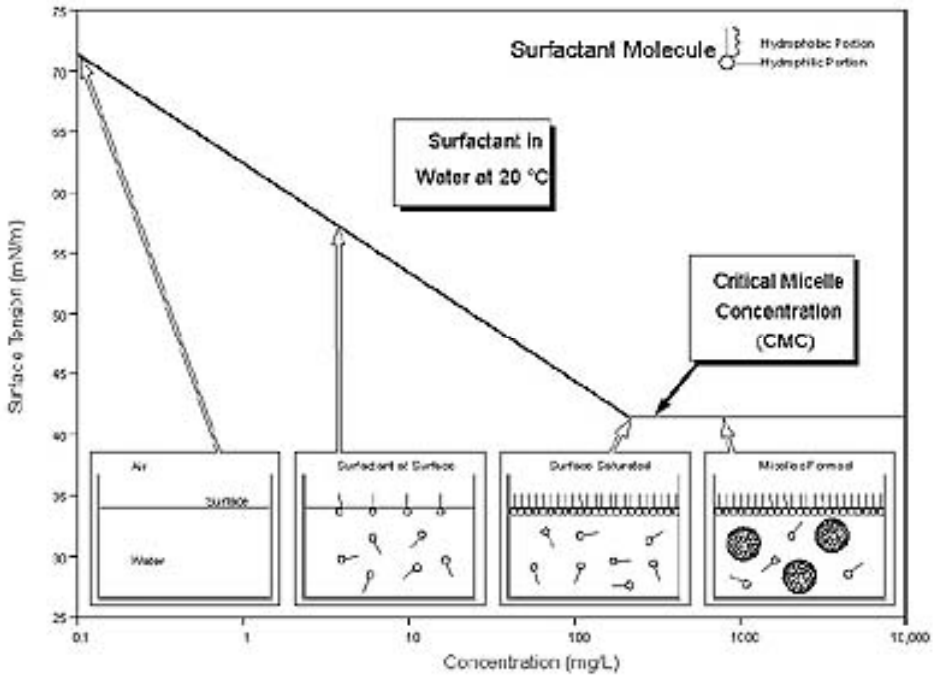
Amphilic Materials in "Solution"

1. A **solution** is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent.

2. A **suspension** is a colloidal dispersion in which a finely-divided species is combined with another species, with the former being so finely divided and mixed that it doesn't rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.

3. An **emulsion** is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

Even within the world of solution chemistry, materials in solution can act quite differently. Consider a fully dissolved 1% solution of sodium chloride in water. This simple system has sodium ion (Na^+), chloride ion (Cl^-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.
Now consider a 1% solution of a surfactant. Surfactant, or surface active agent has a water soluble head and a water insoluble tail. A very well known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, Sodium lauryl sulfate has two opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty group and the water soluble sulfate group makes the molecule amphilic and surface active. The graphic below shows what happens as the concentration of surfactant is increased in water.



Products added to formulations that are surface active have critical performance effects and selection is critical.

Silicone Functionalized Alkyl Polyglycoside

Editor's note: Silicone Spectator welcomes articles about new and exciting technologies that allow for the incorporation of Formulator Friendly® Silicones into formulations. In addition, there is an increasing interest in GREEN PRODUCTS that are bio-derived and are renewable. Alkyl polyglycosides (APGs) are a class of compounds that make use of sugar and natural fatty alcohols. There has been a recent development of new silicone functionalized APG compounds. We are pleased to have the following article contributed by Dr. Bob Coots of Colonial Chemical on this new class of compounds, covered by U.S. Patent 6,762,289.

Formulator Friendly® is a registered trademark of Siltech LLC Dacula, Ga

Contributed by: Robert J. Coots, Ph.D. Colonial Chemical, Inc.

INTRODUCTION

There is an exciting new development of naturally derived surfactants for the personal care industry, based on alkyl polyglucoside (APG) raw materials; these unique products combine the APG structure with a polysiloxane backbone.

These products start from a natural building block, derived from renewable resources. The combination of dimethicone and the alkyl polyglucoside allow for products that provide excellent feel and conditioning. Additionally it provides an out-

standing skin feel when applied from body wash formulations.

These products provide foaming and slip while actually lowering the irritation of formulations. They show excellent toxicological properties as well as an ability to mitigate irritation in harsh formulations, making them a natural choice for many personal care formulations.

Representative of this wide class of materials are two products with widely different molecular weights allowing the formulator to select a product or blend of products to meet individual formulation needs. The structure is shown in figure 1; it has the familiar dimethicone backbone of silicone fluids, with the APG group attached as a branch on this chain. The CTFA designation is PEG-8 PG-Coco-Glucoside Dimethicone.

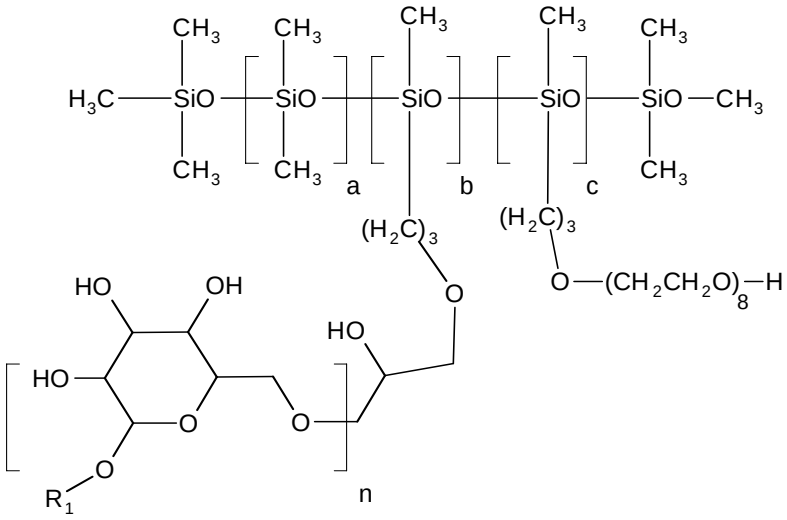


Figure 1. PEG-8 PG-Coco-Glucoside Dimethicone

The sugar (APG) portion of the molecule provides good foam and a high degree of substantivity to hair and skin. Additionally it provides an outstanding skin feel when applied from body wash formulations. The typical properties for the two products are shown in Table 1.

Table 1. Typical Properties

	C-35P	C-800P
Activity, %	35	35
pH (10% aqueous)	6 – 8	6 – 8
Color, Gardner	< 3	< 3

Viscosity at 25°C	28	72
Odor	mild, fatty	mild, fatty
Appearance, (10% aqueous)	Clear	Clear
Ross-Miles Foam Height (1% active), mm		
Immed.iate	150	120
1 minute	140	110
5 minutes	135	95
Draves Wetting (1% active), seconds	6.0	> 200

SAFETY TESTING

Evaluation of eye and skin irritation was performed at an independent laboratory. These tests show that the products are very mild compared to other personal care surfactants.

Eye

The evaluation of C-35P as an eye irritant was performed using the chorioallantoic membrane technique, with C-35P diluted to 2 % activity. C-35P was given a score of 0.0 in this test. For comparison, the leading brand of baby shampoo was rated at 11.0 and a top selling adult shampoo was rated at 24.25. C-35P was rated as having no ocular irritation potential.

Skin

A study was performed adhering to ICH Guideline E6 and 21 CFR parts 50 and 56. The "patch test" was performed with the C-35P diluted to 0.4 % activity. The test sites were evaluated at 48 hours and again at 72 hours. The observation was negative skin changes at both times. Under the conditions of this test, the test material, C-35P did not indicate a potential for dermal irritation.

EVALUATION OF CONDITIONING

The C-35P material was evaluated by an outside laboratory for effects in a typical shampoo formulation. The formula was evaluated with and without the C-35P, by replacing 5.0% of the sulfate surfactant with coco-glucoside dimethicone in the shampoo. The shampoos were then tested side-by-side for foam and feel. The evaluations showed that the addition of the coco-glucoside dimethicone resulted in

a creamy and rich foam, with a smooth, supple feel.

APPLICATIONS

These products are used to replace dimethicone copolyol products in many cosmetic formulations. Other possible applications include:

Skin Care Products: creams, lotions, tonics, shower gels, etc.
Hair Care Products: shampoos, conditioners, hair tonics, hair creams, etc.
Sun Care Products: pre and post sun care creams, lotions, gels, etc.
Make-up Products: foundations, lipsticks, etc.
Health Care

Conclusion

Some unique products that combine APG groups with a polysiloxane backbone have been prepared. This combination results in personal care ingredients that provide excellent feel and conditioning, and it gives outstanding skin feel.

These products show that they provide foaming and slip while actually lowering the irritation of formulations. They show excellent toxicological properties as well as an ability to mitigate irritation in harsh formulations, and they are a great choice for personal care formulations.

Silicone Phosphate Esters

Editor's note: Silicone Spectator welcomes articles about new and exciting technologies that allow for the incorporation of Formulator Friendly® Silicones into formulations. We are pleased to provide the following information on dimethicone co-polyol phosphates contributed by John Imperante of Phoenix Chemical. John has been making exciting new products for many years, many in the field of silicone chemistry.

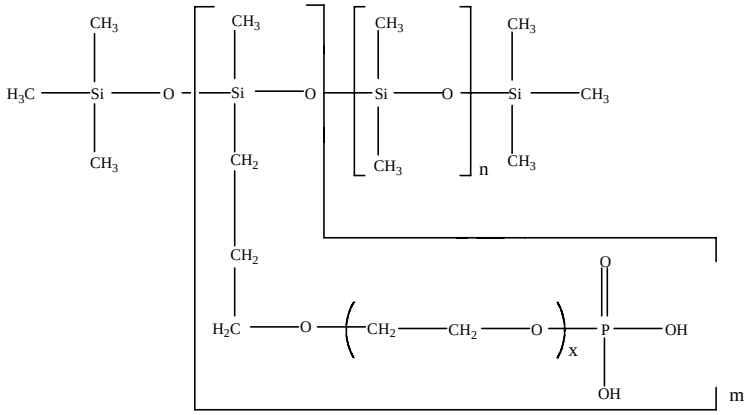
Contributed by:

John Imperante
Phoenix Chemical
Somerville N.J.

Phosphate esters, and in particular mono alkyl phosphate esters have been used in personal care products and are the subject of numerous patents. Silicone phosphate are silicone analogues of these well known materials. The marriage of silicone and phosphate ester chemistry has resulted in a series of unique materials. The products are 100% active, completely water solu-

ble, clear liquids and exhibit a number of properties of interest to the formulator.

They conform to the following structure:



Three products are offered, varying in molecular weight and degree of phosphation.

Pecosil® is a Registered Trademark of Phoenix Chemical, Inc.

Some of the silicone phosphates mentioned in this article are the topic of U.S. Patent 6,756,034 dated June 29, 2004 assigned to Phoenix Research, Inc., a Phoenix Chemical Company.

	Phosphate Groups	Avg. Mol. Wt.
PECOSIL® PS-100	4	2500
PECOSIL® PS-112	12	7500
PECOSIL® PS-100 [i]	24	15000

There is a significant body of data to indicate that as the molecular weight and degree of phosphation increases, the efficiency of these silicone phosphates increases. Specifically, the properties that can be ascribed to these products are:

APPLICATIONS:

WATER-SOLUBLE MOLLIENT

FOAMING AGENT FOR SHOWER GELS AND SHAMPOOS

PIGMENT WETTER AND TiO_2 DISPERSING AGENT

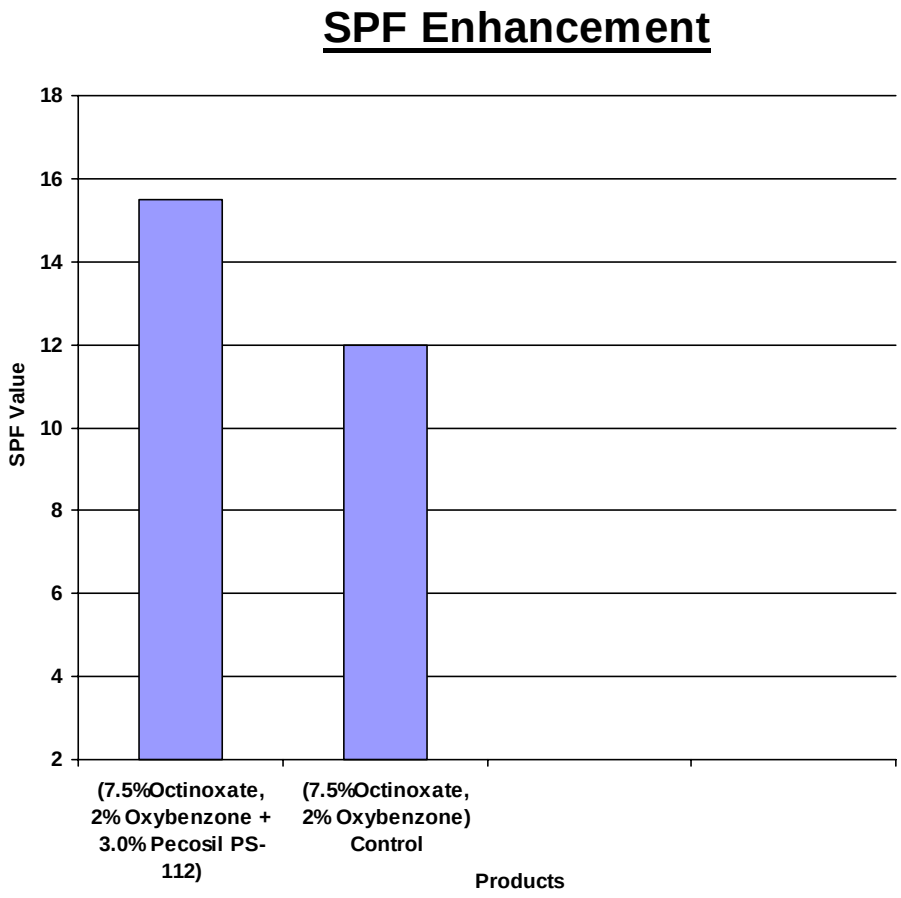
MILD SURFACTANT FOR FACIAL CLEANSES

SHINE-ENHANCER FOR HAIR PRODUCTS

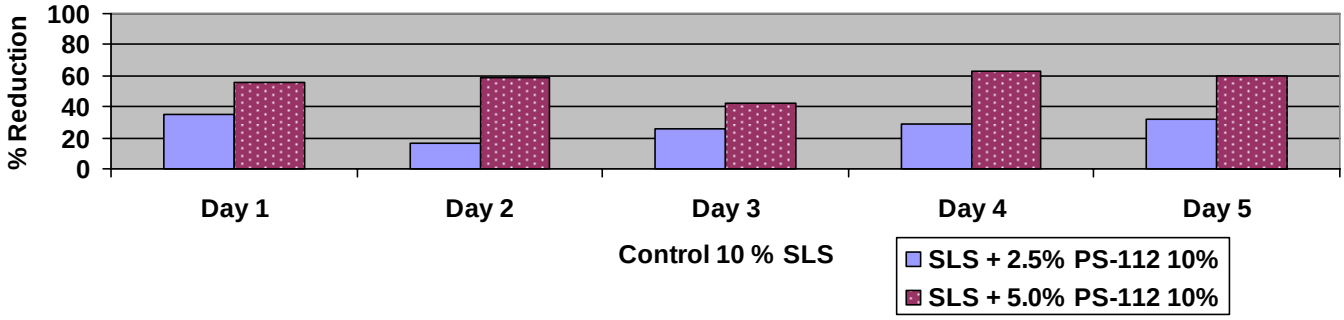
SPF BOOSTER

COUNTER-IRRITANT FOR ALPHA-HYDROXY ACIDS AND SURFACTANTS

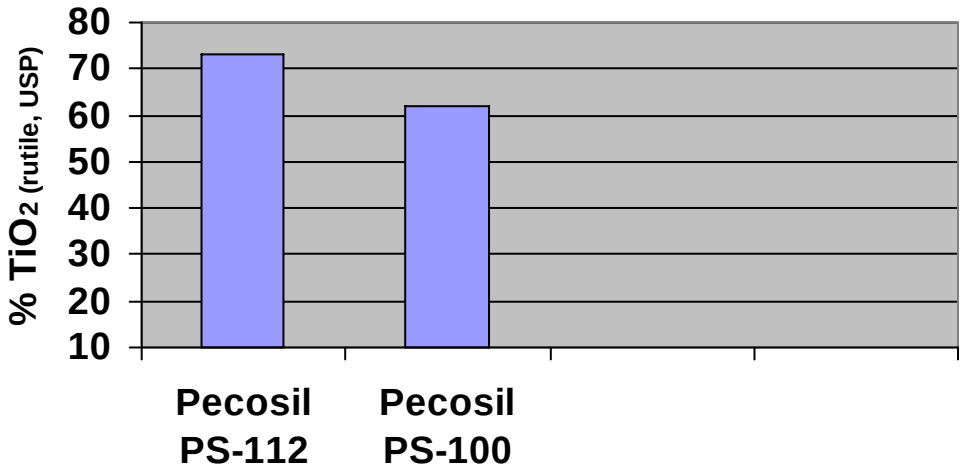
Additional studies show that multiple benefits can be achieved from the use of silicone phosphates.



Irritation Mitigation



PIGMENT WETTING EFFICIENCY

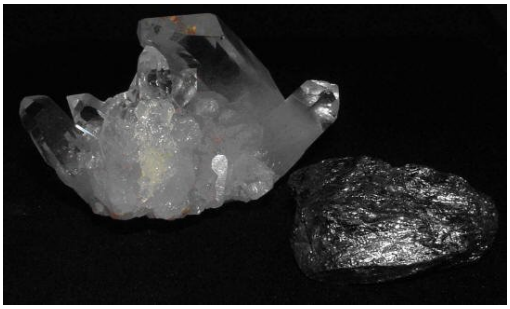


It can be clearly seen that not only do silicone phosphates function as described but that available comparative data show that as degrees of phosphation and molecular weight increase, formulation effectiveness increases, thus, it can be seen that PECOSIL PS-112 is a superior pigment dispersant to PECOSIL PS-100.

Conclusion

It is clear that as the molecular weight of silicone phosphates increase, pigment dispersion effectiveness also increases. Further studies will be undertaken to prove that similar trends can be found for irritation

mitigation and SPF enhancement. The expected superior performance of PECOSIL PS-124 compared to PECOSIL PS-100 and PECOSIL PS-112 will be the subject of a future report.



About Silicone Spectator™

Silicone Spectator™ is electronic newsletters in the field of Silicone Chemistry, placed on the web four times a year. We welcome comments, articles and information on the content of this newsletter.