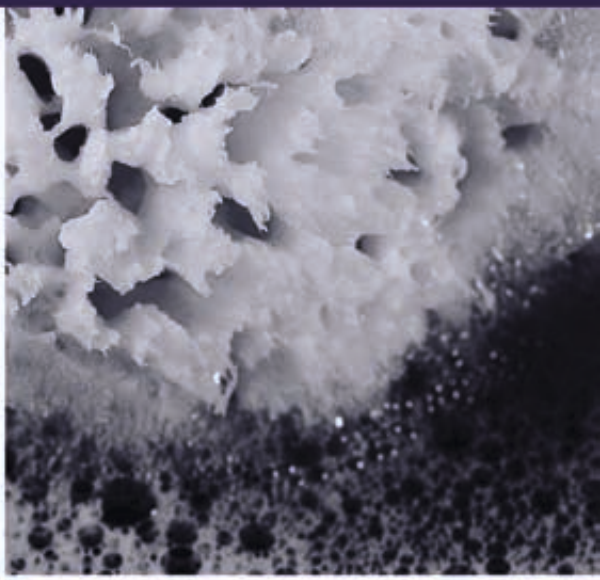
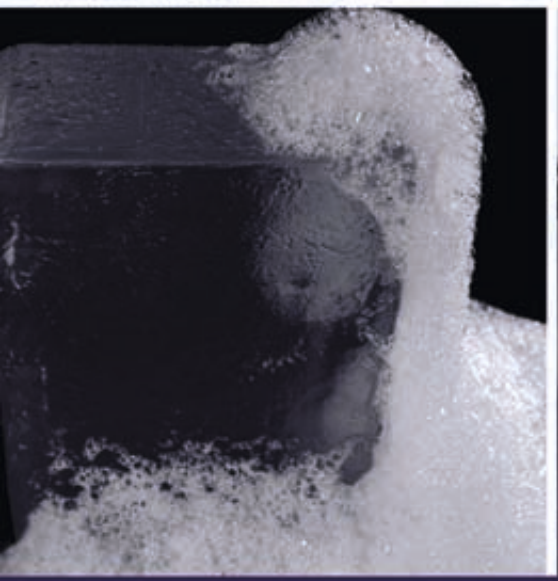
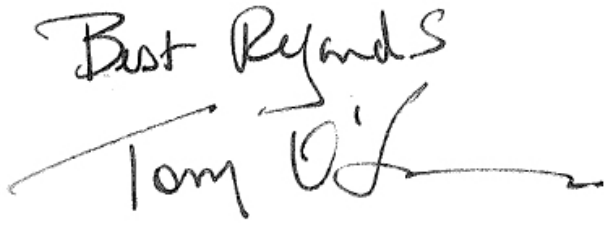
Surfactants:

Strategic Personal Care Ingredients


Anthony J. O'Lenick, Jr.



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by Anthony J. O'Lenick, Jr.

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Preface

The intention of this book is to provide the formulation chemist with a basic understanding of the chemistry, structural attributes and functional properties of the major types of surfactants discussed. In addition, we will propose salient analytical tests for each class of compounds. Once armed with this information, the formulator should be able to make better decisions in dealing with selecting the proper surfactant and in ensuring batch-to-batch conformity to specifications and supplier-to-supplier uniformity. Because the level of exposure to surfactant technology varies so much in industry, I will start with the basics. For those who already have a background in these matters, I am reminded of the words of the Nobel laureate and physicist Enrico Fermi, who once stated that we should never underestimate the pleasure we feel from reading something we already know. I hope that this truism applies in the case of this book.

The surfactants chosen for review in this book are the kinds of personal care products that formulators most commonly encounter. By no means is the data provided intended to be exhaustive of the subject matter. Many volumes have been written to cover the organic and physical chemistry of the various surfactants discussed here. Fortunately for the formulating chemist, a full understanding of all the nuances of the chemistry is not necessary for efficient formulation of surfactant-containing systems.

Contrary to popular perception, the surfactants discussed in this book and the technologies used to manufacture them have been known for quite some time. Many classes date back to the 1930s and before. The section on patents concentrates on those patents that are considered to be the pioneering patents. Many recent commercially significant improvements have been made, but it is important for the chemist to realize that the basic chemistries have been with us for some time. Each inventor builds upon the invention of the previous inventor, and the science as a whole advances.

The Author

Anthony J. O'Lenick, Jr. is currently President of Siltech LLC in Dacula, Georgia. Siltech is a silicone and surfactant specialty company. Prior to that he held technical and executive positions at Lambent Technologies Inc., Alkaril Chemicals Inc., Henkel Corporation and Mona Industries. He has been involved in the personal care market for over 25 years.

Tony has published more than 40 technical articles in trade journals, contributed chapters to three books, and is the inventor on more than 190 patents. He received a number of awards for work in silicone chemistry including the 1996 Samuel Rosen Award given by the American Oil Chemists' Society, the 1997 Innovative Use of Fatty Acids Award given by the Soap and Detergents Association, and the Partnership to The Personal Care Award given by the Advanced Technology Group. Tony was a member of the Committee on Scientific Affairs of the Society of Cosmetic Chemists.

Acknowledgements

The author gratefully acknowledges the encouragement and support of his wife Alice over the years in the writing of this book. The author is grateful to a number of mentors, professors and colleagues, which over the years have helped explain the concepts in this book. Taking liberty with the now famous words of Isaac Newton I say "If we see farther or clearer on any topic, it is because we stand on the shoulders of those who have come before us".

The author also wishes to acknowledge the contributions of Dr. Martin Rieger. Dr. Rieger has made significant contributions to the field of surfactant technology and has graciously allowed his book entitled: *Surfactant Encyclopedia* to be combined into this work to make one expanded work. It is indeed an honor to work with such an individual.

Chapter 1

Raw Materials for Surfactant Preparation

Background

Formulators in the personal care field realize that there are a vast number of surfactants from which to choose in the preparation of new products. There are nonionic, cationic, amphoteric and anionic surfactants available. Within each class there are numerous individual surfactants. A neophyte formulator might ask, "Why are there so many types of surfactants?" The answer is clear: The structure of the surfactant determines its functionality.

Chart 1 shows some of the properties of the major types of surfactants. Selection of the kind of surfactant for use in a particular formulation is a challenge to formulators.

Once this is done, ensuring that the surfactant chosen is the same from lot to lot and manufacturer to manufacturer is quite another challenge. As formulations become more complicated, the need for salient specifications becomes more critical. Salient specifications are defined as those values established for specific chemical analysis that define whether a chemical raw material will function in a given formulation. When a good set of salient specifications for the raw material is clearly defined, products will work more consistently in a given formulation. To understand the salient specifications, one needs to understand not only the chemistry of the surfactant but also the chemistry of potential by-products and residual raw materials.

This work seeks to shed some light on these variables and to provide some guidance on the kind of analysis recommended for each class of product.

Surfactant Classification

One important way to classify surfactants is by the kind of ionic charge present. An example of this kind of classification is as follows:

Class	Example	Charge
Anionic	Phosphate ester	Negative
Nonionic	Nonyl phenol ethoxylate	None
Cationic	Stearyl dimethyl benzyl ammonium chloride	Positive
Amphoteric	Cocamidopropyl betaine	Variable

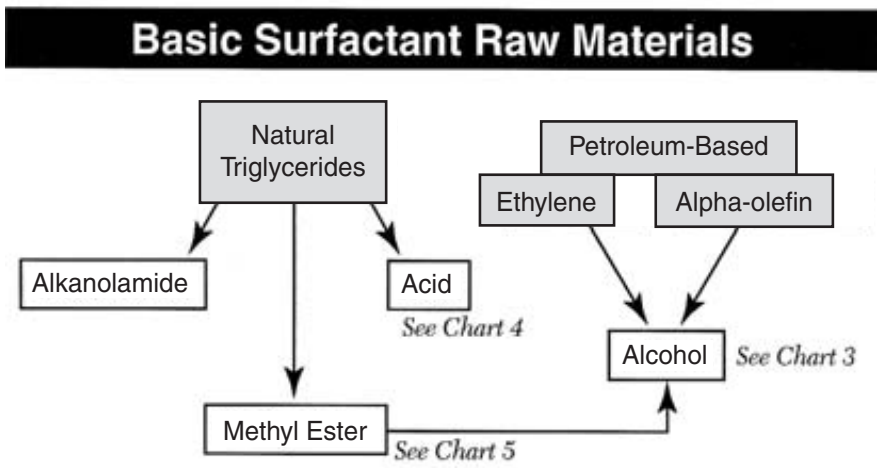
Another way to classify surfactants is by function. This kind of classification is helpful to formulators. Chart 1 shows such a classification system.

Chart 1

PRODUCT CLASSES	RELEASE AGENTS	EMULSIFIERS	DETERGENTS	LUBRICANTS	SOFTENERS	WETTING AGENTS	LEVELING AGENTS	DISPERSANTS	CORROSION INHIBITORS	SOLUBILIZERS	COUPLING AGENTS	FOAMING AGENTS	FOAM STABILIZERS	DISINFECTANTS
Alcohol Alkoxylates Agricultural Surfactants Alkanolamides (1:1)		◆ ◆	◆ ◆	◆		◆ ◆		◆				◆ ◆	◆	
Alkanolamides (2:1) Alkanolamide Ethoxylates Alkylaryl Sulphonates		◆	◆ ◆	◆ ◆	◆	◆	◆		◆			◆	◆	
Alkylphenol Ethoxylates Amine Ethoxylates Amine Oxides		◆ ◆	◆ ◆			◆ ◆	◆ ◆	◆	◆ ◆	◆				
Amphoterics Benzyl Quats Block Co-polymers		◆	◆			◆	◆ ◆	◆	◆	◆				◆
Fatty Acid Ethoxylates Glycerol Esters Higher Alcohol Ethoxylates		◆ ◆ ◆	◆	◆ ◆	◆ ◆									
Imadazolines Imadazoline Quats Lower Alcohol Ethoxylates		◆ ◆ ◆	◆	◆	◆ ◆	◆		◆		◆		◆		
Phosphate Esters Polyethylene Glycols Polyproylene Glycols		◆	◆	◆ ◆ ◆		◆				◆ ◆	◆ ◆			

FUNCTIONS

Chart 2



Raw Materials

The possible number of surfactants useful in formulations is truly staggering. To bring some organization to the surfactant world, we will start with the raw materials. The basic raw materials from which surfactants are prepared find their most basic origins in triglycerides, propylene and ethylene. The process of converting these very basic materials into acids, alcohols or methyl esters is shown in Chart 2.

Acids, alcohols and methyl esters are basic building blocks from which surfactants are derived. Charts 3, 4 and 5 show the various pathways from which these basic raw materials can be transformed into surfactants.

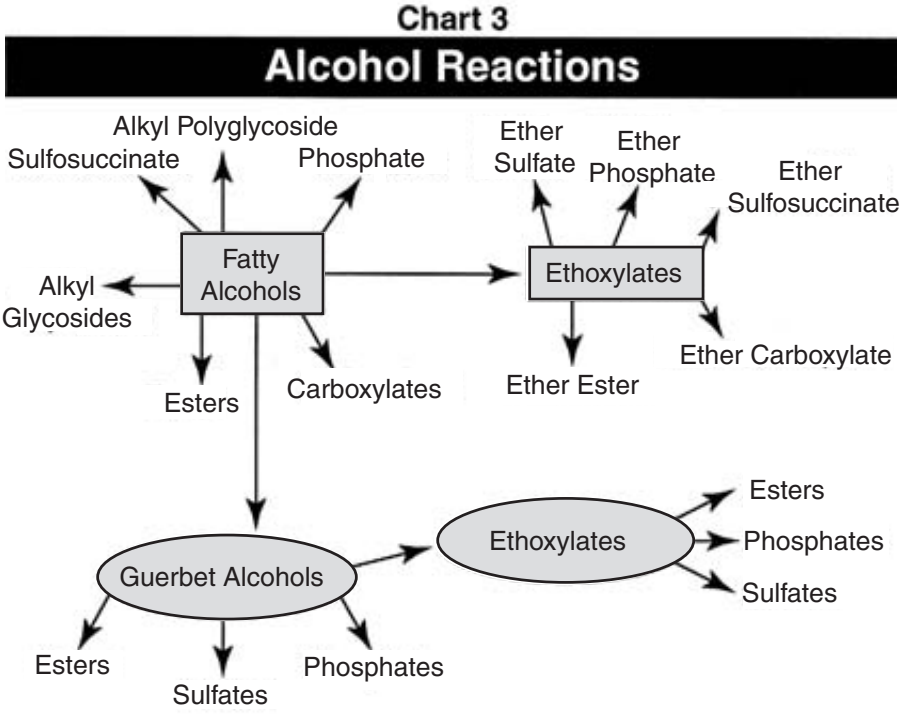
A very important concept that one must understand is that various analogous and homologous series of surfactants are available to formulators.

Analogous series surfactants differ only in the functional groups present. For example, sodium laureth-2-sulfate and sodium laureth-2-phosphate are two analogues. Their common raw material is lauryl alcohol with two moles of ethylene oxide. The substantial difference in properties between these analogues is due only to the different functional groups.

However, if one varies the carbon chain in the group, a series of homologues is prepared. Such a homologous pair is sodium lauryl (C12) sulfate and sodium behenyl (C22) sulfate. The differences in the properties of these two surfactants are due to the differing number of carbon atoms in the molecules.

It is often advantageous for formulators to take into account such differences as these to select a surfactant. The process becomes even more complicated when one considers modifications that change both functionality and carbon chain distribution.

The selection of the surfactant hydrophobe has a profound effect on the functional properties of the molecule and, consequently, the performance of the formulation. In addition, other formulation components influence the performance of the surfactant chosen. The importance of surfactant interaction in preparing formulations is often overlooked by new formulators.



Many interactions and alterations of surfactant properties based on the ionic strength of the solution and other components may be added. In fact, the late Bill Wade, a former professor of the University of Texas at Austin, astutely pointed out that "No surfactant is inherently water-soluble or water-insoluble. The solubility of a surfactant and other surfactant properties are determined not only by the structure of the surfactant in question but also in large part by the other components in the formulation." This is important for formulators to remember because few cosmetic formulations are made up of one surfactant in water.

Before addressing the surfactants themselves, the basic hydrophobic materials from which surfactants are derived must first be addressed.

Triglycerides

The triglycerides of interest for the preparation of surfactants are the naturally occurring triesters of glycerin. Their structures are as follows:

CH_2-O-C(O)-R
|
CH-O-C(O)-R
|
CH_2-O-C(O)-R

Triglyceride

Chart 4

Acid Reactions

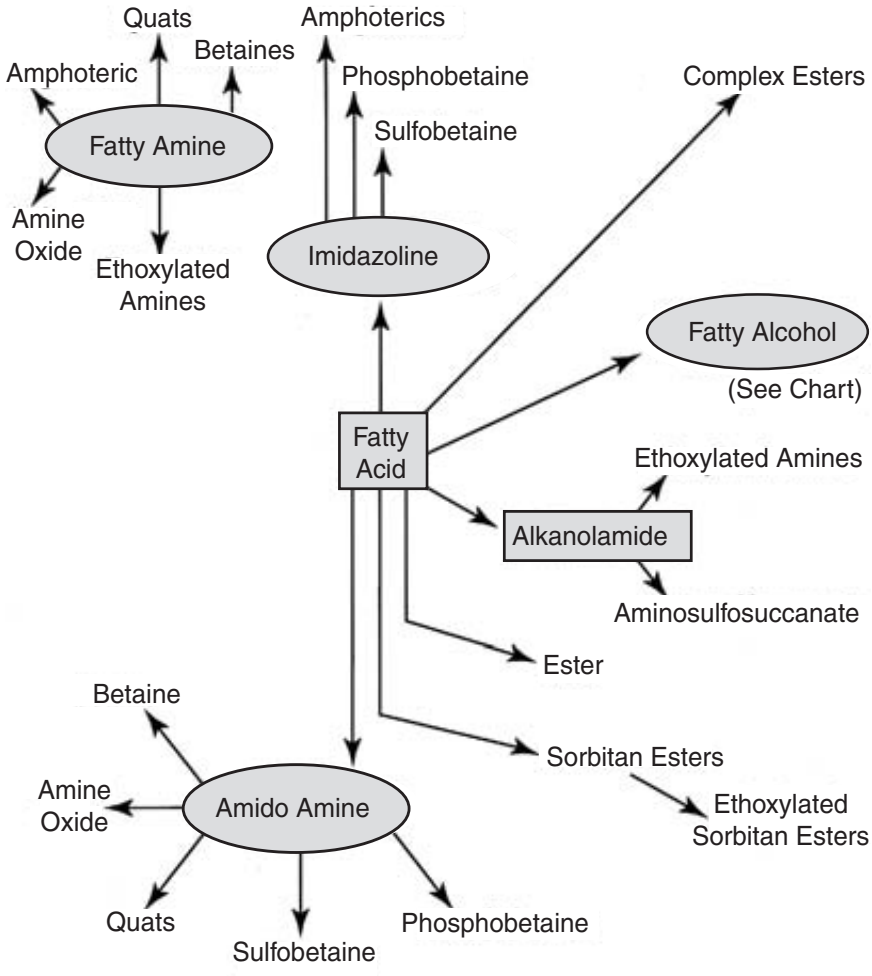
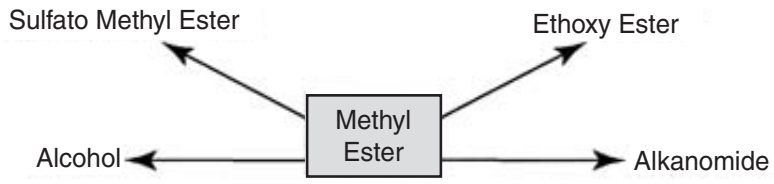


Chart 5

Methyl Ester Reactions



When a triglyceride is reacted to introduce a water-soluble group, a surfactant results.

Classification

Triglycerides can be divided into three classes:

- Class I. Products rich in components below C18.
- Class II. Products rich in C18 unsaturated components.
- Class III. Products rich in components with chain lengths higher than C18.

As will become clear, several kinds of triglycerides have similar carbon chain distributions. One can expect derivatives from oils having a similar carbon chain distribution to have very similar, often nearly identical, functional properties when derivitized into a surfactant in the same way.

Effect of Alkyl Group

One major factor that has an effect on the function of a surfactant is the number of carbon atoms in the chain of the starting hydrophobe. Other factors include the number and location of double-bonds and the presence of additional functional groups.

Generally, as one evaluates the tactile properties of a triglyceride on the skin, the lower the triglycerides molecular weight, the less oily the feel of the compound. The higher the molecular weight, the more "greasy" the feel. In surfactant preparation, detergent products and high-foaming products generally are composed of carbon atom chain distributions that peak between 12 and 14 carbon atoms. Conditioners and softeners usually have more than 16 to 18 carbon atoms. Today, there is a growing trend toward using materials with 22 or more carbon atoms for enhanced conditioning.

Blended surfactants differing only in molecular weight have been marketed for many years. The blends have different properties in formulations than either of the components alone. One good example, for which there is a patent, is a blend of cocamidopropyl betaine and oleylamidopropyl betaine. The cocamidopropyl betaine produces good foam and detergency; the oleylamidopropyl betaine produces good viscosity in many formulations and conditioning effects on hair. The patent deals with the ratios of one betaine to the other in an attempt to optimize the performance in formulations. Formulators are encouraged to consider using different types of surfactants (analogues) in a formulation and to consider using homologous products — those that differ only in the number of carbon atoms in the molecule.

Titer Point

Because the physical form and appearance of a surfactant is the first and easiest property to observe and evaluate, many problems with variation can occur. Some of the variation is a natural property of the surfactant. In dealing with surfactants, particularly those having 16 or more carbon atoms in their hydrophobes, are blends or are highly oligomeric, the surfactant as sold may be neither solid nor liquid at ambient temperature. Some products are semi-solid, and others look like a liquid

that has snow in the bottom. For these products, the concept of titer is very important. It can be illustrated by the simple question, "Is H_2O a solid, a liquid or a gas?" Although this question appears trivial, the answer depends on the conditions. If you ask the question in Alaska in January and are referring to a sample that is exposed to ambient conditions, the answer is "solid." If you ask the same question in Georgia in August under the same conditions, the answer will most likely be "liquid." If you ask that question at Yellowstone National Park's Old Faithful geyser during an eruption and refer to the H_2O in its plume, the answer is "gas." Of course, all these answers refer to atmospheric pressures. If the pressure is altered, all bets are off. This simple question on an everyday ubiquitous material illustrates the problem with asking "is a particular surfactant solid or liquid?"

An additional complication is this: Unlike many surfactants, water is a pure compound, so the transition from solid to liquid to gas occurs at a sharply defined temperature. Unlike pure water, many surfactants are composed of a series of oligomeric species differing in the number of carbon atoms present and the amount of double-bond character present, called *unsaturation*. This results not in a clean melting or freezing point but in a phenomenon called *titer*. Titer is defined as the temperature at which the first component of a compound becomes solid. Often, this can be seen as "snow" in a liquid sample. To those not well-versed in the chemistry and properties of this kind of material, it may appear that something is wrong with the material. To those with the experience, this phenomenon is a perfectly natural and expected effect.

Titer in surfactants can be compared to water in another regard. Just like accumulated snow on the ground does not instantly melt when the temperature reaches 33°F, the titer in a surfactant does not necessarily "melt" at room temperature. Temperature and time are needed to remelt the solid ester, and agitation helps the process.

Once the temperature to which a surfactant composition is exposed drops below the surfactant's titer point, a solid will form. The resulting material will no longer be homogeneous. Even if the temperature is then raised slightly, the solid will remain. Heat needs to be applied along with agitation to ensure redissolution and homogeneity of the sample.

Higher molecular weight esters offer formulators many advantages in properties over the lower molecular weight products. These include improved lubrication, conditioning and skin feel. They also require that users of such products be aware of the property of titer and observe the rules for using this kind of product.

Effect of Iodine Value

Iodine value is a measure of the unsaturation present in a particular chemical. The higher the iodine value, the more double-bonds in the molecule. The preferred test method is known as the *Wijs* procedure. This method measures the absorption of iodine monochloride by the sample and is useful for determining the concentration of nonconjugated double-bonds. A rule of thumb is that for iodine values of less than 10 the percentage of monounsaturation roughly equals the iodine value. It is important to note that some components present in a surfactant composition can

react with iodine monochloride, causing an erroneously high value of unsaturation to be reported.

Generally, as the iodine value increases, the liquidity of the oil increases, and the titer point decreases. Some oils have a high iodine value but are surprisingly resistant to rancidity. Meadowfoam seed oil is one such product. Its unusually good stability occurs because the double-bonds are not conjugated and natural antioxidants are present in the oil.

Double-bonds, in general, lower the titer point of the starting fatty material and the resulting surfactant. Triglycerides composed of chains having double-bonds

Table 1
Fatty Acid Nomenclature

Designation	Name	Formula
C6	Caproic acid	$C_6H_{12}O_2$
C8	Caprylic acid	$C_8H_{16}O_2$
C10	Capric acid	$C_{10}H_{20}O_2$
C12	Lauric acid	$C_{12}H_{24}O_2$
C12:1	Lauroleic acid	$C_{12}H_{22}O_2$
C14	Myristic acid	$C_{14}H_{28}O_2$
C14:1	Myristoleic acid	$C_{14}H_{26}O_2$
C16	Palmitic acid	$C_{16}H_{32}O_2$
C16:1	Palmitoleic acid	$C_{16}H_{30}O_2$
C18	Stearic acid	$C_{18}H_{36}O_2$
C18:1	Oleic acid	$C_{18}H_{34}O_2$
C18:2	Linoleic acid	$C_{18}H_{32}O_2$
C18:3	Linolenic acid	$C_{18}H_{30}O_2$
C20	Arachidic acid	$C_{20}H_{40}O_2$
C20:1	Gadoleic acid	$C_{20}H_{38}O_2$
C22	Behenic acid	$C_{22}H_{44}O_2$
C22:1	Erucic acid	$C_{22}H_{42}O_2$
C22:2	Clupanodinic acid	$C_{22}H_{40}O_2$
C24	Lignoceric acid	$C_{24}H_{48}O_2$
C26	Cerotic acid	$C_{26}H_{52}O_2$
C28	Montanic acid	$C_{28}H_{56}O_2$
C30	Myricic acid	$C_{30}H_{60}O_2$
C32	Lacceroic acid	$C_{32}H_{64}O_2$
C34	Geddic acid	$C_{34}H_{68}O_2$

stay liquid to lower temperatures than those consisting of saturated chains. Conjugated double-bonds — those with only one carbon between two double-bonds (-C=C-C=C-) — are effective in depressing titer point, but they can present problems with rancidity. Rancidity is a degradation process by which the double-bond is oxidized and many different molecules are thereby produced. These compounds generally have objectionable odors. Rancidity can be inhibited by the addition of antioxidants.

Table 1 lists the names of the fatty acids, the designations used in this work and the empirical formulas.

Triglycerides in Personal Care

In dealing with the chemistry of triglycerides used as raw materials in the personal care market, there are two salient factors to consider. They are carbon number and unsaturation (iodine value). The reason these are salient to chemistry is that there are marketing reasons related to using a specific oil rather than one with very similar carbon number and iodine value. Specifically, if you want the name of the oil in the derivative, that specific oil must be used.

Effect of Unsaturation

Iodine value is a measure of the unsaturation present in particular chemical. The higher the iodine value, the more double bonds in the molecule. The preferred method is known as the Wijs procedure. This method measures the absorption of iodine monochloride by the sample and is very useful for non-conjugated double bonds. A rule of thumb for iodine values of less than 10, is that the percentage of monounsaturation roughly equals the iodine value. Therefore a wax with a iodine value of 5 can be predicted to have about 5% unsaturated species present. It is important to note that other components in the composition that can react with iodine monochloride, can falsely increase the indicated amount of unsaturation. Generally, as the iodine value increases, the liquidity of the oil increases and the titer point decreases. Some oils have a high iodine value but are surprisingly resistant to rancidity. Meadowfoam seed oil is one such product. The stability is due to the fact that the double bonds are not conjugated and the presence of natural antioxidants in the oil. Some oil processors add anti-oxidants to their oils. BHT and BHA are some such antioxidants commonly added to oil. BHA is declining in it's use due to it's inclusion in California's Proposition 65 list. Antioxidants can only prevent oxidation, they cannot take a product that has started to oxidize and reverse the reaction. Surprisingly, too much antioxidant can accelerate oxidation.

Carbon Number

Carbon number is an important factor used to select products for use in both derivatives and as the triglyceride per se. Carbon number is the value obtained by multiplying the percentage of a component in a product by the number of carbon atoms in the component, then adding up all the components.

For example if an oil had the following composition:

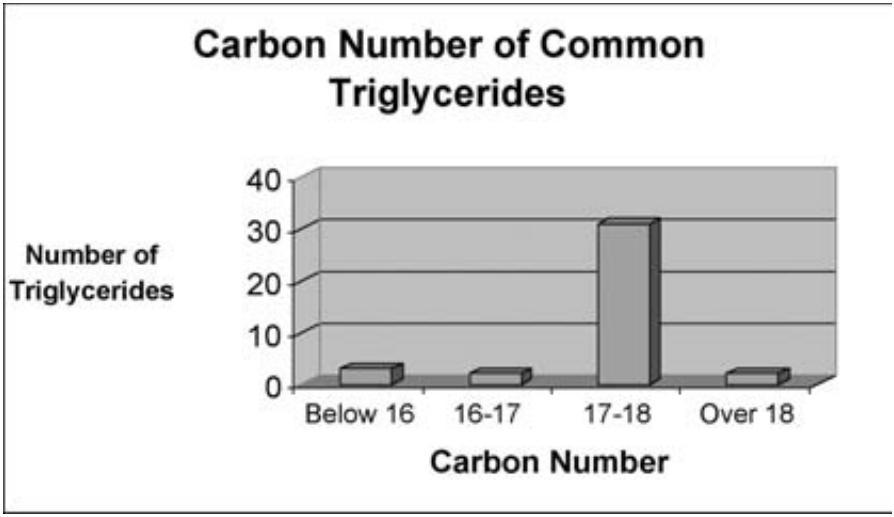
Component	% Weight
C16	20
C18	20
C18:1	20
C20	40
Total	**100**

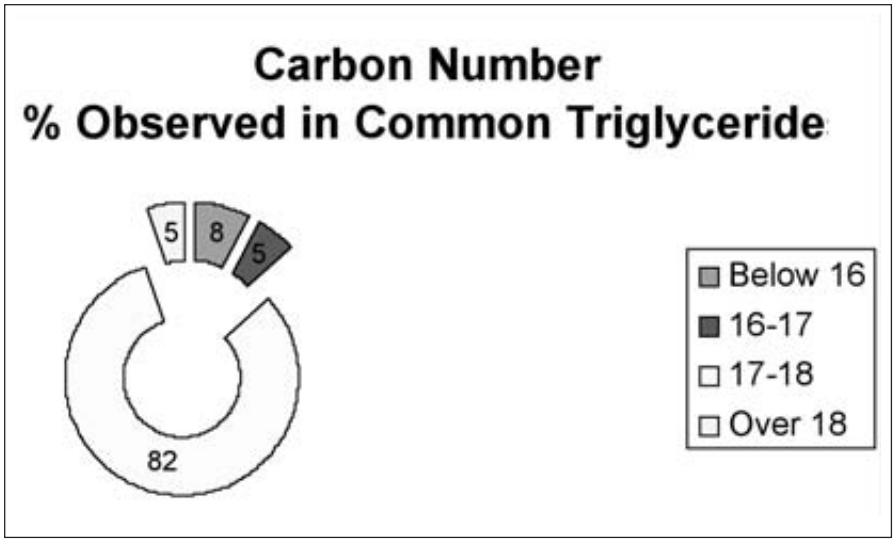
Then the carbon number calculation would be as follows:

Component	(a) % Weight	(b) Carbon Atoms in Component	Calculation (a)*(b)
C16	20	16	3.2
C18	20	18	3.6
C18:1	20	18	3.6
C20	40	20	8.0
Total	100		18.4

Carbon number = 18.4

There are several types of oils that have very similar carbon numbers, which we have then classified by unsaturation, the other salient factor. One can expect





derivatives from oils having a very similar carbon number and very similar levels of unsaturation to have very similar, often identical functional properties. The choice of which of the many oils to choose in this instance depends upon the economics of the oil or the desire of the formulator to name the oil for label and marketing purposes. As will become clear, there are many different fats, oils, waxes and butters which when derivatized result in compounds of strikingly similar carbon distributions, while having their source oil, wax, fat or butter being quite different. Thus, naming the material by the predominant species is not very enlightening to the formulator as to the source of the raw material.

It is also quite interesting that nature has provided many triglycerides that have very similar carbon numbers. In fact, of 38 triglycerides presented here, 31 have carbon numbers between 17 and 18! This also explains why the other important variable unsaturation is critical in choosing an oil for a specific application.

It is very interesting that there are only three triglycerides having a carbon number below 16. Since this is a key number for detergents, it becomes clear why coconut oil is so important to the surfactant industry.

There has been a growing demand for products based upon oils having a carbon number over 18 (for example behenic derivatives). In order to get these products, one must choose a different class of oils. The selection of the oil is a major variable, which normally eludes the formulator, being made more commonly by the derivative manufacturer. Oil selection is assuredly one important factor in formulating cosmetic products.

Effect of Carbon Number

One major factor, which has an effect upon the functionality of both the oil itself, and any potential derivative, is the number of carbon atoms in the chain. Other factors include: the number and location of double bonds and finally, the presence of additional functional groups. Generally, as one evaluates the tactile properties of

an oil on the skin, the lower the molecular weight the less oily the feel of the compound. The higher molecular weight the more greasy the feel. In surfactant preparation, detergent products and high foaming products generally peak between a carbon number of 12 and 14. Conditioners and softeners have a carbon number of 16 to 18. Today there is a growing trend toward using materials with carbon numbers of 22 or more for conditioning. Since few oils offer these high carbon numbers, fractionation of methyl esters to pure compounds if often undertaken, or alternatively hydrogenation of unsaturated oils to make saturated compounds having high carbon number.

Double bonds, in general, lower the titer point of the triglyceride, resulting in a triglyceride that stays liquid to lower temperatures. Conjugated double bonds (i.e. those with only one carbon between two double bonds (-C=C-C=C-), are very effective in depressing titer point, but can present problems with rancidity. Rancidity is a process by which the double bond is oxidized and ultimately broken. This releases many different molecules, many of which have objectionable odors. Rancidity can be mitigated at times with the addition of antioxidants, prior to the start of the rancidity process.

Finally, many oils, fats, butters and waxes, upon additional processing, lose their identity as the oil and become known by the fatty name of the predominant species present after the treatment. These processes include preparation of methyl esters, fractionation of the methyl ester and preparation of a fatty alcohol. For example, if olive oil is completely hydrogenated under high pressure, both reduction of the double bond and hydrogenolysis occurs giving predominantly stearyl alcohol, the predominant material in the mixture. In order to preserve the double bond special catalysts are used.

Carbon Number and Iodine Value for Common Triglycerides

Group 1. Animal derived triglycerides.

Triglyceride	Carbon No.	Iodine Value
Milk Fat	15.5	39

Group 2. Plant derived triglycerides.

Triglyceride	Carbon No.	Iodine Value
Coconut Oil	12.8	8
Palm Kernel Oil	13.3	19
Babassu Oil	13.4	15
Sunflower oil	16.0	130
Japan Wax	16.3	6

Triglyceride	Carbon No.	Iodine Value
Palm oil	17.1	50
Apricot Kernel oil	17.1	102
Tallow	17.3	45
Coca butter	17.5	37
Andiroba Oil	17.5	45
Mango Butter	17.5	46
Avacado oil	17.6	84
Cottonseed oil	17.6	108
Rice bran oil	17.6	105
Shea butter	17.6	60
Wheat germ oil	17.7	130
Illipe butter	17.7	49
Corn oil	17.8	123
Olive oil	17.8	84
Poppyseed oil	17.8	138
Grape seed oil	17.8	135
Sesame oil	17.8	110
Sweet Amond oil	17.9	102
Hazelnut oil	17.9	86
Soybean oil	17.9	130
Safflower oil	17.9	145
Hybrid safflower oil	17.9	140
Walnut oil	17.9	150
Canola oil	17.9	92
Peanut oil	18.0	98
Tall oil	18.0	130
Kokhum Butter	18.0	131
Cupuacu Butter	18.2	40

Group 3. Drying Triglycerides, plant derived

Triglyceride	Carbon No.	Iodine Value
Linseed oil	17.9	190
Tung oil	17.9	170

Group 4. Triglycerides having unusual components.

Triglyceride	Carbon No.	Iodine Value
Borgae oil	17.8	147
Evening primrose	17.9	152
Veronia oil	17.9	106
Ongokea oil	18.0	190
Castor oil	18.0	85
Meadowfoam oil	20.5	95
Rapeseed oil	20.6	100

Triglyceride Preparation and Processing

Triglycerides, often called "oil" are extracted from the pressing of seeds contains many ingredients, some desirable others undesirable. Crude oil is processed to separate the components. We generally take for granted the process that allows for the transformation of a plant seed into clear low odor oil suitable for cosmetic use is a process. The plant chosen for use as well as the processing used determines the properties of the oil.

The oils covered in this article are referred to as "vegetable oil." This differentiates them from "essential oils" which are often good-smelling oil that are steamed out of a variety of plant parts, including flowers, leaves, peels and some seeds. The essential oils are not triglycerides like the vegetable oils but usually "isoprenoids", that is, they come from a different chemical pathway in plants. Plants store vegetable oils (triglycerides) as energy sources for seeds when they germinate.

Steam works well to extract essential oils like coriander oil but not for triglyceride oils. Triglyceride and wax ester oils can be squeezed out of seeds using a turning screw that presses the mashed up seed against a metal barrel with slits in the side. The oil and some fine particles squeeze out the narrow slits. This operation would be called an oil expeller or seed oil press. The oil from the seed oil press can be filtered and called "virgin" oil, especially if it isn't heated up to get more oil out. The oil from the seed oil press can also be called crude oil. Alternatively, oil can be dissolved in solvent, followed by evaporating of the solvent leaving the extracted oil.

Often, seeds are flaked to increase surface area. The seeds are processed into thin flakes before pressing or solvent extraction. The flaking improves oil yield by breaking open the small oil pockets in the seeds. Sometimes the seeds are heated before flaking so that the proteins in the seed won't break down the oil or other things in the seed. The preheating is also called preconditioning. The oil comes out more easily if it is hot, but too much heat damages the oil quality.

Sometimes the seeds are crushed and formed into pieces called "collets" that have lots of holes or openings. This step also is done before solvent extraction to make the oil easier to flow out. Solvent extracted oil with some solvent still in it is called the "miscella."

Crude oil can be good enough for chemical uses, usually. A well-filtered "virgin" oil can be kept cold to remove any solid waxes that might crystallize out in a process called "winterization."

Many cosmetics applications require cold-pressed, virgin oil. On the other hand, some seeds are too low in oil to economically remove the oil by pressing. In any case, once you have the crude oil, you can move onto refining.

Refining is done by filtering the oil through clay or silica (like fine sand), which can remove color. In an operation called "degumming" alkali in water is added to the oil and some ingredients, especially fatty acids and one called""phospholipids" go into the water or settle out or are filtered out. Finally steam can be passed through the oil to remove odor in an operation called deodorization. This step also breaks down oxygen attached to the oil, which might lower oil quality.

Hopefully, after all of this refining the oil is light in color, has no odor, no oxygen breakdown products and no solid wax. The amount of oil you have left after refining is often related to the amount of crude oil you started with or to the amount of oil in the seed by the "yield" of oil from each step in the process.

The oils that are commonly used in cosmetic products are complex mixtures of different triglycerides, but also contain various other components that are useful. For example olive oil can be processed to contain highly desirable tocopherols. Solvent extraction or steam distillation would remove much of this material. If the oil was in the formulation for the benefit derived from the tocopherols, the potential variations in the processing could have dramatic consequences. The winterizing of oils, that is cooling and filtration of solids from the liquid results in a loss of the higher molecular weight fractions. Many times it is exactly these fractions that provide the unique skin feel or conditioning to the product. It should be clear that the different processes used in the preparation of an oil may be critical to functionality.

Fractionation

There are many applications in which a pure compound, rather than a mixture called a composition is desired for a particular application. In this case, the oil is derivitized into a more volatile compound, most commonly a methyl ester, then distilled into its components

Triglycerides may be easily turned into methyl esters by reaction with methanol and catalyst. Base catalysts are preferred. As the reaction proceeds, the reaction mixture turns hazy as glycerin is liberated. Once complete, the excess methanol is distilled off, glycerin removed from the bottom after it settles and the methyl ester is distilled into its fractions.

The methyl ester formed by the reaction, if not distilled is still referred to by the oil name (for example methyl cocoate). However, once fractionated the material is named by carbon distribution. Methyl cocoate is fractionated into methyl laurate, methyl myristate and so on. The triglyceride source is lost in the name of the methyl ester. The names for the common alkyl groups are given below. Distillation is a major operation used to fractionate the methyl ester mixture gotten from oils into specific defined methyl esters having the desired alkyl groups.

Class I. Products Rich in Components Below C18

Coconut Oil (Cocos nucifera)

Source

Coconut oil is the most abundant natural oil processed. Coconut oil comes from the seeds of the *Cocos nucifera* plant. It is the most common oil raw material used in the cosmetics industry. Geographically, coconut oil is cultivated principally in Southeast Asia and the Philippines. It is the major source of lauric acid (C12).

Chain Distribution

Component	Typical % by Weight
C8	8
C10	7
C12	48
C14	19
C16	8
C18	3
C18:1	5
C18:2	2

CAS Number: 8001-31-8 EINECS Number: 232-282-8
Iodine Value: 8 Titer Point: 22°C (free fatty acids)

CTFA Status

Coconut oil is listed in the Cosmetics, Toiletries and Fragrances Association (CTFA) dictionary, both *per se* and in 162 derivatives.

Palm Kernel Oil (Elaeis guineenis)

Source

Palm kernel oil is a triglyceride derived from the seed of the coconut palm (*Elaeis guineenis*). It comes from Southeast Asia.

Carbon Chain Distribution

Component	Typical % by Weight
C8	6
C10	5
C12	49
C14	15
C16	7
C18	2
C18:1	15
C18:2	2
CAS Number: 8023-79-8	EINECS Number: 232-282-8
Iodine Value: 19	Titer Point: 24°C (free fatty acids)

CTFA Status
Palm kernel oil is listed in the CTFA dictionary, both *per se* and in 19 derivatives.

Class II. Products Rich in C18 Unsaturated Components

Soybean oil (Glycine soja)

Source
Soybean oil is a triglyceride derived from the soybean (*Glycerin max*). The soybean originated in China as far back as 2,300 B.C. It later was widely cultivated in North America, most importantly in the United States, where it is a major food crop today.

Carbon Chain Distribution

Component	Typical % by Weight
C16	7
C18	4
C18:1	29
C18:2	54
C18:3	5
CAS Number: 8001-22-7	EINECS Number: 232-274-4
Iodine Value: 130	Titer Point: 21°C (free fatty acids)

CTFA Status
Soybean oil is listed in the CTFA dictionary, both *per se* and in 10 derivatives.

Corn Oil (Zea mays)

Source

Corn oil is a triglyceride derived from the wet milling of corn (*Zea mais, graminae*). It is cultivated in all temperate areas of the world. Corn oil's major use is in foods.

Carbon Chain Distribution

Component	Typical % by Weight
C16	8
C18	4
C18:1	46
C18:2	42
CAS Number: 8001-30-7 Iodine Value: 123	EINECS Number: 232-281.2 Titer Point: 17°C (free fatty acids)

CTFA Status

Corn oil is listed in the CTFA dictionary, both *per se* and in eight derivatives.

Olive Oil (Olea europaea)

Source

Olive oil is a triglyceride obtained by pressing olives. It has occupied a unique position in civilization and is the oldest oil known to man. It is produced throughout the area that once was the Roman Empire.

Carbon Chain Distribution

Component	Typical % by Weight
C16	8
C18	2
C18:1	84
C18:2	6
CAS Number: 8001-25-0 Iodine Value: 84	EINECS Number: 232-277-0 Titer Point: 20°C (free fatty acids)

CTFA Status

Olive oil is listed in the CTFA dictionary, both *per se* and in 21 derivatives. Silicone derivatives are available.

Class III. Products Rich in High Molecular Weight Components

Meadowfoam Seed Oil (Limnanthes alba)

Source

Meadowfoam oil is a triglyceride derived from the herbaceous winter plant, *Limnanthes alba*. It is grown in the southern portion of Oregon. Viewed from a distance, the flowers have an appearance of a canopy of white foam, so the name meadowfoam was given to the plant. Meadowfoam seed oil is a relatively new raw material. It is unique because it has a high concentration of fractions at or above 20 carbons and it has a unique arrangement of double-bonds. Because the double-bonds in the doubly unsaturated chain are not conjugated, as they are in linoleic acid, the oil is liquid to very low temperatures and is exceptionally stable, which reduces the likelihood of oxidation and rancidity occurring.

Carbon Chain Distribution

Component	Typical % by Weight
C20:1(n=5)	63
C20:2(n=5,13)	12
C22:1(n=5)	3
C22:1(n=13)	12
C22:2(n=5,13)	10

CAS Number: 153065-40-8 EINECS Number: N/A
Iodine Value: 95 Titer Point: 18°C

CTFA Status

Meadowfoam oil is listed in the CTFA dictionary, both *per se* and in two derivatives. Silicone functional meadowfoam derivatives and meadowfoam surfactants are likewise available.

Rapeseed (High Erucic) oil (Brassica campestris)

Source

Rapeseed oil is a triglyceride derived from the plant *Brassica napus L.* The oil is commonly called HEAR oil (high erucic acid rapeseed). It is cultivated in North America, predominantly in Canada. Recently, there has been an effort to bio-engineer the crop to produce a carbon chain distribution more like that of soybean oil. This newly engineered oil has been called *canola*. The driving factor to lower the percentage of the higher molecular weight fractions is the desired use of the material in cooking applications. In food applications, higher molecular weight fractions are considered less desirable from a health point of view. However, these fractions are desirable in surfactant products, where they provide improved substantivity and conditioning.

Carbon Chain Distribution

Component	Typical % by Weight
C16:0	2
C18:0	1
C18:1	20
C18:2	20
C18:3	2
C20:0	1
C22:1	52
C24:0	2

CAS Number: 8002-13-9 EINECS Number: 232-299-0
Iodine Value: 100 Titer Point: 13°C

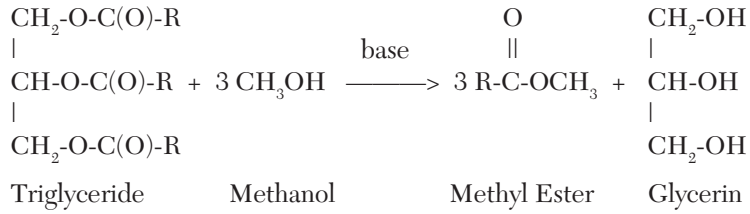
CTFA Status

Rapeseed oil is listed in the CTFA dictionary, both *per se* and in eight derivatives.

Methyl Esters

Reaction

Methyl esters are made by the reaction of triglycerides with methanol in the presence of a catalyst, as shown below.



Commercial manufacture of methyl esters is accomplished by using a continuous process. In such systems, the quality of the triglyceride is a key factor in the efficiency of the process. Henkel, a major commercial producer of methyl esters, practices the continuous process throughout the world.

Methyl esters are then separated from the glycerin and distilled to give narrow fraction products useful as raw materials for the preparation of surfactant products.

Fatty Acids

Natural Acids

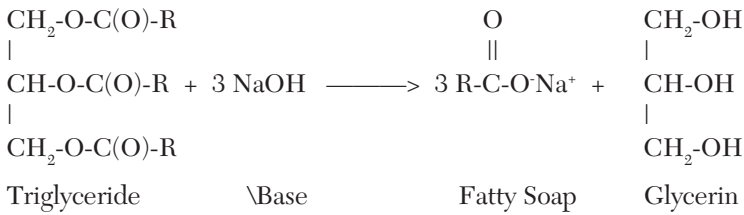
Natural acids can be made by saponification of either methyl esters or triglycerides followed by acidulation.

Reaction

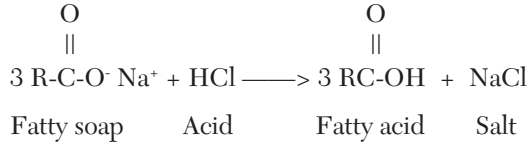
The reaction sequence, whether using methyl ester or triglyceride as a raw material, has two steps. The first is saponification with base, and the second is acidulation. If a triglyceride is used, glycerin results as the by-product. If methyl ester is used, methanol is the by-product.

Triglycerides

Saponification

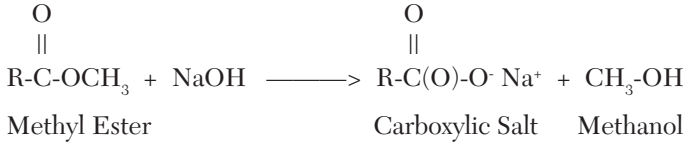


Acidulation

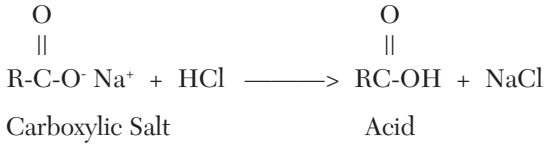


From Methyl Ester

Saponification



Acidulation



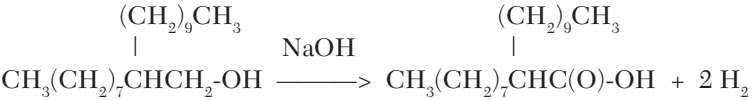
The carbon chain distribution of the resulting acid is the same as the starting raw material from which the acid is made. Consequently, if a distilled, fractionated methyl ester having a narrow carbon chain distribution is reacted to make acids, a narrow-range acid is produced. On the other hand, if a triglyceride having a wide-range carbon chain distribution is used, an acid having an equally wide carbon chain distribution results.

Guerbet Acids

The term *Guerbet* refers to a particular branch pattern that results from an aldol condensation. The compounds have a beta branch and are highly regioselective and high in purity. This unique branch pattern results in many of the desirable properties of Guerbet derivatives.

Guerbet acids are prepared by the oxidation of Guerbet alcohols to produce primary carboxylic acids. Additional information on the Guerbet reaction is provided later in the Guerbet alcohol section of this book. (See page 124.) One method by which a Guerbet acid is made is the dehydrogenation of the alcohol with alkali metal salts, a process called *oxidative alkali fusion*, which gives excellent yields of carboxylic acids.

Reaction



Octyldodecanol
(a Guerbet alcohol)

Octyldodecanoic Acid
(a Guerbet acid)

Raw Materials

The raw materials used to make Guerbet acids are Guerbet alcohols, which are oxidized to the corresponding acid.

Properties

The regiospecificity, purity and liquidity of the Guerbet acids make them useful in the synthesis of highly branched products. The effect of the branching is clearly seen when one compares the melting point of Guerbet acids with the melting point of linear acids having the same number of carbon atoms, as shown below.

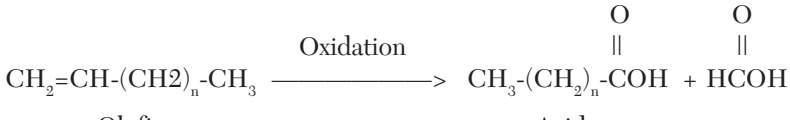
Melting Points of Various Acids

Carbon Number	Linear	Guerbet
12	44°C	- 15°C
16	63°C	17°C
20	75°C	35°C
24	84°C	48°C

Synthetic Linear Acids

One method useful for preparing synthetic fatty acids is oxidation of alpha olefins. The oxidation reaction results in the loss of one carbon atom from the alpha olefin.

Reaction



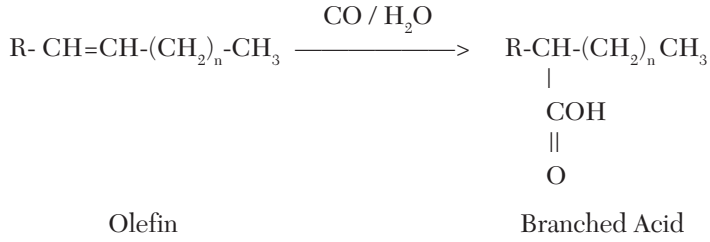
Raw Materials

Alpha olefin is a readily available raw material derived from ethylene. Alpha olefins are readily available from petroleum feedstock.

Synthetic Branched Acids

One method useful in the preparation of synthetic fatty acids is the oxidation of internal olefins. The so-called *Monsanto process* for the carbonylation of olefin is a one-step process. It is so versatile and cost-effective that it is replacing other synthetic routes to creating acids. The process adds one carbon to the starting olefin.

Reaction



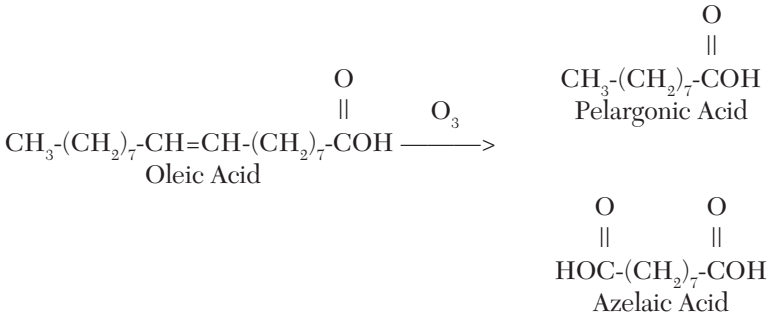
Raw Materials

Internal olefin is a readily available raw material derived from ethylene. Internal olefins are readily available raw materials from petroleum feedstocks.

Ozone Acids

Ozone acids are produced by the reaction of unsaturated acids with ozone. Ozonolysis of oleic acid is the major source for pelargonic and azelaic acids.

Reaction



The process was developed and patented in the 1950s by Emery, now Henkel. It is important because it produces diacid and odd-carbon chain acids, which are not readily available from nature.

Raw Materials

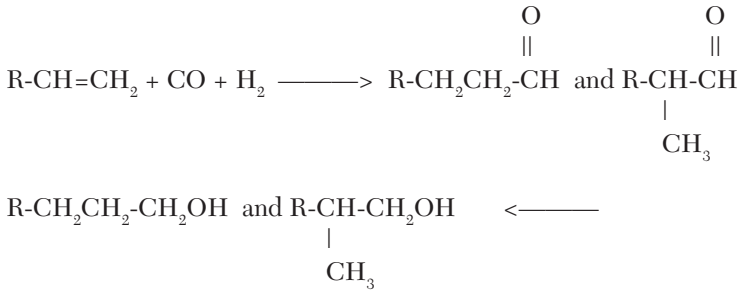
Basically, any unsaturated acid can be subjected to the process to cleave the double-bond and produce a diacid and pelargonic acid. The reaction of erucic acid results in pelargonic acid and brassylic acid 13-carbon diacid.

Fatty Alcohols

Oxo Alcohols

Reaction

Oxo alcohols are prepared by the reaction of alpha olefin with hydrogen and carbon monoxide using a catalyst, commonly a cobalt compound. The reaction occurs in two parts. The first is the preparation of the aldehyde, and the second is reduction of the aldehyde to the alcohol. What is important is that two different aldehyde compounds — one linear and the other with a methyl branch — form in the first part of the reaction. Both then rearrange into alcohols, as shown below.



Raw Materials

The raw material used in the reaction is alpha olefin, which is made from ethylene. The key factor among alcohol properties is the exact "R" distribution of the alpha olefin. Typically, the alpha olefin can be either a narrow range or a wide range.

Ziegler Alcohols

Ziegler alcohols are made by the oxidation of trialkyl aluminum alkoxylates, chain growth and subsequent hydrolysis. Continental Oil Co., Ethyl Corporation and Condea[12] developed the technology in the mid-1960s. Because ethylene is the material used in the chain growth portion of the reaction, the molecules, unlike oxo alcohols, are linear. Because of their lack of branching, Ziegler alcohols are more similar to natural alcohols than to oxo alcohols.

Reaction

$$Al(C_2H_5)_3 + 3n\ CH_2{=}CH_2 \xrightarrow{\text{Chain Growth}} Al\text{-}(R^1)(R^2)(R^3) \xrightarrow{\text{oxidation}} Al\text{-}(OR^1)(OR^2)(OR^3)$$

$$Al\text{-}(OR^1)(OR^2)(OR^3) \xrightarrow{\text{Hydrolysis}} 3ROH + \tfrac{1}{2}\,Al_2O_3$$

Ziegler alcohols are the most similar to natural alcohols both in structure and properties.

Natural Alcohols

Natural fatty alcohols are made by the reduction of methyl esters using high-pressure hydrogen. The process has been known for almost 70 years and has undergone extensive fine-tuning by the key producers. The catalyst used for the reaction determines the products prepared. If copper chromite is used as a catalyst with an unsaturated methyl ester, hydrogenation of any C=C unsaturation also occurs, resulting in a saturated species alcohol. However, if a group-specific catalyst like certain aluminum oxide is used, the unsaturation is unaffected, resulting in an unsaturated alcohol. This is the route used to make oleyl alcohol.

Reaction

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_3 + H_2 \xrightarrow[250\ C]{\text{catalyst}} RCH_2\text{-}OH + CH_3OH$$

Raw Materials

The process for preparing high-purity alcohol requires a clean triglyceride from which a methyl ester is derived. Certain materials poison the catalyst used to make the fatty alcohol. These include sulfur compounds and chlorine-containing materials. The resultant methanol is distilled off. The methyl ester used as the raw material might be a wide-cut product or fractionated into narrow-cut products. This allows for the preparation of a variety of fatty alcohol products tailored for specific surfactant synthesis.

Guerbet Alcohols

Guerbet alcohols have been known since the 1890s when Marcel Guerbet first synthesized these materials.[13]

Reaction

The Guerbet reaction sequence, which bears the inventor's name, is related to the aldol reaction and occurs at high temperature under specific catalytic conditions. The reaction can be represented by the following equation:

$$2\ CH_3(CH_2)_9OH \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3(CH_2)_9CHCH_2OH + 2\ H_2O$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (CH_2)_7CH_3$$

Decanol 2-octyldodecanol

A Guerbet alcohol has twice the molecular weight of the reactant alcohol, minus a mole of water. The overall reaction appears simple. The reaction actually proceeds by a number of sequential steps. These steps are as follows:

- Oxidation of alcohol to aldehyde.
- Aldol condensation after proton extraction.
- Dehydration of the aldol product.
- Hydrogenation of the allylic aldehyde.

Properties

The regiospecificity, purity and liquidity of Guerbet alcohols make them good raw materials for synthesis of highly branched products. The effect of the branching is clearly seen when one compares the melting point of Guerbet alcohols with the melting point of linear alcohols having the same number of carbon atoms, as shown below.

Melting Points of Various Alcohols

Carbon Number	Linear	Guerbet
C12	24° C	- 30°C
C16	50° C	- 18°C
C18	8° C	- 8°C
C20	62° C	0°C
C24	69° C	19°C

General Properties

Guerbet alcohols are high molecular weight. Therefore, they:

- Have low eye and skin irritation properties.
- Are branched, so they are liquid to extremely low temperatures.
- Have low volatility.

Fatty Alcohol Properties			
Designation	**Prepared From Carbon**	**Numbers Possible**	**Branching**
Natural	Triglycerides (Oils)	Even only C8 to C18	Essentially none.
Oxo	Hydroformylation of olefin	Odd or even	Present, sometimes extensive.
Ziegler	Aluminum alkyl oxidation of ethylene	Even	Little present.
Guerbet	Linear alcohol Oxo alcohol	Even Even	Beta branched. Beta and methyl branched.

- Are primary alcohols, so they are reactive and can be used to make many derivatives.
- Are useful as superfatting agents to re-oil the skin and hair.
- Are good lubricants.

Guerbet alcohols are essentially saturated. Therefore, they:

- Exhibit very good oxidative stability at elevated temperatures.
- Have excellent color, initially and at elevated temperatures.
- Exhibit improved stability over unsaturated products in many formulations.

Guerbet alcohols are used commonly in personal care applications, most notably lipsticks.

Chapter 2
Amphoteric Surfactants

Compounds classified as "amphoteric surfactants" are an important class of surfactants. There are several members of the class, but the nomenclature used to classify these materials has been confused and debated over the years. Initially, amphoteric surfactants were defined as compounds having a structure that under some aqueous condition has both a positive and negative charge within the same molecule.

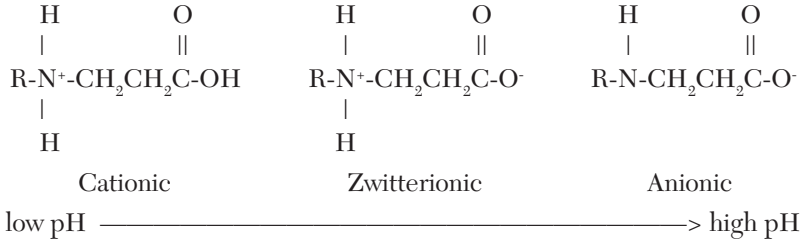
Over the years, the definition of amphoteric surfactants has been modified and expanded to provide more information on the exact nature of the surfactant as a function of pH. This has led to some confusion. The overall classification of amphoteric surfactant has several subgroups. They include true amphoterics and ampholytes. There is also reference made to so-called *zwitterionic compounds*.

As will become clear, the subdivisions of the amphoteric class are determined by the ability to support one, two or three types of charges as the pH of the solution changes. True amphoterics can exist with anionic (-), cationic (+) or zwitterionic (- and +) charges, depending on the pH. Ampholytes have a fully quaternized nitrogen and consequently cannot lose their positive charges. As a result, they exist as either zwitterionic or cationic compounds. They cannot exist in an anionic (-) state because the positive charges on the nitrogen are always present. Certain molecules have their positive and negative charges so closely related that they continue to exist as zwitterionic compounds regardless of the pH. Sulfobetaines are an example of zwitterionic compounds.

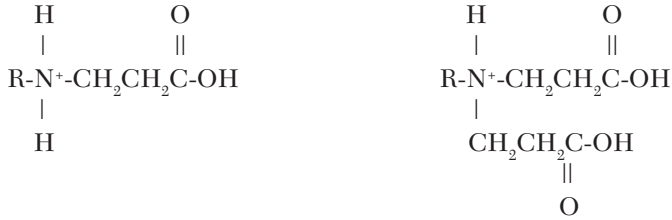
The consumption of amphoteric surfactants for personal care formulations is relatively low compared with other classes of surfactants. However, living systems, like cells, make use of naturally occurring amphoteric surfactants almost exclusively. It is likely that in the future more amphoteric surfactants that mimic biologically active surfactants will be developed for use in personal care applications. It is also quite likely that these amphoteric surfactants will be less irritating and more biodegradable than many of the surfactants they replace in formulations.

Propionates

The propionates are true amphoteric surfactants — they are capable of existing in three distinct forms as a function of pH, as shown on the next page.



The propionates are further divided into two classes, the monocarboxylic form called the amino and the dicarboxylic called the imino. The following is a representative structure of the two classes in aqueous solution at an acidic pH.



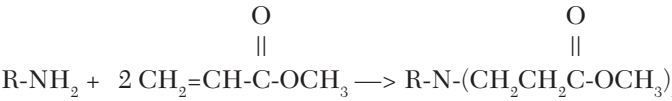
Amino **Imino**

Reaction

The propionate preparation reaction is carried out in two steps as follows:

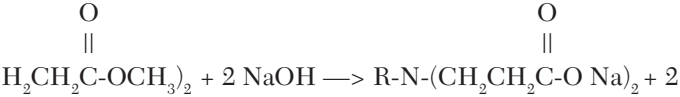
Step 1: Synthesis of the Acrylate Ester

In this step the amine is added across the double-bond of the methyl acrylate to produce a methyl ester. The reaction is carried out under anhydrous conditions, generally with a catalyst, as shown below.



Step 2: Saponification of the Acrylate Ester

In this step the methyl ester is saponified with base to make the desired salt and methanol. The reaction is carried out in aqueous solution, and the methanol is generally distilled off, as shown below.



In the case of the monocarboxylic product (the amino form), one mole of base is reacted with the adduct from Step 1. In the case of the dicarboxylate (the imino form), two moles of base are reacted with one mole of the adduct from Step 1.

Applications

The applications properties of the propionates depend on the ratio of amino to imino. The principal functional differences are as follows:

(Predominant Species)		
Function	**Amino**	**Imino**
Wetting	Fast	Slow
Water solubility	Lower	Higher
Surface Activity	Higher	Lower
Lipophilicity	Higher	Higher
Solubilization	Lower	Higher

Propionates have what is referred to as *zwitterionic ranges*. (See the graphic below for the zwitterionic ranges of several common propionates.) Within the zwitterionic range, the compound has a positive and negative charge within the molecule and, therefore, is ionically balanced without a counter ion. Within their zwitterionic pH range, propionates have minimal solubility. This range varies with the product chosen, but it is usually between two and four. The exact value observed for the isoelectric range for a product is determined by the exact alkyl distribution of the amine used as a raw material, the amino, imino ratio, and impurities and by-products. The isoelectric range is a salient property for this class of compounds. A dilute aqueous solution of surfactant will exhibit a haze in this range. This lack of solubility can be used to obtain maximum substantivity — attachment of a surfactant to a surface — within this pH range.

The propionates are primarily cationic below the isoelectric range, amphoteric within it and anionic above it. Actually, an equilibrium of all three forms exists at all except the most extreme conditions of acidity and basicity. At pH values near the isoelectric range, the propionates are strongly amphoteric. As the pH tends further toward acidity or basicity, amphoterism decreases, and the cationic or anionic species predominate.

At a pH of approximately 4.5-8.5, propionates can perform more than one function at the same time. The cationic nitrogen group, for example, will provide substantivity, and the carboxyl group will provide detergency and foaming action.

ZWITTERIONIC RANGES	
Propionate	**Isoelectric Range pH**
N-Coco B Amino Propionic Acid	2.9–4.5
Disodium N-Tallow B Imino Dipropionate	1.3–4.7
Disodium N-Lauryl B Imino Dipropionate	2.4–4.0
Partial Sodium salt of N-Lauryl B Iminodipropionic Acid	2.4–4.2

Propionates are stable over a wide pH range. Consequently, they can be used for their conditioning and detergency attributes in products having either high or low pH.

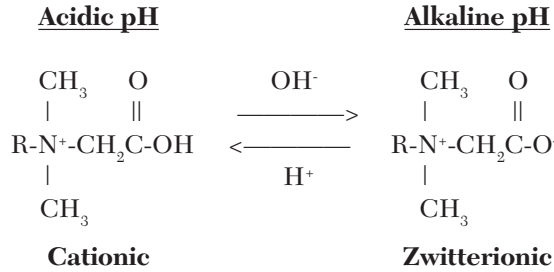
Propionates are good detergents, but they are not as mild as the imidazoline derived amphoteric surfactants or amidoamine-based products. This is thought to be related to the amido function present in the imidazoline and amido betaine products. A recent patent describes the existence of an amido propionate that is claimed to be very mild. The lack of the amido function makes these materials more stable to hydrolysis at extremes of pH.

The pH of the formulation has a dramatic effect on the foam of propionates. At neutral and alkaline pH values, the compounds foam well. At their isoelectric range, the foam is essentially zero, and below the isoelectric range conditioning properties are observed. Below their isoelectric range, the compounds are protonated and exist as cationic surfactants. This explains their substantivity.

Alkyldimethyl Betaines

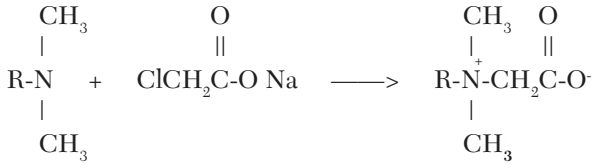
The class of ampholyte compounds classified as betaines was discovered in 1876. The first known member of the class was isolated from beets (*beta vulgaris*). The importance of this class of surfactants has grown in recent years with the growing interest in mild surfactants.

Betaines have a quaternized nitrogen function and a carboxylic function. The compounds are ampholytes because they exist in only two forms as a function of pH. This distinguishes them from amphoterics. The nitrogen is always quaternized, making it impossible for it to lose its charge. Consequently, the structure of the betaine varies with pH of the aqueous solution. The structures are as follows:



Reaction

To prepare a betaine, alkyldimethyl amine is reacted with sodium chloroacetate in water. The organic chlorine reacts, and inorganic chloride ion is generated, as shown below.



Properties

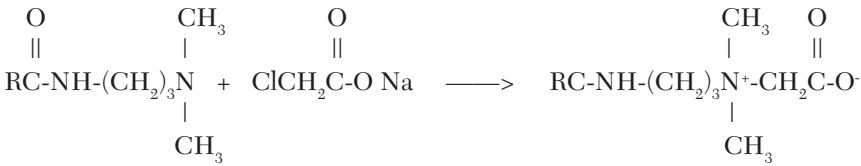
Alkyl betaines, unlike their amido analogues, are a class of compounds that are very stable under conditions that would hydrolyze the amido group in the alkylamido betaine. These conditions include strong acid or base and an oxidizing environment. The personal care applications where this may be useful include hair permanent formulations, hair relaxer formulations and alkaline conditioners. The alkyl betaine has a tendency to be more irritating to the skin and eyes than the comparable amido compound. Cocobetaine produces a good level of foam and has good substantivity to hair and skin.

Alkylamido Betaines

This class of betaine has an added amido function present, which alters the performance of the molecule. This class generally has increased foam stability, is milder and can be formulated to a higher viscosity than the nonamido products. It has less hydrolytic stability when formulated at extremes of the pH range.

Reaction

To prepare an amido betaine, an alkylamidoamine is reacted with sodium chloroacetate in water. The organic chlorine on the sodium chloroacetate is reacted to become chloride ion. The tertiary amine concentration drops as the reaction continues, as shown below.



Amidoamine Sodium chloroacetate Amido betaine

Properties

Cocamidopropyl betaine is a very important surfactant used in the personal care market. The amido betaine products are very mild, high-foaming detergents that are used extensively in shampoos, bubble bath products and other cleansing products. Cocamidopropyl betaine is a very mild detergent that has some conditioning effects. Being an amphoteric, cocamidopropyl betaine is compatible with many anionic surfactants in many different ratios.

In working with cocamidopropyl betaine, one must be aware that there are two kinds of products commonly referred to as *cocamidopropyl betaines*, one derived from coconut oil and the other derived from fatty acid. The big difference is the by-product produced by the reaction. If the acid raw material is used to produce the amidoamine, then water is the by-product. Water is removed during the reaction. However, if coconut oil, a triglyceride, is used, the by-product glycerin remains in the product and acts as a diluent. The presence of glycerin in the final product can affect the viscosity-building capabilities of the resulting betaine.

Products having other alkyl chain products have been offered over the years, attempting to capitalize on particular functional attributes. For example, lauramidopropyl betaine is said to have a higher foam level than the cocamidopropyl betaine product. In addition, several manufacturers have developed low-salt versions of the amido betaines. These products have a tendency to be less corrosive to metal tanks at low pH and can be formulated into systems in which chloride ion would reduce viscosity. The negative effect of salt on the formulation viscosity would be particularly noticed in highly concentrated, high-viscosity products. One must be careful to determine if any solvents are present in the low-salt versions of these compounds.

Alkylamido Betaines

Often an improvement to an existing surfactant occurs as a result of insightful minor changes that fulfill a customer need. Betaines in general and cocamidopropyl betaine in particular have become a workhorse of the cosmetic industry. They are truly a workhorse. From time to time, there arise opportunities to modify them to meet specific customer needs.

1. Low Salt Betaines

Betaines are synthesized by the reaction of sodium monochloro acetate and a tertiary amine. The reaction is carried out most commonly in water, and produces sodium chloride as a by-product.

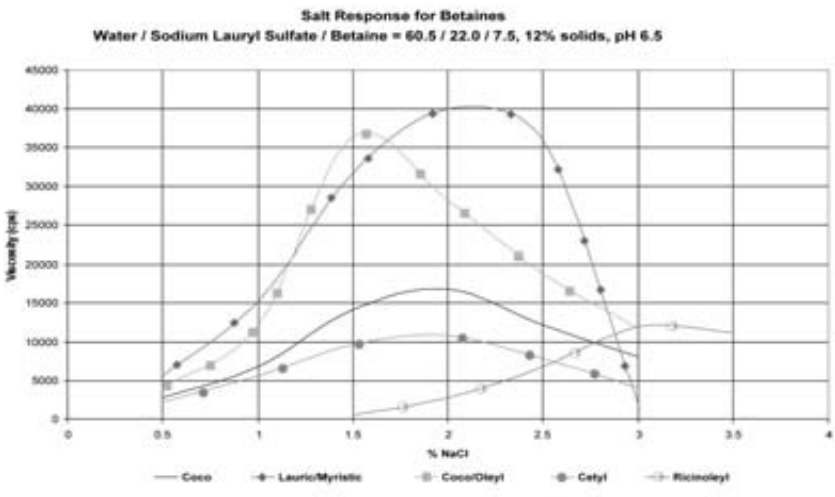
The salt containing betaine can be corrosive, most importantly in steel vessels. In order to overcome this problem and to produce a low salt version, several manufacturers have prepared the betaine, not in water, but in polar solvents in which sodium chloride is insoluble. Such a solvent is isopropanol. As the reaction progresses, the sodium chloride forms a solid and is subsequently filtered off. The lower limit of the sodium chloride concentration is determined by the amount of water that gets into the reactor. After filtration or centrifugation to remove the salt, the product is placed into water and the isopropanol is removed.

The low salt products generally have less than 1% NaCl as opposed to over 5% NaCl with the standard technology. The resulting betaine is not only less corrosive, but has found use in formulations where the salt curve requires less salt than the sum of the salt in the formulation's ingredients. This is commonly seen in gelled systems using amphoteric surfactants and betaines.

2. Lauric Myristic Amido Betaine

Many times customers become interested in the performance of the raw material and not merely the cost. Cocamido propyl betaine can be replaced in formulation by a a number of products, including a 70% Lauric 30% Myristic amido propyl betaine that does not contain glycerin (that is the product is not made from coconut oil, but a fractionated product having a narrower alkyl chain, or even a castor based betaine.

The Lauric Myristic amido propyl betaine is very efficient in increasing viscosity and stabilizing foam in shampoo and related systems. While this technology is not new, it has not received the exposure to formulators that it should.



FOAM PROPERTIES

COCO:	Cocamidopropyl betaine Highest overall foam height but the least stable, generates the quickest flash foam.
LAURIC/MYRISTIC:	Lauramidopropyl betaine Densest foam of all but less voluminous than coco, requires more mixing time to disperse.
CETYL:	Cetyl betaine Second to lauric in foam density but has the longest sustained foam.
COCO/OLEYL:	Cocamidopropyl betaine and Oleamidopropyl betaine Moderate foaming with good flash foam, open bubble structure.
RICINOLEYL:	Ricinoleamidopropyl betaine Moderate but dense foam with creamy texture.

3. Cetyl Betaine

There has been a recent trend toward increasing the carbon number in many surfactants. That is going from C12 to C16, or even C22. This trend has implications on many functional attributes, for example conditioning. A C-22 betaine will provide conditioning, but very little foam.

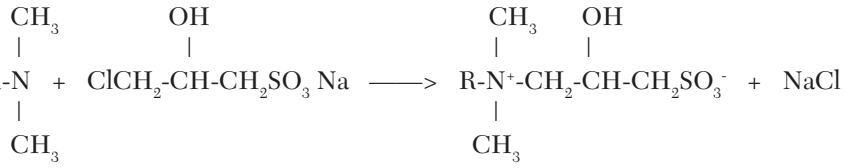
The increasing of the carbon number from 12 to 16 in an alkyl betaine (that is one without an amido group), results in an excellent product. The product gives a dense foam that has an outstanding skin feel. The product is mild and provides detergency. This type of product finds use in many types of products including hand wash formulations.

Sulfobetaines

Sulfobetaines are a class of surfactants that are sulfur-containing analogues of betaines. They have a quaternized nitrogen function and a sulfonate (SO_3) function. The compounds are ampholytes because they exist in two forms as a function of pH.

Reaction

To prepare an alkyl sulfobetaine, alkyldimethyl amine is reacted with 3-chloro-2-hydroxypropyl sulfonate in water, as shown below.



Surfactants with a hydroxypropyl-linking group require special attention to potential toxicity issues associated with oxirane chemistry. Specifically, the 3-chloro-2-hydropypropyl sulfonate is made by the reaction of epichlorohydrin and sodium sulfite. Because the chemistry is based on oxirane reactions, the potential for residual epoxy content must be addressed. Properly controlling the reaction conditions will result in a material that has very low levels of residual epoxide.

Properties

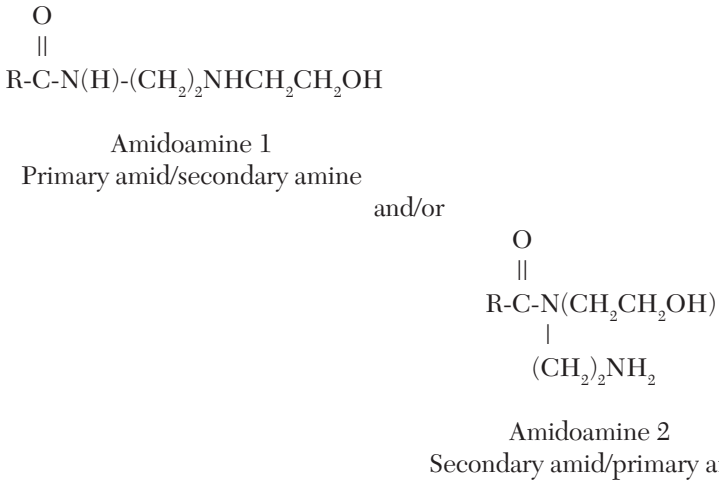
Sulfobetaines are claimed to be some of the most substantive materials to hair and skin. Historically, sulfobetaines, sometimes referred to as *hydroxy-sultaines*, were used as conditioners for wool. They provide moderate foam and conditioning properties. Cocamidopropyl sulfobetaine has the Cosmetics, Toiletries and Fragrances Association name Cocamidopropyl sultaine. This material is used in shampoos and bubble bath products.

Imidazoline Amphoterics

Chemistry

Amphoterics based on imidazolines were disclosed before World War II, but they attracted little commercial interest until the 1950s. Imidazoline-derived amphoteric surfactants are made in a two-step process. Generally, the imidazoline is hydrolyzed under conditions of controlled pH to give the indicated amidoamine. Much work has been done in recent years to elucidate the exact structure of the imidazoline-based amphoteric, but the exact chemistry remains elusive. In fact, as analytical sophistication grows, more components are discovered. The key in using these products is to buy the product that is the most consistent and is made by a process that remains unchanged by the manufacturer.

There are many different specific process steps used to make imidazoline-based amphoterics. The specific condition under which the imidazoline is hydrolyzed is an area of extreme interest. This is because there are two kinds of amidoamine compounds that can by made by hydrolysis, as shown below.



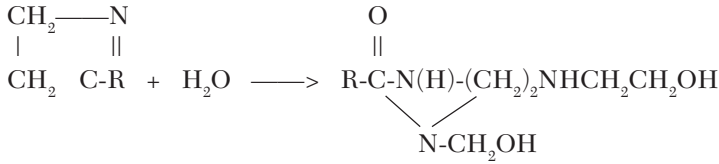
Amidoamine 1 can react with only one mole of sodium chloroacetate, adding only one carboxyl group. Amidoamine 2 can react with two moles of sodium chloroacetate, adding two carboxyl groups. To the extent that amidoamine 1 forms, the attempt to react it with two moles of sodium chloroacetate will result in the formation of one mole of amphoteric and one mole of sodium glycolate. The amphoteric of amidoamine 1 is less water-soluble and less desirable than the amphoteric derived from amidoamine 2.

The ratio of the different amidoamines determines the stability and performance of the resulting amphoteric. The ratio of compound affects viscosity, foam, performance and stability. The imidazoline compounds are not truly amphoterics

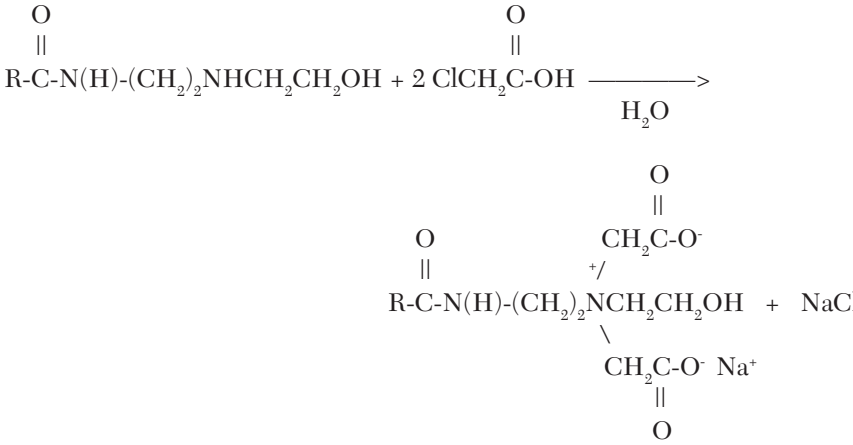
for the same reason that betaine compounds are not amphoterics: If the nitrogen is fully reacted with the sodium chloroacetate, the resulting surfactant is capable of existing in only two forms, cationic and zwitterionic. The difference in the amidoamine ratios and the conditions under which the amidoamine is chloroalkylated can result in batch-to-batch and vendor-to-vendor variation. Extreme care must be exercised in selecting a compound member of this class of compounds.

Reaction

Hydrolysis



n-Chloroalkylation



Properties

Imidazoline-derived amphoteric polymers are mild detergents. They are generally formulated with nonionic surfactants, such as sorbitan esters, for use in mild formulations like baby shampoos.

Because the exact structure of imidzoline amphoterics varies as a function of the process used to make them, care must be exercised to avoid manufacturer-to-manufacturer variation. Because several by-products can be found in imidazoline-derived amphoterics, it is recommended that all materials be placed in a refrigerator as purchased and cut 50/50 with water. No separation should be observed at 30 days.

Analysis of Amphoteric Surfactants

Instrumental Analysis

All amphoteric surfactants should be evaluated by Fourier transform infrared analysis. This instrumental technique is highly automated and when coupled with a computer analysis interface can locate small differences in products. These small differences might not be observable to the naked eye, so the use of sophisticated analytical instruments is strongly suggested. These techniques save time and money and are quite sensitive.

Wet Analysis

The evaluation of surfactants in this class is based on the fact that the surfactants possess carboxylic acid groups and amino groups. The ratios of these are important. The following analyses are recommended:

- Acid value
- Alkali value
- Zwitterionic point
- Solids
- NaCl
- Glycerin
- Bleaching agents
- Refrigerator stability

Information from Dr. Martin Rieger's Surfactant Encyclopedia: Amphoteric Surfactants

Substances are classified as amphoteric only if the charge on the hydrophobe changes as a function of the pH. Surfactants that carry a positive charge in strongly acidic media, carry a negative charge in strongly basic media, and form zwitterionic species at intermediate pHs are amphoteric:

$[RNH_2CH_2CH_2COOH]^+ X^-$
Low pH; Cationic Hydrophobe

$[RN^+H_2CH_2CH_2COO^-]$
Intermediate pH; Zwitterionic Hydrophobe

$[RNHCH_2CH_2COO]^- B^+$
High pH; Anionic Hydrophobe

In these structures, X– represents an unidentified anion (such as Cl-) and B+ an unidentified cation (such as K+). In light of this definition, the number of truly amphoteric surfactants used in cosmetics is quite small. Amphoteric surfactants are subdivided into two major classes:

A. Acyl/dialkyl ethylenediamines and derivatives
B. N-Alkyamino acids

A. Acyl/dialkyl ethylenediamines and derivatives

Chemical Properties

The amphoteric compounds in this class originally were viewed as heterocyclic derivatives of imidazolines. Later chemical studies demonstrated that imidazolines are formed during the synthesis of these substances from a long-chain carboxylic acid(or a derivative) with aminoethyl-ethanolamine (NH2-CH2-CH2-NH-CH2-CH2OH).

The resulting 2-alkyl hydroxyethyl imidazoline is subsequently hydrolyzed during the alkylation step (commonly with chloroacetic acid or ethyl acrylate). During alkylation, one or two carboxyalkyl groups react to form a tertiary amine and an ether linkage. Different alkylating agents can yield different tertiary amines, such as the hydroxypropyl sulfonates.

The nomenclature of these compounds is further confused by several name changes mandated by regulatory review.

Substances in this group are closely related and may be supplied as salts or as free acids. They are not pure chemical entities but contain various compounds formed during their synthesis. The structures believed to be the principal components of these surfactants are shown later. The cation normally associated with the "ampho" compounds is Na+.

Despite the presence of impurities, these substances perform as amphoteric substances during use and are present as zwitterions in the neutral pH range. The principal impurities are amine soaps, alkylation products of the starting amine, and various complex secondary amines.

As a rule, all members of this class are water-soluble.

Physical Properties

These surfactants are commonly distributed as aqueous solutions or pastes.

Uses

The amphoterics in this class are mild detergents but relatively poor emulsifiers. They are compatible with all other types of surfactants and can tolerate hard water. They can form complexes with anionic surfactants. They reduce the tendency of the anionics to produce eye irritation but do not interfere with foaming.

As a result, they are widely used in shampoos, especially those designed to minimize eye irritation and eye stinging. They leave the hair soft and manageable and act as antistatics. These desirable properties depend on the pH of the finished product, which normally should be between 6.5 and 7.5.

Stability

The amphoterics in this class all possess an amido group that may be hydrolyzed at extreme pH conditions. Because such conditions are not encountered normally in cosmetic practice, these materials may be considered stable.

Safety

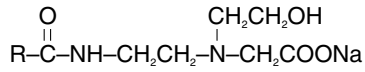
The mildness of these surfactants is concentration-dependent, and they may cause eye irritation in concentrated solutions (above 20%). At more normal concentrations, they are well-tolerated by skin and mucous membranes.

B. N-Alkylamino acids

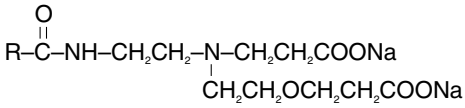
This class of amphoteric surfactants is derived from various amino acids, and its members do not possess the hydroxyethyl grouping. Alkylation of the primary amino groups of an amino acid leads to secondary and tertiary amines that, as a rule, are more basic than the original primary amine. In addition, some of the alkyl substituents may carry a second amino group that provides an additional basic center.

Many N-alkylamino acids are simple alkyl derivatives of b-alanine or of b-N(2-carboxyethyl)-alanine. Others exhibit structures analogous to those of the natural a-

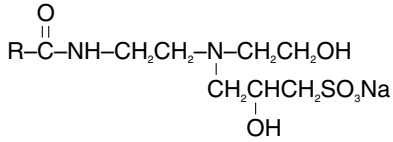
Generic acyl/dialkyl ethylenediamines



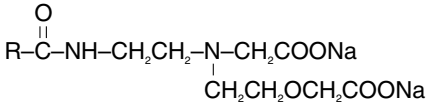
Sodium acylamphoacetate



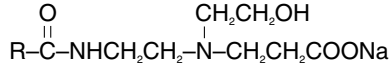
Disodium acylamphodipropionate



Sodium acylamphohydroxypropylsulfonate



Disodium acylamphodiacetate



Sodium acylamphopropionate

Specific members

Disodium cocoamphocarboxymethylhydroxy-propyl sulfate
Disodium cocoamphodipropionate (CIR)
Sodium cocoamphoacetate (CIR)
Sodium lauroampho PG-acetate phosphate
Sodium tallowamphopropionate
Sodium undecylenoamphopropionate

amino acids. The compounds in this group are available as free carboxylic acids or, more commonly, the corresponding sodium salts. When fully neutralized with alkali, these substances behave as amines. Only when the pH is adjusted to about 6 do they exhibit their zwitter-ionic character.

The sodium salts of the alkylamino acids possess high water solubility. The zwitterionic forms, especially those of the alkylaminopropionic acids, are not as water-soluble as the iminopropionates.

Physical Properties

Although these amino acids and their salts are available as solids, they are also distributed in solution form.

Uses

The alkylamino acids foam copiously in the alkaline or neutral pH range. At low pHs, they behave as cationics and lose their foaming power. In their zwitterionic, forms they are substantive to hair and find use in all types of hair products. They also can be used as emulsifying agents.

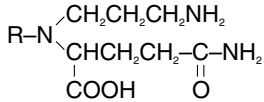
Stability

N-Alkylamino acids are not readily hydrolyzed by acids or bases and exhibit excellent stability under normal use in cosmetics.

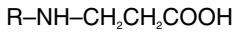
Safety

Based on their usage, it is concluded that N-alkylamino acids are safe in cosmetics.

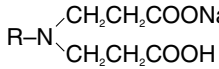
Generic N-alkylamino acids



Aminopropyl alkylglutamide



Alkyl aminopropionic acid



Sodium alkyliminodipropionate

Specific members

Aminopropyl laurylglutamide
Dihydroxyethyl soya glycinate
Lauraminopropionic acid

Chapter 3
Anionic Surfactants

Fatty Alcohol Sulfates

To the cosmetic chemist, fatty alcohol sulfates and their ethoxylated relatives (fatty alcohol ether sulfates) are perhaps the most commonly used class of anionic surfactants. The importance of this class of materials is apparent when one realizes that they are components in all 10 of the leading shampoos. Sulfates are also ubiquitous in other personal care products.

The term *sulfate* refers to any product that has an SO_4 group linked to a fatty moiety. The linkage is carbon to oxygen to sulfur (C-O-S). This distinguishes the class from the sulfonate group (SO_3) in which the carbon is directly linked to the sulfur atom. The presence of the C-O-S bond means that sulfates can be hydrolyzed at low pH to obtain alcohol and inorganic sulfate. By contrast, sulfonates are stable in acid.

Reaction

The sulfation reaction is conducted in two steps. The first is the reaction of the fatty alcohol with sulfating reagent, generally SO_3, to produce a so-called *sauer ester*. Sauer is German for acid. This sauer ester is metastable and must be neutralized within a short time of preparation, or hydrolysis will occur.

Neutralization is the second step. Here the sauer ester is neutralized with base in water to make the desired sulfate.

Sulfation

$$ROH + SO_3 \longrightarrow ROSO_3H \text{ (Sauer Ester)}$$

Neutralization

$$ROSO_3H + NaOH \xrightarrow{H_2O} ROSO_3Na + H_2O$$

The same process is carried out for the preparation of the ether sulfate.

Sulfation

$$RO(CH_2CH_2O)_3H + SO_3 \longrightarrow RO(CH_2CH_2O)SO_3H \text{ (Sauer Ester)}$$

Neutralization

$$RO(CH_2CH_2O)_3SO_3H + NaOH \xrightarrow{H_2O} RO(CH_2CH_2O)_3SO_3Na + H_2O$$

Chlorosulfonic acid (CSA) is also used as a sulfating agent. CSA is HSO_3Cl. It is a milder sulfating reagent than SO_3. Under similar conditions, fewer by-products at lower concentrations can be expected using CSA. However, equally as important as the sulfation reagent chosen are the conditions under which the sulfation is run. Products equally well suited to use in personal care products can be made using either reagent. The formulator may encounter a number of product nuances using products from the different processes.

Properties

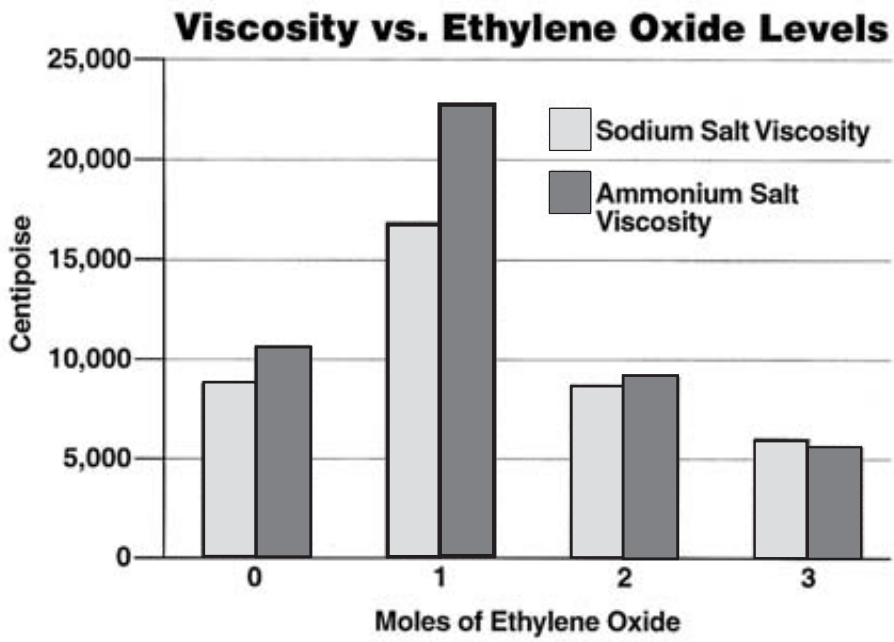
Foam and viscosity of the formulation are two important properties to formulators when selecting which fatty alcohol sulfates or fatty alcohol ether sulfates will be used in a given cosmetic product. Using a simple formulation, shown below, it is possible to show the effect of the structure of the sulfate on several key performance properties.

FORMULA "A"

Test Sulfate or Ether Sulfate	12.0
Cocamid DEA (triglyceride-derived)	2.0
Sodium Chloride	3.0
Water	QS
	100.0

Moles of Ethylene Oxide	Sodium Salt Viscosity	Ammonium Salt Viscosity
0	8,700 cp.	10,500 cp.
1	17,200 cp.	22,400 cp.
2	8,800 cp.	9,100 cp.
3	5,800 cp.	5,500 cp.

As shown in the chart on the next page, the number of moles of ethylene oxide present in the fatty alcohol ether sulfate has a dramatic effect on viscosity.



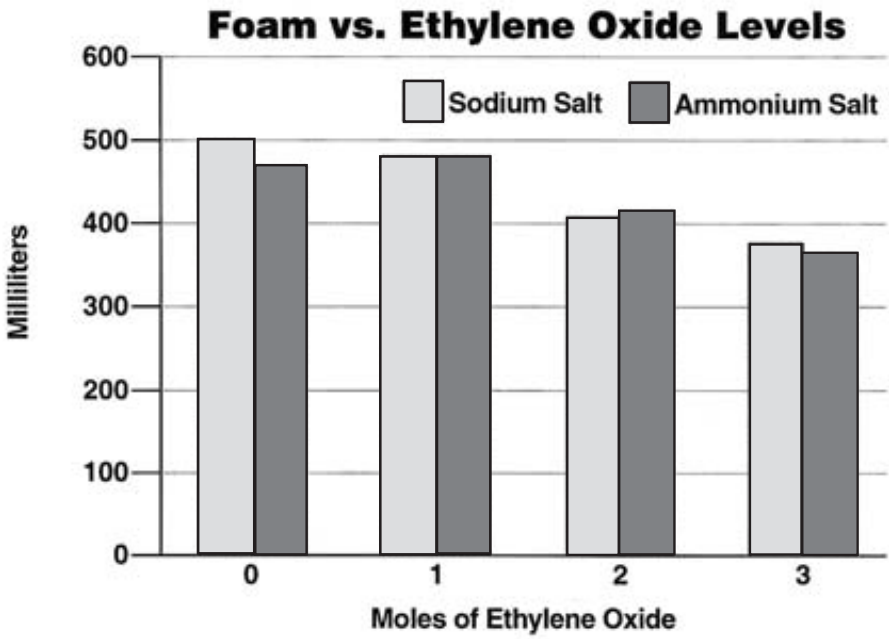
Foam Methodology

The foam methodology is as follows: 150 ml of a 0.5% active aqueous solution of the test material is prepared using water having 50 ppm hardness. The solution is heated to 30°C. The solution is added to a blender and stirred at medium speed for 10 seconds. The foam is then placed in a graduated cylinder and measured.

Moles of Ethylene Oxide	Sodium Salt Foam	Ammonium Salt Foam
0	500 ml	450 ml
1	475 ml	475 ml
2	415 ml	420 ml
3	365 ml	350 ml

As shown in the chart on the next page, the number of moles of ethylene oxide present in the fatty alcohol sulfate also has a dramatic effect on foam.

Fatty alcohol sulfates *per se* are, by themselves, irritating to eyes and defatting to skin. Consequently, they are not used as the only surfactants in most formulations. The sulfate is an excellent detergent, produces copious, dense foam, and provides some emulsification and wetting properties. To maximize the beneficial effects of the sulfate, formulators generally combine them with other surfactants to minimize



the irritation and defatting effects they have on skin and to maximize the desirable properties of the sulfate. Anionic silicone surfactants are known to lower the irritation effects of sulfates. Fatty alcohol ether sulfates are less irritating and defatting than nonethoxylated sulfates.

Many additives will affect viscosity and foam. The following is a list of additives that are known to alter foam, solubility and viscosity:

- Counter ion of the active sulfate.
- Inorganic salts (type and concentration).
- Unsulfated alcohol (type and concentration).
- Ethoxylation level of the hydrophobe.
- Solvents and processing aids.

The ability to vary the number of carbon atoms present in a fatty alcohol sulfate results in a series of products, some of which are of only limited interest to the cosmetic formulator. If the number of carbon atoms is 10 or fewer, the resulting surfactant is a good wetting agent, but it produces an unacceptable level of foam. If the number of carbon atoms in the fatty alcohol sulfate exceeds 16, the water solubility is substantially and undesirably low. High-foaming surfactants based on fatty alcohols having 16 or more carbon atoms can be produced using ethoxylated versions of these higher fatty alcohols.

Sulfates' stability in alkaline environments is used advantageously in the synthesis of surfactants used in highly alkaline formulations. Fatty alcohol sulfates, being stable in base, provide good foam in alkaline formulations, such as hair relaxer formulations. If low-foam compounds are desired, a highly ethoxylated alcohol like laureth-14-sulfate sodium salt is used.

The choice of the source of fatty alcohol is a key factor in the selection of a sulfate for use in formulation. The difference between natural, Ziegler, oxo and Guerbet alcohols for making sulfates is a key variable. Ether sulfates have an additional factor to consider. Not only are the number of moles of ethylene oxide reacted with the fatty alcohol before sulfation important, but the oligomer distribution also is important. The formulator needs to have control of these parameters to maintain the needed quality on the finished formulations.

Alpha Olefin Sulfonates

To the organic chemist, sulfonates and sulfates are closely related materials. Sulfation and sulfonation both result in anionic surfactants that are made using SO_3, often in the same kind of reactor, using different feedstocks. To formulators, however, the products are different in several aspects. Sulfonates and sulfates having the same number of carbon atoms and no ethylene oxide in the backbone are analogues of each other. It is helpful for formulators to understand the relationship between this class of analogues.

Sulfonates are based on alpha olefin, and sulfates are based on fatty alcohol. Alpha olefin comes from petroleum feedstocks. Therefore, the derivatives are by definition unnatural products. Fatty alcohol sulfates can be derived from natural or synthetic alcohols. Many branched alcohols that are not available in alpha olefins also are available. (See the Fatty Alcohols section in Chapter 1.)

Alpha olefin sulfonates tend to be somewhat more irritating than their fatty alcohol sulfate counterparts. Alpha olefins are better detergents, having a greater defatting effect on the skin. Alpha olefin sulfonates have minimal usage in the personal care market. Historically, they have been used in liquid hand soap and shampoos. But today, alpha olefins are not commonly used in personal care products. It should be clear that it is impossible to ethoxylate alpha olefins before sulfation. Consequently, there are no alpha olefin analogues of fatty alcohol ether sulfates.

The incorporation of irritation-mitigating silicone surfactants is one way to make alpha olefin sulfonates more cosmetically acceptable. However, these additives are expensive and may result in blends that are cost-prohibitive.

The principal advantage that alpha olefin sulfonates offer over fatty alcohol sulfates is their stability in acid, which is not always of interest to the cosmetic formulator.

Reaction

The sulfonation reaction is conducted in two steps. The first is the reaction of the olefin with sulfonation reagent, SO_3. Neutralization is the second step in this process; the product of sulfonation is neutralized with base in water to make the desired sulfonate.

Sulfonation

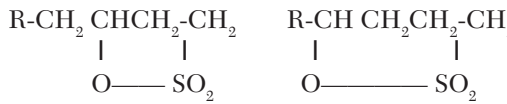
$$CH_3\text{-}(CH_2)_{13}\text{-}CH{=}CH_2 + SO_3 \longrightarrow CH_3\text{-}(CH_2)_{13}\text{-}CH_2CH_2\text{-}SO_3H$$

Neutralization

$$CH_3\text{-}(CH_2)_{13}\text{-}CH_2CH_2\text{-}SO_3H + NaOH \xrightarrow{H_2O} CH_3\text{-}(CH_2)_{13}\text{-}CH_2CH_2\text{-}SO_3Na + H_2O$$

The synthesis of alpha olefin sulfonate, as shown in the preceding equation, has a complicating side reaction — the formation of a sultone on sulfonation. Sultones are cyclic inner esters. As shown below, sultones can be either five- or six-member rings, and the positional isomer distribution is process-dependent and can be quite complex. These esters can be produced in significant concentrations and must be hydrolyzed before use of the surfactant.

Sultone Structures



5-member sultone 6-member sultone

Properties

Despite several technical advancements related to dealing with sultones, the use of alpha olefin sulfonates in personal care applications has been quite limited even though they have an interesting property: The compounds are stable in acidic solution whereas sulfates are not.

The C14-C16 olefin sulfonate is the product of most potential interest to the personal care formulator. This surfactant provides good levels of stable foam, exhibits good detergent properties and is rather mild to the skin and eyes.

It was thought that this material would replace fatty alcohol sulfates several years ago, but this has not occurred for several reasons. One reason relates to the process control needed to successfully and effectively hydrolyze the sultones and their reproducibility. Second, the thickening of alpha olefin sulfonate-based formulations is different than the thickening techniques employed for sulfate-based formulations. Salt and amid addition are of marginal value to generate thick formulations in alpha olefin sulfonate-based formulations. Betaines, sarcosinates and other related compounds are generally employed. Because these thickeners are more costly than salt and amid on an active basis, the cost-effectiveness of the formulation might be compromised. Alpha olefin sulfonate might well see new life in personal care formulations as a result of the strong effort to replace diethanolamine-based amid products in personal care formulations. Finally, it might very well be argued that for most formulations fatty sulfates and fatty ethoxy sulfates work quite well, and replacement is unnecessary, given the history of the use of sulfates and the lack of history for alpha olefin sulfonate-based products.

Sulfosuccinates

The use of sulfosuccinate surfactants in personal care products has increased recently with the advent of very mild shampoos. However, their usage is still quite limited. The sulfosuccinate half ester has good foam, is mild and has a pleasing feel on the skin. The diester is used in formulations to improve the wetting of many substrates, including hair and skin. The presence of the ester linkage in these materials makes them biodegradable in wastewater.

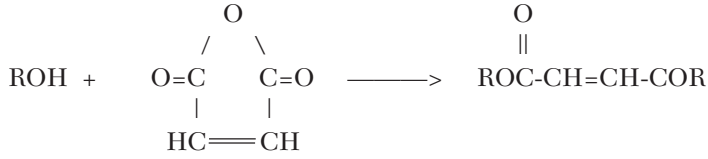
Sulfosuccinate Half Esters

Sulfosuccinate half esters have been used in the formulation of shampoo products for many years. Most important in this class of products is the alkylamido sulfosuccinate half ester.

Reaction

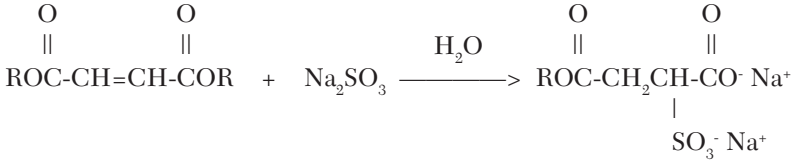
Sulfosuccinate monoesters are prepared in a two-step reaction. The first is the reaction of the alcohol with maleic anhydride. The second step is the aqueous sulfonation of the monoester with sodium bisulfite.

Maleate Ester Step



Sulfonation Step

The second step of the preparation is reaction with sodium sulfite in aqueous solution, as shown below.



Properties

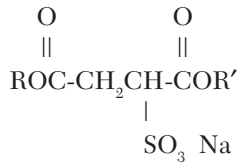
Half ester sulfosuccinate surfactants are better foaming and poorer wetting agents than the diester products. They are also generally less irritating to the skin and eye. Due to the presence of the hydrolyzable ester function in the molecule, sulfosuccinate surfactants are limited to a pH range of 5-10.

Sulfosuccinate Diesters

Sulfosuccinate diesters are another member of the anionic class of surfactants. They are sulfonated diester derivatives of maleate esters. Because they are sulfonates, they have a stable carbon-sulfur bond. However, they also have ester linkages in the molecule, so, unlike alpha olefin sulfonates, sulfosuccinates are not stable in acid or base.

Sulfosuccinate diesters are used principally for their wetting properties in personal care applications.

Sulfosuccinate diesters conform to the following formula:

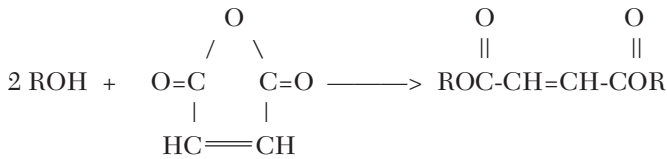


R and R′ can be the same alkyl group or different alkyl groups.

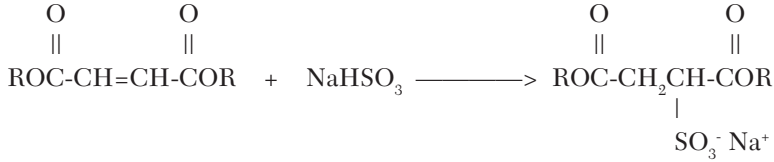
Reaction

Sulfosuccinate diesters are prepared in two steps. The first is the preparation of the maleate diester. The second is sulfonation of the maleate diester with sodium metabisulfite. The two distinct steps are:

Maleate Ester Step



Sulfonation Step



The same two steps are carried out in the preparation of both the diester and monoester sulfosuccinate, but, different sulfonation reagents are used. Process monitoring and control of the reaction sequences is vital to obtain a product that has the desired functional properties in critical formulations. Impurities, which can affect performance, include starting alcohol (ROH), unsulfonated ester and residual bisulfite.

To obtain a product with surface activity, it is necessary to have both a hydrophobic and a hydrophilic portion within the same molecule. The hydrophobe, or fatty soluble portion of the molecule, comes from the fatty alcohol. If the hydrophobe lacks sufficient molecular weight, the resulting sulfosuccinate will have minimal surface activity. Likewise, if the hydrophobic portion of the molecule is too high in molecular weight, a water-insoluble, oil-soluble sulfosuccinate is produced that has essentially no surface activity.

The hydrophilic portion of the molecule comes from the sulfonate group. Most commonly, the sulfonic acid groups are in the form of sodium salts, but the ammonium, potassium and calcium salts have been made. The solubility properties of the products change as a function of counter ion.

General Structural Properties of Sulfosuccinates

The following general structure/function relationships for sulfosuccinates have been established:

- Sulfosuccinate diesters having eight carbon atoms or less in the two hydrophobes are too water-soluble to be of interest as surfactants. For example, dibutyl sulfosuccinate has eight carbonatoms in the two hydrophobes, four in each.
- Sulfosuccinate diesters having 20 or more carbon atoms in the two hydrophobes, such as didecyl sulfosuccinate, are generally too water-insoluble to be of interest as surfactants.
- As the number of carbon atoms in the surfactant increases, the solubility in water decreases, and the wetting power increases until about 18 carbon atoms are present in the nonpolar hydrophobe.
- The best wetting agents in the diester class are products that have between 14 and 18 carbon atoms in the two hydrophobes.
- When branched alcohols are used in synthesis of diester sulfosuccinates, the resultant products are more water-soluble than the homologous diester sulfosuccinates based on linear alcohols.
- Symmetrical sulfosuccinate diesters — those made from the same alcohol, R = R′ — generally have the best wetting properties.

Stability

Diester sulfosuccinates are unstable in both acidic and alkaline solutions. This is because of the hydrolytic instability of the ester linkage present in the molecule. The range of pH over which a sulfosuccinate is stable is usually quoted at 5-10. If a high or low pH is experienced for a substantial period of time, hydrolysis will occur, and the product will eventually split into oil-soluble and water-soluble phases.

Many personal care formulations exist in which diester sulfosuccinates can be used successfully. These include pigmented products, where the wetting properties are critical to pigment grind. The ability of diester sulfosuccinates to lower surface tension also makes these materials of interest where improved spreading on skin and hair is a desired effect. This would include most shampoos, bubble baths, body oils and skin care products.

The wetting properties of sulfosuccinates are maximized at or near their critical micelle concentration. Consequently, using them at high concentrations to obtain a wetting effect is not necessary.

Phosphate Esters

Phosphate esters are a class of surfactants that has been known for many years. They have been used historically as emulsifiers, and their application has been restricted primarily to end uses other than personal care products. Recently, however, there has

been a trend to use monoalkyl phosphate esters in a variety of personal care formulations. The proper selection of a phosphate ester for use in personal care applications is likely to result in wider use of this class of compounds as emulsifiers and detergents in personal care applications. Additionally, these materials are likely to be used as raw materials for synthesis of surfactants resembling naturally occurring phospholipids such as phosphatdylcholine.

Phosphate esters are part of a class of anionic surfactants. The commercial products are complex mixtures of the following components:

O || RO-P-OH | OH	O || RO-P-OR | OH	O || HO-P-OH | OH	ROH
Monoester	Diester	Phosphoric Acid	Nonionic

The kind or kinds of starting alcohol used determine the "R group." Modification of this group is a major factor in the functionality of a phosphate ester.

Generally, two different phosphating agents are used commercially. They are polyphosphoric acid (PPA) and phosphorous pentoxide (P_2O_5). The selection of phosphating reagent has an effect on the ratio of the components and on the functional properties of the resulting phosphate esters.

Reaction

The reaction used to make phosphate esters is referred to as *phosphation*. It is conducted with either polyphosphoric acid or phosphorus pentoxide.

$$\text{R-OH} + P_2O_5 \xrightarrow{\text{Excess ROH}} \text{R-O-P(=O)-(OH)}_2 \text{ Monoester}$$

$$(\text{R-O})_2\text{-P(=O)-OH} \text{ Diester}$$

and

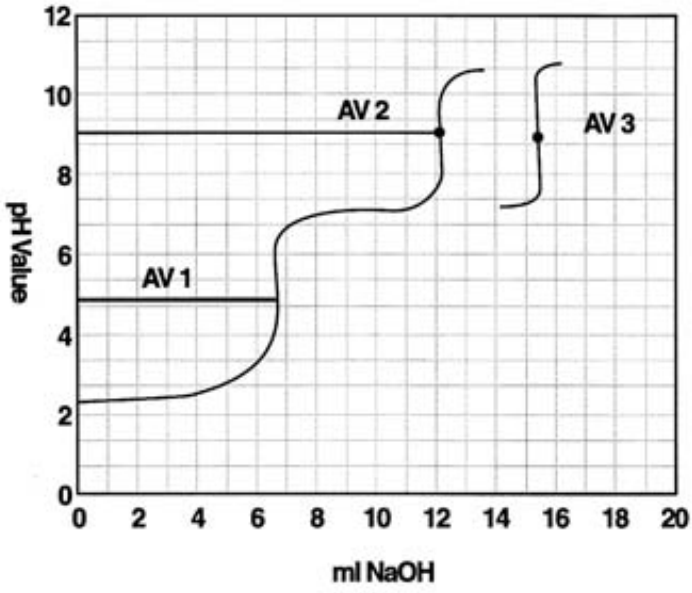
$$O{=}P\text{-(OH)}_3 \text{ Phosphoric Acid}$$

Properties

Because phosphate esters are complex mixtures of various products, analysis is important.

Phosphate esters can be analyzed partially by an acid value titration. This titration doesn't fully identify the product, but it does give valuable insights on the

Acid Value Titration of Phosphate Esters



product's quality. The titration is run using a standardized solution of base, most commonly sodium hydroxide. There are three distinct endpoints in the titration. By evaluating each, valuable information on product quality can be obtained. Two endpoints can be determined directly by titration to a pH using a pH electrode. The third can be determined indirectly after the addition of calcium chloride; the acid generated by the addition is titrated.

The acid value calculations are made using the following formula.

Acid Value #1

$$\text{Acid Value} = \frac{(\text{mls of NaOH to Point A})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})}$$

Acid Value #2

$$\text{Acid Value} = \frac{(\text{mls of NaOH to Point B})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})}$$

Acid Value #3

$$\text{Acid Value} = \frac{(\text{mls of NaOH to Point C})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})}$$

The three acid values result from the three types of phosphate protons available on each species. Species with three acid groups, such as phosphoric acid, have an acid value #1, 2 and 3. Those with two acid functions, such as monoesters, have an acid value #1 and 2, and those with only one acid functionality, such as diester, have an acid value of only #1.

O || RO-P-OH | OH	O || RO-P-OR | OH	O || HO-P-OH | OH
Monoester	Diester	Free Phosphoric
Contributes to:		
Acid Value 1 and 2	Acid Value 1 only	Acid Value 1, 2 and 3

Knowing these values, it is then possible to calculate the monoester, diester and free phosphoric acid content.

The exact composition of the phosphate ester is a major factor in the functional properties of the product. The free nonionic present in the product is a function of the mole ratio of nonionic to phosphating agent. Free nonionic is a major factor affecting performance.

For example, if the nonionic is an auxiliary surfactant in and of itself, the detergency and wetting properties of the phosphate ester will be improved. However, if the nonionic is hydrophobic and water-insoluble, a defoaming effect will result. The use of ethoxylated nonionic surfactants as raw materials increases the caustic stability of the product.

The monoester component of a phosphated product is most commonly the fastest wetter in the series. When a nonionic surfactant is replaced with one of a higher molecular weight in the phosphation process or if process modifications are used to increase monoester concentration, the wetting speed is increased. It is highly desirable to keep the free phosphoric acid content as low as possible in most applications because free phosphoric acid adds nothing to the surfactant properties of the surfactant. Most phosphate esters used in personal care are so called *MAP*, or monoalkyl phosphate, products.

Analysis of Phosphate Esters

A shorthand for the designation of the hydrophobe phosphated has been adopted. The shorthand is as follows:

Alcohol	Phosphate Fatty Alcohol Designation
Hexyl alcohol	Hexyl 0 EO phosphate
Octyl alcohol	Octyl 0 EO phosphate
Decyl alcohol	Decyl 0 EO
Decyl 2.5 mole ethoxylate	Decyl 2.5 EO
Decyl 6 mole ethoxylate	Decyl 6.0 EO
Decyl 8 mole ethoxylate	Decyl 8.0 EO
Tridecyl alcohol	Tridecyl 0 EO
Tridecyl 6.5 mole ethoxylate	Tridecyl 6.5 EO
Myristyl alcohol	Myristyl 0 EO phosphate
Myristyl 3 mole ethoxylate	Myristyl 3 EO phosphate
Myristyl 7 mole ethoxylate	Myristyl 7 EO phosphate
Myristyl 9 mole ethoxylate	Myristyl 9 EO phosphate
Myristyl 12 mole ethoxylate	Myristyl 12 EO phosphate

Phosphate Ester Composition

	Mono	Diester	Free Ester Phosphoric
Hexyl 0 EO phosphate	53.4	41.2	5.6
Octyl 0 EO phosphate	49.7	49.7	0.6
Decyl 0 EO phosphate	58.3	41.5	0.2
Decyl 2.5 EO phosphate	60.3	37.7	2.0
Decyl 6.0 EO phosphate	67.1	25.3	7.6
Decyl 8.0 EO phosphate	66.7	23.7	9.6
Tridecyl 0 EO phosphate	46.2	53.0	0.8
Tridecyl 6.5 EO phosphate	64.0	32.0	4.0
Myristyl 0 EO phosphate	58.2	40.7	1.1
Myristyl 3.0 EO phosphate	59.3	39.4	1.3
Myristyl 7.0 EO phosphate	59.0	36.1	4.9
Myristyl 9.0 EO phosphate	62.3	27.9	9.9
Myristyl 12.0 EO phosphate	67.7	17.8	14.5

Product Composition

The table above shows the concentration of monoester, diester and free phosphoric acid for the phosphate esters. The data demonstrate that, as one increases the amount of ethylene oxide on the decyl alcohol hydrophobe from zero to seven moles of ethylene oxide, the concentration of monoester and free phosphoric acid

increases in an almost linear fashion. Similarly, diester content drops as one increases the amount of ethylene oxide on the hydrophobe. Because all hydrophobes were dried before phosphation, the increase was not attributed to water present.

As one increases the amount of ethylene oxide on the myristyl alcohol hydrophobe from zero to seven moles of ethylene oxide, the concentration of monoester and diester varies only slightly. The trend is for less diester and free phosphoric acid as the amount of ethylene oxide on the hydrophobe increases. Once the amount of ethylene oxide added exceeds seven, a dramatic drop in diester and increase in monoester and free phosphoric acid result. Because all hydrophobes were dried before phosphation, the increase was not attributed to water present. However, it appears that the more polar alcohol ethoxylates phosphate less well, producing more monoester and free phosphoric acid than those phosphation reactions run using more hydrophobic fatty alcohols or fatty alcohol ethoxylates. It has also been suggested that this effect may relate to steric hindrance.

Wetting Speed

One of the major uses of phosphate esters stems from their fast wetting times. The data presented in the following table is Draves Wetting data. It measures the amount of time in seconds to wet out a cotton skein.

Wetting Speeds

Phosphate Type	Hydrophobe C Atoms	Wetting Time (sec.)
Hexyl 0 EO phosphate	6	15
Octyl 0 EO phosphate	8	17
Decyl 0 EO phosphate	10	28
Decyl 2.5 EO phosphate	10	8
Decyl 6.0 EO phosphate	10	23
Decyl 8.0 EO phosphate	10	33
Tridecyl 0 EO phosphate	13	34
Tridecyl 6.5 EO phosphate	13	29
Myristyl 0 EO phosphate	14	34
Myristyl 3.0 EO phosphate	14	30
Myristyl 7.0 EO phosphate	14	39
Myristyl 9.0 EO phosphate	14	49
Myristyl 12.0 EO phosphate	14	42

Alkyl Group

The previous table shows that as the molecular weight of the hydrophobe increases the wetting time likewise increases. The lowest molecular weight hydrophobe (hexyl phosphate) with no ethylene oxide was the best wetter in the series of nonethoxylated species. In fact, as the molecular weight of the hydrophobe containing no ethylene oxide increases, the phosphate produced will have a longer wetting time. This is true for hydrophobes having six to 14 carbon atoms.

Ethoxylation Degree
Within each set of hydrophobes, the ethoxylated materials all reached the fastest wetting times with between two and three moles of ethylene oxide added.

Commercial Products
Phosphate esters are marketed at 100 percent activity in their free acid form or can be neutralized to any desired pH with alkali metals, such as sodium or potassium hydroxide; amines, such as mono-, di- and tri-ethanolamine; ammonia; and other bases. Additionally, several products are available as partially neutralized forms.

Most phosphate esters are pale yellow to amber, sweet-smelling, viscous liquids or pastes and combine many important properties, including:

- Stability to extremes of acidity and alkalinity.
- Excellent heat stability.
- High electrolytic tolerance.
- Good solubility in alkali.
- Outstanding coupling ability.

Effect of Neutralizing Agent
The phosphate esters marketed in their free acid form can be neutralized to any desired pH with any basic material. The pH of the final formulation has little effect on the foaming, surface tension reduction, wetting, detergency, coupling, and caustic tolerance properties of the phosphate ester within the formulation. However, the pH does affect the solubility of the phosphate ester, with the partly neutralized phosphate ester showing solubility characteristics intermediate between those of the free acid and the completely neutralized phosphate ester.

The order of water solubility for variously neutralized or partially neutralized phosphate esters is as follows:

$$\text{TEA} < \text{DEA} < \text{MEA} < \text{NH}_3 < \text{KOH} < \text{NaOH}$$

Comparison of the properties of phosphate esters neutralized with various bases shows that the sodium and potassium salts have slightly better foaming, detergency, coupling and caustic tolerance properties.

Analysis
In addition to the analyses specified at the end of this chapter, applicable to all anionic surfactants, there are several analyses specific to phosphate esters. One noteworthy analytical technique is phosphorus nuclear magnetic resonance (NMR) spectroscopy. Recently, phosphorus NMR has been applied to phosphate esters. The data generated by this analytical tool have provided tremendous and heretofore unavailable information on the composition of phosphate esters. This has allowed for better structure elucidation and the development of improved process control used to make phosphate esters.

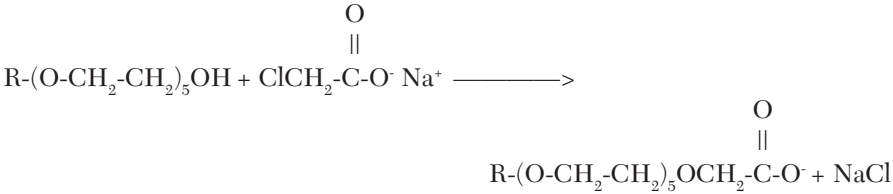
This technique gives clean, first-order spectra. Based on the information gleaned, it appears likely that this technique will become an important one in the future as access to the equipment and familiarity with the method become more commonplace. More information on the technique is provided in Chapter 7.

Carboxylates

The group of surfactants classified as carboxylated surfactants contains a –COOH group. They may be based either on alcohols or alcohol ethoxylates. This class of products is used as emulsifiers.

Reaction

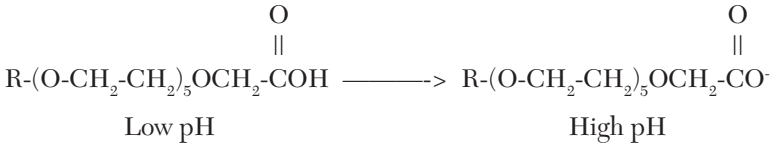
Carboxylated surfactants are prepared by the reaction of an alcohol or alcohol alkoxylate with sodium chloroacetate, generally in the presence of alkaline catalysts. The reaction is illustrated below.



Properties

Carboxylated nonionic surfactants are effective anionic detergents that exhibit good detergents over a wide range of pH values. This makes them important detergents because fatty sulfates hydrolyze at pH values of below five.

Carboxylated nonionic surfactants are used as emulsifiers. Their emulsification properties are affected by the pH of the formulation. The best emulsification occurs on the alkaline side, where the products are true anionic surfactants. At low pH values, carboxylated surfactants are nonionic, as illustrated below.



Pioneering in the use of computer-generated models to predict surfactant properties of this class of materials, scientists working at Sandoz (now Clariant) have done the functionality of carboxylated surfactants. This predictive tool is highly recommended for formulators using this class of products.

The carboxylated nonionic surfactants exhibit good compatibility with all other ionic classes, which is unusual for anionic products. If one carefully selects the ratio of carboxylated surfactant, soluble complexes can be obtained even with cationic surfactants. The complex of the cationic surfactant and the carboxylated nonionic exhibit improved deposition on hair when formulated in anionic shampoo systems.

Many of the carboxylated nonionic surfactants are provided as high active products having about 90 percent actives in the acid form and about 70 percent for the sodium salts. This high actives property offers some additional formulation latitude where formulations with low concentrations of water are required.

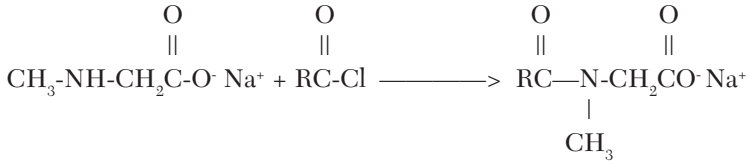
Sarcosinates

Sarcosinates are a class of anionic surfactants based on acylated glycine derivatives. They are good cleansing agents and are reported to be very mild. These surfactants are structurally similar to amino acids and soap.

Sarcosinates are made by the acylation of glycine. The reaction must be conducted using acyl chloride. It cannot be satisfactorily carried out using a fatty acid.

Reaction

An acyl chloride is reacted with N-methyl glycerin to get the desired product, as shown below.



Properties

Sarcosinates are soap-like anionic detergents. They are mild detergents that are reported to be substantive to skin. Sacrosinates are moderate-foaming surfactants, and their foam is unaffected by the pH of the solutions in which they are employed.

Analysis of Anionic Surfactants

Instrumental Analysis

All anionic surfactants should be evaluated by Fourier transform infrared analysis. This instrumental technique is highly automated and when coupled with a computer analysis interface can locate small differences in products. These small differences might not be observable to the naked eye, so the use of sophisticated analytical instruments is strongly suggested. These techniques save time and money and are quite sensitive.

Wet Analysis

The evaluation of surfactants in this class is based on the fact that the surfactants are anionic groups. The following analyses are recommended:

- Acid value
- Alkali value
- Anionic actives
- Solids
- Inorganic salts
- Sodium sulfite

Surface Active Phospholipids for Personal Care

Introduction

Phospholipids are a class of compounds that have grown in importance in recent years. They resemble compounds in the cell including being constituents of cell membranes. A series of products based upon this chemistry has been developed and recently expanded. These materials offer many desirable surfactant properties including foaming, detergency, and conditioning.

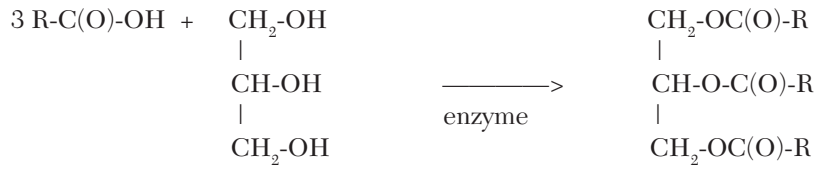
Over the last quarter century, a great deal of work has been done to develop surface-active agents that contain phosphorous. This is due in part to the natural occurrence of phospholipids, a necessary chemical for life, as we know it. Synthetic phosphorous-based surface-active agents can provide a number of properties to formulations including;

1. wetting
2. emulsification
3. foam
4. conditioning
5. anti-microbial properties

While there is no single compound with all of these various properties, the properties are a direct consequence of the structure of the compounds. There are three very different classes of phosphorus-based compounds with different properties. These include the mild high foaming, detergent molecules called phosphobetaines, the emollient conditioning compounds, which have become known as phospholipids and the antimicrobial super conditioning agents called phospho-quats.

Natural Lipids

Naturally occurring lipids are actually triglycerides made by the reaction of a fatty acid and glycerin. These materials can be made in the laboratory with catalyst at high temperature (180-200° C). However, the reaction occurs in living cells at low temperatures using specific enzyme systems.



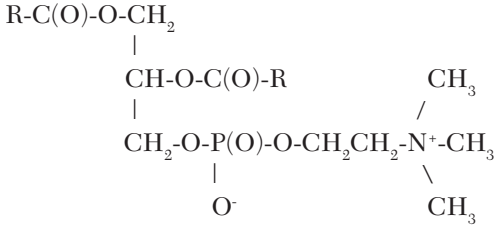
Triglycerides are the storehouse of energy in the cell. They exist in a wide variety of plants, and animals. Related terms are oils, and butters. These terms are often confused.

Lipids are water insoluble, oil soluble compounds that dissolve only very sparingly in water. This property is a direct consequence of the energetics of the hydrogen bond in water. Water is a very unique material and is essential to life as we know it. The polarity of water results in the formation of hydrogen bonding between molecules of water. This bonding results in the variety of unusual properties of water. The high surface tension, the ability to dissolve polar molecules and the relatively high boiling point in relation to molecular weight, are all a direct result of the hydrogen bonding of water.

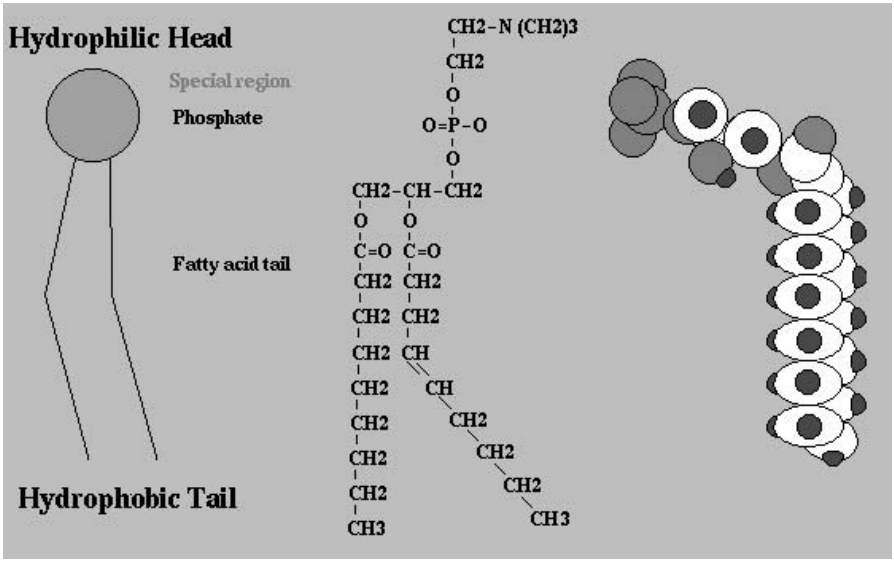
The lowest free energy state of water is the state in which oil floats on top and the water is in the lower phase. This is why separated oil on water is common. It takes energy to disrupt the hydrogen bonding in water to allow for mixing in oil.

Phospholipids

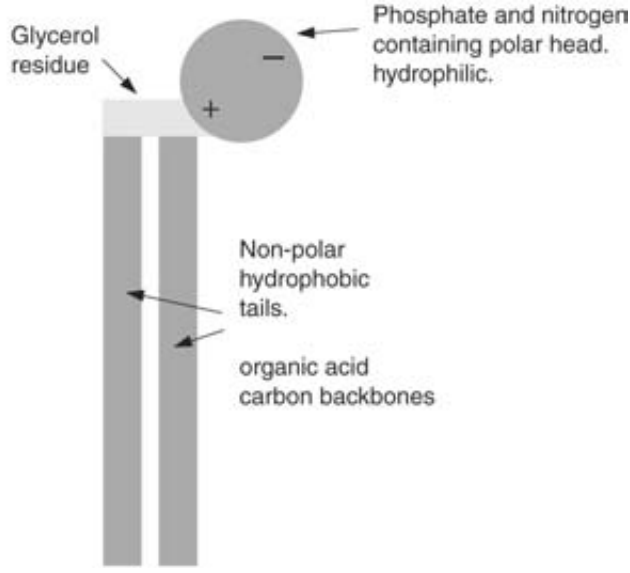
Natural Phospholipids are a vital class of compounds found in cell membranes. These compounds are related to lipids, but have a polar phosphate group and a polar quaternized nitrogen molecule present.



Phosphatidyl Choline

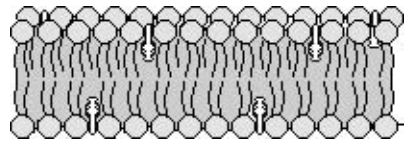


As can easily be seen, the compound is far more polar than lipids. Graphically the compounds are:



Unlike the lipid compounds, the phospholipids shown above have both water loving polar groups and oil loving groups. This allows the compounds to be much more water-soluble. It is both interesting and important to functionality that the two groups on the compound are different, one saturated and the other unsaturated. This results in the proper combination of properties to make the necessary cell membrane.

The phospholipid bilayer, which the cell membrane is an example of, is composed of various cholesterol, phospholipids, glycolipids and proteins. Below is an example of a simple phospholipid bilayer:

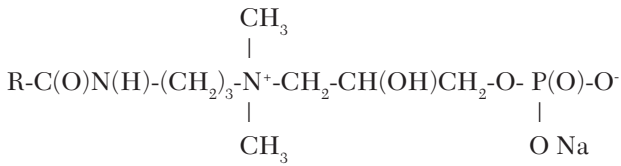


Surfactant Products

Phosphobetaines

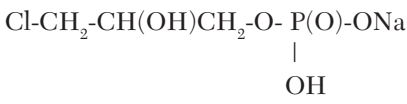
The first set of materials that are of interest in this class of materials is the so-called phosphobetaines. These compounds were first described in 1981 in U.S. Patent 4,283,542. The patent, now expired, deals with compounds that have the following structure;

Alkylamido Phosphobetaine Structure

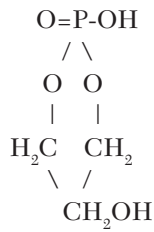


The products from this class differ in the "R" composition. The common attribute is that the products are all mono substituted and are amphoteric products since they bear one and only one + and one and only one"– charge in the same molecule.

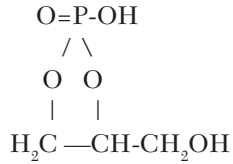
The process patent describes the effect of ring closure upon foam and solubility. The intermediate used to make the product is prepared by reacting sodium phosphate and Epichlorohydrin. The intermediate that forms exists in a linear and two cyclic forms depending upon the pH at which the reaction is conducted.



Linear Structure



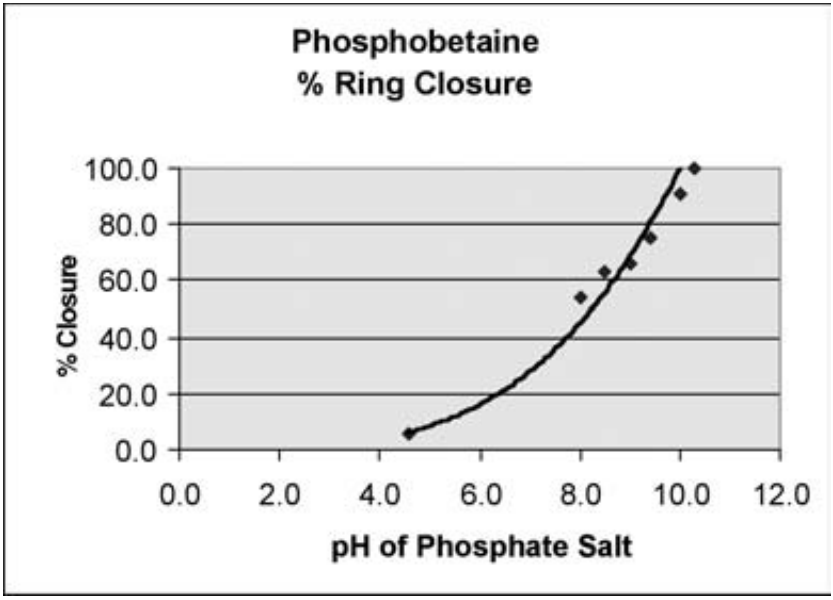
6 member cyclic compound



5 member cyclic compound

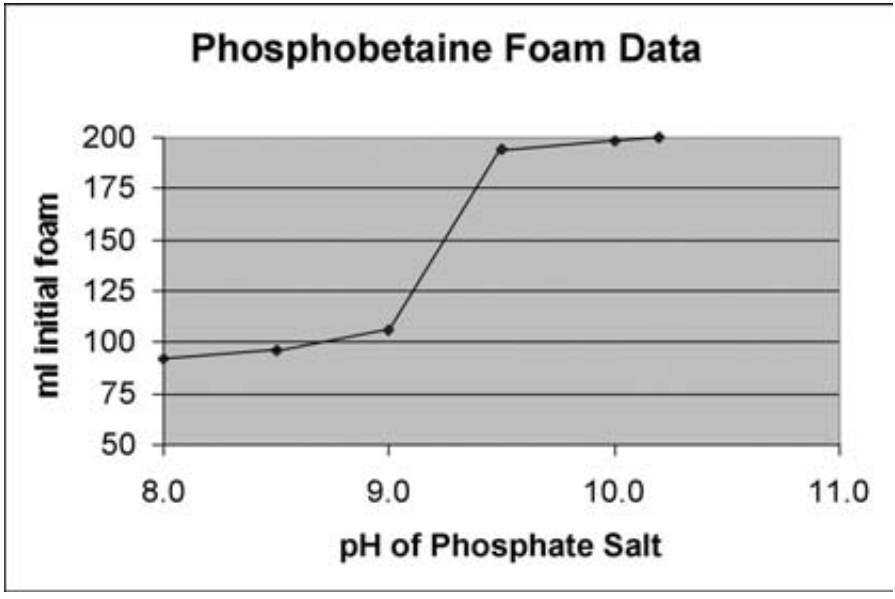
The % ring closure can be monitored by chromatographic analysis, but it has been found that the % NaCl generated during the reaction is a good indication of the degree of cyclization. The difference is the location of ring closure. As the pH of the reaction increases, the amount of cyclic product likewise increases.

pH	Ring Closure via % NaCl
4.6	5.5
8.0	54.0
8.5	63.0
9.0	66.2
9.4	75.0
10.0	91.0
10.3	100.0



The foam properties of the product prepared by the reaction of the intermediates made at different pH values also varies as a function of pH. The foam value is initial foam for a cylinder shake foam test using 0.4% active product in deionized water.

pH Phosphate Salt	Foam
8.0	92 ml
8.5	96 ml
9.0	106 ml
9.5	194 ml
10.0	198 ml
10.2	200 ml



The phosphobetaines are detergent systems that are mild and have good foam. They form anionic cationic complexes with sulfates and ether sulfates. These complexes are more substantive to hair, are very mild and are good for personal care products where mildness is of interest, like baby products.

Other patents, now expired, which name Mayhew, and O'Lenick as inventors are as follows:

Phospholipid Patents

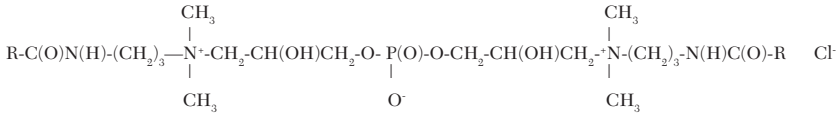
	Number	Date of Issue	Topic
#1	4,209,449	24-Jun-80	Phosphate Quats
#2	4,215,064	29-Jul-80	Phosphobetaines
#3	4,243,602	06-Jan-81	Phosphate Quat
#4	4,261,911	14-Apr-81	Phosphitaines
#5	4,283,542	11-Aug-81	Phosphobetaine Process
#6	4,336,385	22-Jun-82	Phosphate Quats from Imidazolines
#7	4,336,386	22-Jun-82	Phosphite Quaternaries
#8	4,380,637	19-Apr-83	Imidazoline Phosphobetaines
#9	4,503,002	05-Mar-85	Phosphate Quat Compounds

Phospholipids

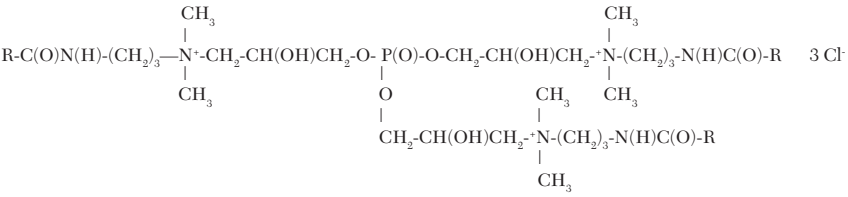
The term phospholipid is properly reserved to compounds in which there is more than one functional group. While at first this sounds unimportant, looking at the structure, one becomes aware of the differences.

Alkylamido Phospholipid Structures

Difunctional



Phosphate quaternary



The phospholipid structures listed above show that as the degree of substitution around the phosphate group increases the product is no longer an amphoteric and becomes more and more cationic. The difunctional material has two + charges and

one – charge, leaving a net charge of +1. The phosphate quaternary has three positive charges and no negative charges, having a net charge of +3.

This change in charge has profound affect upon the properties of the material. As the product becomes more functionalized;

1. the molecular weight increases;
2. the skin penetration decreases;
3. the cationic nature increases;
4. the skin and hair substantivity increases;
5. the amount of fatty in the molecule increases;
6. the skin feel improves.

This explains why the phospholipids are used in skin care as emollients and conditioners and not as detergents.

Emollients work in one of two ways (1) prevent transepidermal water loss, or (2) provide hydration to the skin. Oily materials function in the first way, and to a great extent phospholipids function in the latter way. A good way to show that the compounds provide hydration is the fact that they provide self-preserving properties to aqueous solutions.

Complexation with Anionic Surfactants

One of the critical functionalities observed with phosphobetaine and phospholipid technology is the interaction between the products and sodium laureth sulfate. When the two are combined, a complex forms. The more cationic the phosphobetaine, the less soluble the complex with ether sulfate.

Cocamidobetaine

The first material to consider is an ampholyte, namely a cocamidobetaine. Sodium Trideceth sulfate and cocamidobetaine were combined at differing ratios. All Solutions were prepared at 10% active in water.

STDES / Cocamidobetaine	Result
90 / 10	Clear, high foam, low viscosity
80 / 20	Clear, high foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Clear, high foam, low viscosity
50 / 50	Clear, high foam, low viscosity
40 / 60	Clear, high foam, low viscosity
30 / 70	Clear, high foam, low viscosity
20 / 80	Clear, high foam, low viscosity

Over all ranges, the mixture was clear and homogeneous.

Phosphobetaine (Mono Product)

The mono-substituted product functions like the cocamidobetaine.

STDES / Cocamido phosphobetaine	Result
90 / 10	Clear, high foam, low viscosity
80 / 20	Clear, high foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Clear, high foam, low viscosity
50 / 50	Clear, high foam, low viscosity
40 / 60	Clear, high foam, low viscosity
30 / 70	Clear, high foam, low viscosity

Over all ranges, the mixture was clear and homogeneous.

Phospholipid (Di-Product)

A distinct difference is noted with the di-product, due to the greater amount of cationic charge.

STDES / Cocamidophospholipid	Remarks
90 / 10	Clear, high foam, low viscosity
80 / 20	Cloudy, moderate foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Cloudy, moderate foam, low viscosity
50 / 50	Cloudy, moderate foam, low viscosity
40 / 60	Cloudy, moderate foam, low viscosity
30 / 70	Clear, moderate foam, low viscosity
20 / 80	Clear, moderate foam, low viscosity

Phospholipid (Tri-Product)

The increasing amount of cationic charge is noted in the product that is predominately tri-ester, and the compatibility with anionic is even lower. The product called tri-product is actually a mixture of di and tri functional product.

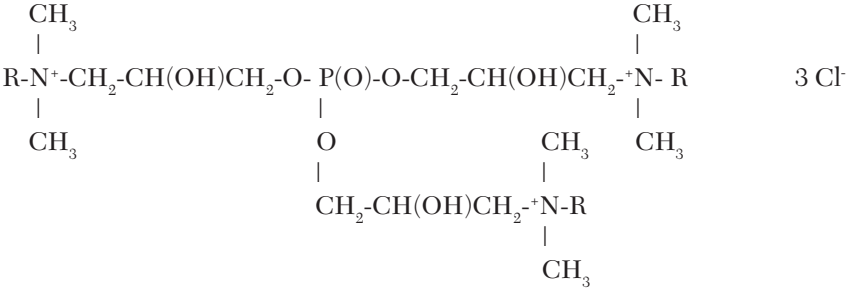
STDES / Cocamidophospholipid	Remarks
100 / 0	High dense lasting foam, solution is clear and thin
90 / 10	High dense lasting foam, solution is clear and thin
80 / 20	dense lasting foam, solution is clear and thin
70 / 30	High very dense lasting foam, solution is viscous
60 / 40	Low thin foam, solution is clear and viscous
50 / 50	Low thin foam, solution phase separates into two distinct layers
20 / 80	High moderately dense less durable foam, solution is opaque and thin
10 / 90	High moderately dense less durable foam, solution is clear and thin
100 / 0	High moderately dense foam, solution is clear and thin

Antimicrobial properties

Recently, there have been several patents, naming Fost and Perella as inventors, directed to specific alkyl functional phosphate quaternary compounds that have spermicidal, or antimicrobial activity. Recalling the structure of the alkylamido given above, the alkyl products have the following structure;

Alkyl Phosphate Quaternary Compounds

In these products, the "R" group is alkyl. Commonly C_{12} to C_{14}. This is the same distribution as found in germicidal quats.



R is $C_{12}H_{25}$.

The patents of interest assigned to Mona Industries, now Uniquema are as follows:

Patent #	Topic	Issued
5,215,976	Phospholipids as Spermicidal Agents	1-Jun-93
5,286,719	Phospholipids as Viricidal Compositions	15-Feb-94
5,648,348	Phospholipids as Antimicrobial Agents	15-Jul-97
5,650,402	Phospholipids as Antimicrobial Agents	22-Jul-97

While these alkyl substituted materials are not registered antimicrobial compounds, and consequently cannot be used as the sole antimicrobial in formulations, they do enhance performance of the antimicrobial and are self-preserving. It is very interesting that the antimicrobial activity is limited strictly to prokaryotic life, with complete selectivity towards eukariotic life. The explanation appears to be that the mode of action is that these materials increase the permeability of the cell wall to water, thereby causing lyses. Since eukarotic life has no cell wall, the cells are not affected. This phenomenon is of interest, since it shows that these compounds do in fact provide emmoliency by hydration, rather than decreasing trans epidermal water loss.

The most interesting class of products for personal care is the amido functional products. These products are multifunctional, natural oil derived phospholipids composed predominantly of diester and triester phosphates. Through the careful selection of specific natural oils as raw materials, the products deliver a broad range of functional properties which include gentle cleansing, anti-irritation effects, unusually high substantivity, long lasting conditioning, emulsification attributes, and exceptional mildness to skin and eyes.

Information from Dr. Martin Rieger's Surfactant Encyclopedia: Anionic Surfactants

Substances are classified as anionic only if the charge on the hydrophobe is negative. Surfactants, in which the hydrophobe carries no charge unless the pH is elevated to neutrality or above, like carboxylic acids, are also categorized as anionic.

Anionic surfactants are further subdivided into five major chemical classes and additional groups:

A. Acylamino acids (and salts)
   1. Acylglutamates
   2. Acyl peptides
   3. Sarcosinates
   4. Taurates

B. Carboxylic acids (and salts)
    1. Alkanoic acids (and alkanoates)
    2. Ester carboxylic acids
    3. Ether carboxylic acids
C. Phosphoric acid esters (and salts)
D. Sulfonic acids (and salts)
    1. Acyl isethionates
    2. Alkylaryl sulfonates
    3. Alkyl sulfonates
    4. Sulfosuccinates
E. Sulfuric acid esters
    1. Alkyl ether sulfates
    2. Alkyl sulfates

A. Acylamino Acids and Salts

Surfactants in this class are prepared by the acylation of the amino group of amino acids. The acylation is conducted primarily with naturally occurring fatty acid derivatives. Acylation of the amino group of an amino acid eliminates its basicity, yielding a free carboxylic acid which requires neutralization. Depending on the length of the acylating moiety, the resulting amides are anionic surfactants.

Four types of acylamino acids can be differentiated chemically. The acylglutamates are derived primarily from glutamic acid, and this group includes some aspartic acid derivatives. The sarcosinates are obtained from sarcosine (N-methylglycine). The acyl peptides are prepared from proteins or protein hydrolysates. The acyl taurates, the smallest group, are prepared by acylation of N-methyltaurine ($CH_3NHCH_2CH_2SO_3H$).

A.1. Acylglutamates

Chemical properties

Glutamic acid is a dicarboxylic acid, and its N-acyl derivative, can form mono- or di-salts with alkalies. The aqueous solutions of the mono-basic salts are slightly acidic (pH 5-6), while the di-salts are alkaline. Both salts are readily soluble in water. The chirality of the a-amino group is generally specified as the l-form, i.e., that of the natural amino acid.

The acylglutamates are amides and may undergo hydrolysis under adverse pH conditions.

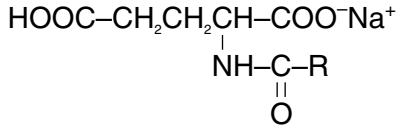
Physical properties

The sodium salts are solids, while the TEA salts are generally marketed as 30% aqueous solutions. The acylglutamates foam relatively poorly.

Uses

The acylglutamates are used in skin-cleansing products and shampoos because of their general mildness. They also are found in syndet bars and reportedly provide a soft feel to the skin.

Generic alcyglutamates



Sodium acylglutamate

Selected members:

Di-TEA-palmitoyl aspartate
Sodium hydrogenated tallow glutamate

Stability

The acylglutamates are amides but evidently possess adequate resistance to hydrolysis in cosmetic products.

Safety

The available data suggest that the glutamates as a group are non-irritating and non-sensitizing.

A.2. Acyl Peptides

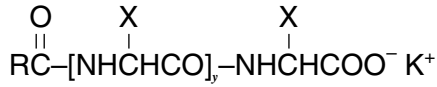
Chemical properties

The acyl peptides are prepared by acylation of partially hydrolyzed proteins. Collagen was and still is the most common source of the protein. Hydrolyzed keratin, rice, soy and wheat proteins and other hydrolyzed polypeptides have recently achieved popularity. The nature of the hydrolyzing agent is not identifed and may be chemical (acid or base) or enzymatic. The molecular weight of the hydrolyzed starting polypeptide ranges from about 350 to 2000. The level of hydrolysis is rarely specified, and the presence of free amino acids is likely. The members of this group, therefore, may include acylation products derived from partially or fully hydrolyzed proteins.

The ratio of the amount of alkanoic acid to the amount of peptide (amino acid) depends primarily on the degree of hydrolysis. Each peptide fragment (or amino acid) displaying an amino group can be expected to react with one mole of the alkanoic acid derivative. Thus, the amount of "protein" in the product may vary from product to product. Reactive side groups (for example, OH on the protein, especially hydroxyproline or serine) can also be acylated to form a variety of acylation products.

The acylation is generally carried out with a nature-derived fatty acid derivative. Reaction with the amino group of the peptide or amino acid leaves the carboxyl group free. As a rule, neutralization after reaction is required, and various alkalies

Generic acyl peptides



Potassium acyl-hydrolyzed protein
(**X** represents various amino acid side chains;
y represents the number of repeating peptide units.)

Specific members:

Palmitoyl hydrolyzed milk protein
Sodium cocoyl hydrolyzed soy protein
TEA-abietoyl hydrolyzed collagen
TEA-cocoyl hydrolyzed collagen (CIR)

have been employed. Purification of the final product is difficult, and the presence of soap and of other residues (Cl^- if an acid chloride is used) are to be expected.

The derivatives of low-molecular-weight peptides exhibit considerable solubility in organic solvents, especially ethanol.

Physical properties

The acyl peptides are solids but are generally available as aqueous solutions and occasionally as alcoholic solutions.

Uses

The acyl peptides are mild cleansing agents and find important applications in hair-care products. They, or at least some constituent(s) of the raw material, are reported to be substantive to hair keratin and provide hair conditioning. They have been employed in skin-care products for related reasons and especially for their ability to tolerate hard water. They are not widely used as emulsifiers.

Stability

he acyl peptides exhibit good stability in water at near neutral pHs. They are amides and subject to hydrolysis at extreme pHs. These substances can support the growth of microbial species and can be enzymatically degraded. Since they also have a tendency to inactivate some preservatives, the stability of these surfactants depends to a large extent on effective preservation.

Safety

The raw materials of the acyl peptide type have a long history of safe use-more than 50 years. It is claimed that these surfactants have a reduced tendency to defat the skin. Some acyl peptides have been reviewed by the CIR Expert Panel.

A.3. Sarcosinates

Chemical properties

The sarcosinates comprise a small group of anionic surfactants derived from the acylation of sarcosine (N-methyl glycine). Their salts differ from the salt of the parent acid by only three carbon atoms, and their overall behavior is similar to that of ordinary soaps. On the other hand, the polar end is larger, and the salts of the sarcosinates exhibit high water solubility.

In addition, the terminal carboxylic acid has a lower pKa than that of the ordinary fatty acid. This accounts for their salt formation (and resulting solubility and utility) at a pH range as low as 4 to 5.

Their ability to foam is unaffected by water hardness. Sarcosinates are compatible with various surfactants and reportedly can be combined with quaternary germicides.

Physical properties

The free acids are solids, but the water-soluble salts are generally available as aqueous solutions. The sarcosinates foam well.

Uses

The sarcosinates are mild cleansing agents with reported substantivity to skin and hair. They are used in shampoos and various types of skin-cleansing products. The substantivity of these anionics at slightly acid or neutral pH ranges may be due to the presence of some unneutralized acyl sarcosine as the free acid.

Stability

The sarcosinates are amides and subject to hydrolysis at extreme pH ranges. Under normal-use conditions in cosmetics, the sarcosinates are stable.

Safety

The reported skin mildness suggests that the sarcosinates are safe in cosmetic usage.

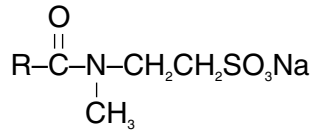
Generic sarcosinates

Ammonium acyl sarcosinate

Specific members:

Myristoyl sarcosine
TEA-lauroyl sarcosinate

Generic taurates



Sodium methyl acyltaurate

Specific members:

Sodium lauroyl taurate
Sodium methyl cocoyl taurate

A.4. Taurates

Chemical properties

The taurates form a small group of anionic surfactants derived from taurine or N-methyl taurine by acylation. These sulfonic acids are strong acids and very water-soluble. In the acid form, their aqueous solutions hydrolyze to the corresponding alkanoic acid, and they are available only as the sodium salts.

In contrast to their ester analogues, the alkyl isethionates, are resistant to hydrolysis at a relatively low pH range. As a rule, commercial surfactants of this class contain large amounts of sodium sulfate.

Physical properties

The taurates are available as solids and as aqueous solutions. They foam well, especially in the presence of other anionic surfactants.

Uses

The taurates have limited use in cosmetics, and are found primarily in bubble baths.

Stability

The taurates are stable under cosmetic-use conditions.

Safety

Specific information on the safety of the taurates as a group is not available.

B. Carboxylic Acids and Salts

Carboxylic acids are the organic compounds that possess the COOH function. Surfactant-type carboxylic acids are weak acids, and their water solubility and functionality, with few exceptions, depend on neutralization with a suitable alkali. As a class, they are compatible primarily with anionic and nonionic surfactants. This class of surfactants is divided further into three chemical groups: alkanoic acids, ester carboxylic acids and ether carboxylic acids.

B.1. Alkanoic acids

Chemical properties

The fatty acids derived from animal and vegetable glycerides make up most of the alkanoic acids. In addition, some alkanoic acids are prepared synthetically. Most naturally occurring fatty acids possess even-numbered carbon chains and are monofunctional. The naturally occurring unsaturated fatty acids normally display the cis-configuration; one of these, ricinoleic acid, not only is monounsaturated but also carries a hydroxyl group.

Polyunsaturated acids, such as g-linoleic acid, appear to play a special role in the formation of skin lipids in vivo. As a result, the acids and their derivatives (including surfactants) have received much attention by cosmetic formulators.

The natural alkanoic acids are prepared from fats and oils by hydrolysis, generally by alkalies. After saponification, the acids are precipitated by acidification, subjected to various types of purification, and isolated as individual or mixed alkanoic acids. When no isolation is carried out, the mixture of fatty acids from a particular lipid is identified by its source, such as soya or coco fatty acids.

Alkanoic acids are important raw materials in the cosmetic industry and the sources of many types of surfactants. As a rule, the fatty acids are identified by their classical names that reportedly reflect their historical sources. Most of the commercially available acids are not pure. The presence of unsaturated acids can be particularly troublesome because these acids tend to form peroxides.

The free acids are useful as surfactants only in rare instances, but the salts of the acids not only are the oldest but also the most widely used surfactants. "Soluble" salts are derived from alkali metals and short-chain amines. The insoluble salts are formed from alkaline earths and heavy metals. The salts of alkanoic acid, the alkanoates, are generically known as soaps. The ingredient listing at the end of this class includes separate listings for the alkanoic acids and for their salts, because formulators use the acids and form the soaps in situ rather than use preformed soaps.

Alkanoic acids are weak acids. Their pKas are estimated to be about 5 or 6. The free acids are relatively insoluble, and their use in aqueous acidic media for surfactant purposes is not practical. These acids and their neutral soaps form 1:1 association complexes; these so-called acid soaps may make an important contribution to the utility of alkanoic acids in cosmetics. These association complexes may also play an important role in the performance of toilet soaps. Free fatty acids are normal constituents of the skin lipids and may be converted to acid soaps during washing with alkali carboxylates. The study of these complex interactions is of current concern to investigators exploring the liquid crystalline state of skin lipids.

The insolubility of heavy metal and alkaline earth salts limits the utility of alkanoic acids in hard water systems. The fatty acids (and the soaps) form insoluble precipitates with long-chain alkylamines.

Physical properties

The alkanoic acids may be liquids or solids at room temperature. The commercial mixtures generally melt at much lower temperatures than the pure acids. The salts are solid. Aqueous soap solutions foam copiously.

Generic alkanoic acids

$R–COOH$

Alkanoic acid

$(R–COO)_2Mg$

Magnesium alkanoate

$(R–COO)_2AlOH$

Aluminum dialkanoate

Specific members:

Lauric Acid (CIR)
Aluminum stearate (CIR)
Cottonseed acid
Zinc undecylenate

Uses

The water-soluble soaps are used in a wide variety of cosmetic products. The sodium soap of stearic acid-a blend of 55% hexadecanoic and 45% octadecanoic acids'is used to make viscous emulsions, while the oleic acid soaps are preferred for fluid emulsions.

Soaps are used in shaving products and a wide variety of skin cleansers, especially the conventional soap bars. Potassium soaps and the salts of alkanolamines are more soluble than the sodium soaps and yield less viscous products. Sodium stearate gels ethanol and is used in deodorant stick products.

Magnesium soaps and other water-insoluble soaps are used as lubricants and gel formers in nonaqueous systems. These insoluble soaps can be used for the preparation of w/o (water-in-oil) emulsions. The metallic alkanoates are commonly used in face and body powders to provide hydrophobic characteristics to the application site.

Stability

Alkanoic acids are not chemically altered by exposure to acids or alkalies. Deterioration frequently is the result of oxidative (light-induced) reactions that cause rancidity and yellowing of the (poly)unsaturated members of this class.

Safety

Alkanoic acids are natural constituents of the human body and do not cause adverse effects. The salts with alkali metals are slightly basic and have been reported to be more irritating than other, less alkaline anionic surfactants. It is also generally

believed that dodecanoic acid, or its salts, has a greater propensity to cause irritation than do the longer-chain alkanoic acids. Several alkanoic acids and alkanoates have been reviewed by the CIR Expert Panel.

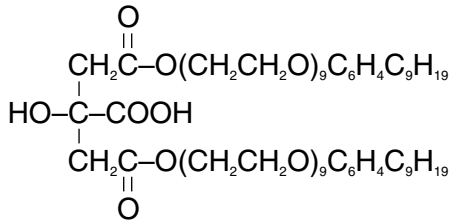
B.2. Ester Carboxylic Acids

Chemical properties

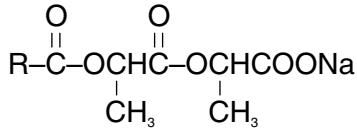
Ester carboxylic acids are a small group of monoesters of di- or tri-carboxylic acids. The ester may be formed by an alcohol and a polycarboxylic acid, such as dinonoxynol-9 citrate, or by an acid that reacts with a hydroxyl group on the carboxylic acid, such as the acyl lactylates. The salient chemical features are a neutralizable anion-forming carboxylate group as the hydrophile, and an ester-link generally as part of the hydrophobe. The ester group is subject to hydrolysis under adverse pH conditions.

Self-esterification of lactic acid leads to lactide, the cyclic ester formed between two molecules of lactic acid, and possibly to lactyl lactate. Lactide can be transesterified to a noncyclic acyl lactylate. These esterification reactions are not likely to go to completion. Instead, lactic acid, one of its dimers (lactide or lactylic acid), and polymeric polylactylates may be formed and remain as impurities in marketed actyl lactylates.

Generic ester carboxylic acids



Dinonoxynol-9 citrate



Sodium acyl lactylate

Specific members:

Calcium stearoyl lactylate
Laureth-6 citrate

The finished acyl lactylates are likely to contain substances derived from these impurities. Some of the acyl lactylates are GRAS food additives. They are commonly marketed as sodium or calcium salts.

Physical properties

The ester carboxylic acids are waxy solids. Salts of the short-chain lactylates foam well. It has been claimed that they are substantive to hair and provide humectant qualities.

Uses

The ester carboxylates are useful o/w and w/o emulsifiers. They can be used in shampoos, depending on their foaming ability.

Stability

The members of this group are esters but are considered stable under cosmetic-use conditions.

Safety

Ester carboxylic acids are reported to be mild on the skin.

B.3. Ether Carboxylic Acids

Chemical properties

The ether carboxylic acids are an increasingly important group of carboxylic acids derived from ethoxylated alcohols or phenols by oxidation of the terminal OH group. The resulting acids possess a lower pKa than the typical alkanoic acids, are not affected appreciably by hard water, and exhibit water solubilities depending on the length of the POE chain. Salt formation is only part of the criteria for water solubility. These carboxylic acids are compatible with all types of surfactants, including some cationics. The HLB of these compounds depends on the length of POE chains and the degree of salt formation.

Physical properties

The free acids are soft waxy solids, while the sodium salts are harder. The commercial products are aqueous suspensions or solutions. Aqueous solutions of the salts foam well.

Generic ether carboxylic acids
$R–(OCH_2CH_2)_nOCH_2COONa$ Sodium PEG-*n* alkyl carboxylate
Specific members:
Nonoxynol-8 carboxylic acid Sodium trideceth-13 carboxylate

Uses

The ether carboxylates are useful as emulsifiers and emulsion stabilizers.

Stability

Ether carboxylic acids and their salts are stable under normal cosmetic-use conditions.

Safety

The ether carboxylates are reported to be mild.

C. Phosphoric Acid Esters and Salts

Chemical properties

Surfactants of the phosphoric acid class are primarily the mono- and di-esters of phosphoric acid and their salts.

The normal route of synthesis involves reaction between an alcohol and phosphorus oxychloride. The product is a mixture of esters which requires purification to provide mono-, di- and tri-esters.

Phosphoric acid esters can be prepared from any alcoholic OH grouping in the precursor molecule. Thus mono- and di-glycerides, simple and complex alcohols, and a variety of ethoxylated derivates can be converted into phosphates. The alkyl groups of the esterifying alcohols can carry complex substituents, including quaternary functionalities. The resulting mono- and di-phosphates are then zwitterionic. Tri-phosphates, as a rule, are water-insoluble unless the esterifying alcohol carries a sufficiently powerful water-solubilizing group. The diesters are more lipophilic than the monoesters, and overall lipophilicity depends on the nature of the substituent alcohol. The neutralized esters (the salts) are soluble in water. However, they frequently exhibit some solubility in organic solvents. Some phosphoric acid esters are dispersible in water and are soluble in essentially nonpolar solvents.

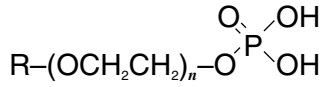
Phospholipids are particularly important members of this group. The most common of these is lecithin, more descriptively identified as phosphatidylcholine. The structure of a phospholipid is shown in the generic structures for this section. In the case of lecithin, one of the two protons on the 1,2-diacylphosphoglyceride is replaced by a choline grouping, R". This leaves one proton of the phosphoric acid component free to neutralize the amino grouping in the choline portion of the molecule. The R" grouping in phospholipids may include multifunctional components, such as ethanolamine or inositol. Naturally derived phospholipids and synthetically prepared phospholipids exhibiting differing R, R', and R" groupings are used today as emulsifiers in foods, drugs and cosmetics. It is noted that the central C-atom in the glycerin portion of the phospholipids is chiral.

Physical properties

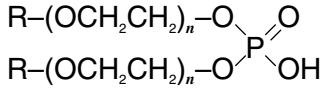
The free esters may be solids or tacky viscous fluids at room temperature. The sodium salts are solids. The phosphoric acid esters do not foam well.

Phosphoric-acid-derived surfactants have achieved a high level of interest in the

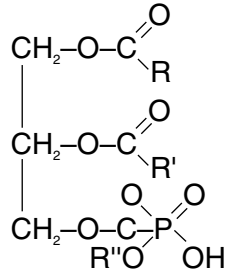
Generic phosphoric acid esters (and Salts)



PEG-*n* alkyl phosphate



Di-PEG-*n* alkyl phosphate



Phospholipid

Specific members:

DEA-oleth-10 phosphate
Dilaureth-4 phosphate
Lecithin

cosmetic industry in recent years. They have been reported to resemble the lipid components in various biomembranes.

Uses

Phosphates as a group are widely used as emulsifiers and cleansers. Simple monoalkyl phosphates reportedly are safe and non-irritating skin cleansers and are effective emulsifying agents. Natural and synthetic phosphoglycerides are prominently used in the formation of liposomes.

Stability

Phosphoric acid esters are readily hydrolyzed in acidic media but exhibit acceptable stability at neutral and slightly alkaline pHs. Natural phospholipids generally contain unsaturated fatty acids. Their applications in cosmetics generally require use of a suitable antioxidant.

Safety

No generic safety data for these phosphate esters is available. Some of them, especially lecithin, are edible and are important emulsifiers in food and drug products.

D. Sulfonic Acids and Salt

Surfactants of the sulfonic acid type are distinguished from other sulfur-containing surfactants by the presence of a chemically stable C-S bond and by the fact that the sulfur atom is tetravalent (by the classical definition). The sulfonic acids, as a group, are strong acids and are used in cosmetics only in the form of salts. They are divided into four groups. The acyl isethionates comprise a very small number of substances that are of particular importance in skin-cleansing products. The remaining larger groups are the alkylaryl sulfonates, the alkyl sulfonates and the sulfosuccinates.

D.1. Acyl Isethionates

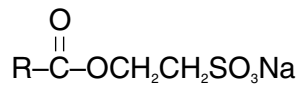
Chemical properties

Acyl isethionates are the esters formed between simple alkanoic acids and isethionic acids ($HOCH_2CH_2SO_3H$). Isethionic acid is formed by the addition of sodium bisulfite to ethylene oxide. The acyl isethionates are fairly strong acids and they are subject to autohydrolysis in aqueous solution unless their pH ranges are adjusted to near-neutrality with alkali. All commercially important isethionates are esters and are, therefore, marketed as sodium salts. It is a remarkable and totally unexplained fact that the acyl isethionates are milder than the sulfuric acid esters, most other alkyl sulfonates, and, evidently, even soaps.

Isethionates can be blended with anionic and nonionic surfactants. They possess the type of water solubility that permits their use in detergent bars, and they are not affected by hard water.

Physical properties

Acyl isethionates are solids and generally marketed as powders or flakes. They foam well, and their blends with soaps are particularly useful.

Generic acyl isethionates

Sodium acylisethionate
Specific member:
Sodium cocoyl isethionate

Uses

Although only a few types of acyl isethionates are available, they have been used extensively in shampoos and skin-cleansing products. They play an important role in the formulation of syndet bars.

Stability

The acyl isethionates are esters and may undergo hydrolysis at extreme pH conditions.

Safety

The unusual mildness of the acyl isethionate on the skin has been repeatedly confirmed.

D.2. Alkylaryl Sulfonates

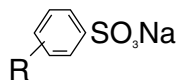
Chemical properties

Alkylaryl sulfonates are alkyl-substituted aromatic sulfonates. Most of them can be viewed as chemical derivatives of benzene sulfonic acid. Sometimes, the alkyl group(s) of the hydrophobe may be quite short, not exceeding three carbon atoms. Thus, some alkylaryl sulfonates may be derived from cumene, toluene or similar substances. The longer chain alkyl groups are synthetically prepared. The original alkylaryl sulfonates were based on alkyl groups ranging from about 12 to 15 carbon atoms derived from the polymerization of gaseous olefins (propylene and butylene). The resulting alkyl chains were of the branched type such as tetrapropylene, and were not readily biodegradable.

By contrast, modern alkylaryl sulfonates use straight-chain alkylates, such as olefins or chlorinated straight-chain paraffins from various sources. Then these are condensed with benzene, using the Friedel-Crafts reaction. The resulting alkyl benzene is finally sulfonated with sulfuric acid, SO_3 or related materials.

The alkylaryl sulfonates are derived from water-soluble strong acids; they are commercially available, primarily as salts. Their performance is not affected adversely in the presence of hard water.

Generic alkylaryl sulfonates



Sodium alkylbenzene sulfonate

Specific member:

Sodium dodecylbenzene sulfonate

Physical properties

Alkylaryl sulfonates derived from long-chain alkyl groups foam well and are efficient wetting agents. The sulfonates with short-chain alkyl groups also lower surface tension. They do not foam well but increase the solubility of other surfactants in the presence of inorganic salts. This property, hydrotropy, is particularly important in heavy-duty (built) detergents. It is less critical for cosmetic products, but hydrotropes of the alkylaryl sulfonates type can be used to lower the cloud point of surfactant-containing products.

Uses

Long-chain alkylaryl sulfonates are not widely used in cosmetic products. They have a tendency to cleanse excessively and leave a dry, harsh feeling on the skin and the hair. Their detersive properties are generally modified with other additives for use in cosmetics. They have, nevertheless, been used in bubble baths and antiseborrheic products.

Stability

The alkylaryl sulfonates exhibit excellent stability even under adverse conditions.

Safety

The reported tendency of alkylaryl sulfonates to remove lipids from the skin appears to be associated with the observation that alkylaryl sulfonates also tend to be moderate skin irritants.

D.3. Alkyl Sulfonates

Chemical properties

This group includes a few chemical substances of diverse structures. Some are derivatives of propylene glycol, although they carry names based on their derivation from glycerin. Others are derived from the sulfonation of alcohols or acids, while others are POE derivatives in which the terminal OH group is replaced by an SO_3 function.

The most important alkyl sulfonates are the a-olefin sulfonates that are prepared by sulfonation of linear olefins from petroleum cracking or oligomerization of ethylene. These compounds are mixtures of alkene and hydroxyalkane sulfonic acids and may contain some disulfonates. The reaction of the olefin with SO_3 first yields $RCH^2CH+-CH^2SO^3$. This intermediate may form a 1,2 or 1,3 sultone that ultimately produces a 2-OH or 3-OH alkane sulfonic acid.

The more prevalent reaction is the transfer of the positive charge along the carbon chain that finally yields various alkene sulfonic acids, the major constituent of commercial olefin sulfonates. The alkyl sulfonates are strong acids and are marketed primarily as the sodium salts.

The so-called alkyl glyceryl ether sulfonates represent one of the oldest classes of synthetic surfactants. They are obtained by the reaction of epichlorohydrin with a fatty alcohol, which is then converted to the desired end product by reaction with, for example, sodium sulfite. An analogous reaction with ethoxylated fatty alcohols

yields sodium alkylether sulfonates.

The one ester of sulfoacetic acid used in cosmetics is sodium lauryl sulfoacetate. This compound is an alkyl sulfonate in which the alkyl group has been modified.

Physical properties

Most alkyl sulfonates foam well and exhibit good detersive properties. They are generally available as aqueous solutions.

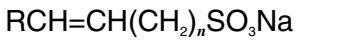
Uses

Alkyl glyceryl ether sulfonates or alkyl sulfoacetates have been used in dentifrices in the past. The a-olefin sulfonates are, however, widely used in shampoos. The sodium alkylether sulfonates have recently been introduced as primary surfactants for shampoos.

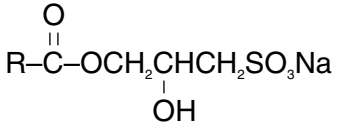
Stability

The sulfonates are very stable towards hydrolysis unless their structure includes functionalities of the ester type. The close proximity of the double bond to the sulfonate group in olefin sulfonates stabilizes the former against peroxidation.

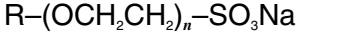
Generic alkyl sulfonates



Sodium alkenyl sulfonate
(major constituent of olefin sulfonate)



Sodium alkylglyceride sulfonate



Sodium alkylether sulfonate

Sodium lauryl sulfoacetate

Specific members:

Sodium cocomonoglyceride sulfonate
Sodium $C_{12\text{-}14}$ olefin sulfonate
Sodium $C_{12\text{-}15}$ pareth-15 sulfonate
Sodium lauryl sulfoacetate (CIR)

Safety

As a group, the alkyl sulfonates are relatively mild and non-drying on skin and mucous membranes. They cause less defatting than alkylaryl sulfonates. At moderate concentrations, the irritation potential reportedly is similar to that of soap. a-Olefin sulfonates should be free of sultones to assure the absence of troublesome idiosyncracies. One of these sulfonates has been examined by the CIR Expert Panel.

D.4. Sulfosuccinates

Chemical properties

Sulfosuccinates constitute a diverse group of derivatives of sulfosuccinic acid ($COOH\text{-}CH_2\text{-}CHSO_3H\text{-}COOH$). They may be considered to be alkyl sulfonates, carboxylic acids and esters or amides; their common origin makes them a cohesive chemical group.

The reaction of maleic anhydride with a hydrophobe, such as an alcohol or less frequently with an amine, leads to a mono-ester or an amide. If the reaction conditions are right, a disubstitued derivative of maleic acid may be formed. Any one of these compounds then can be further reacted with sodium sulfite or sodium bisulfite to produce a sulfosuccinic acid salt. The hydrophobe may be an alkyl alcohol, an alkyl ether, ethoxylated amide or amide derived from alkanolamines. The use of a (hydrophobic) amine in the initial reaction with maleic anhydride is rare.

The most common sulfosuccinates in cosmetics are mono-esters, which are almost exclusively marketed commercially as the disodium salts. Di-esters are generally derived from lower-molecular-weight alcohols (C4 to C10) and exist as the mono-salts of the sulfonic acid group. Branched-chain alkyl di-esters exhibit higher water solubility than the straight-chain homologs.

Sulfosuccinates are the salts of strong acids and as a rule, exhibit good water solubility. The water solubility of sulfosuccinates is enhanced by the presence of POE-groupings.

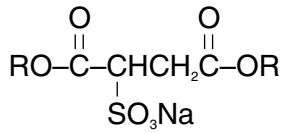
Physical properties

Sulfosuccinates are solids, but most of them are distributed as 30 to 40% aqueous solutions. Mono-esters lower the surface tension of water but do not produce stable foams. The di-esters produce more stable foams.

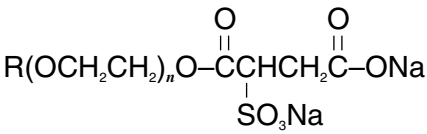
Uses

Sulfosuccinates, especially the alkanol amide derivatives, are used mostly in shampoos. They are lime soap dispersants and also can be used as o/w emulsifiers. As a result of their remarkable mildness, they can be used in bubble-bath formulations and skin cleansers. Sulfosuccinate mono-esters reportedly can reduce the irritation potential of other anionic surfactants. The mechanism for this action is obscure but has been attributed to the binding of the sulfosuccinate mono-esters to skin proteins.

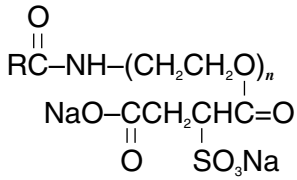
Generic sulfosuccinates



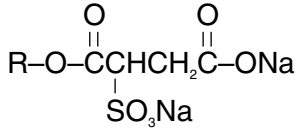
Dialkyl sodium sulfosuccinate



Disodium alkyl PEG-*n* sulfosuccinate



Disodium alkylamido PEG-*n* sulfosuccinate



Disodium alkyl sulfosuccinate

Specific members:

Dioctyl Sodium Sulfosuccinate
Disodium oleamido MEA-sulfosuccinate

Stability

The sulfosuccinates are esters and may contain other hydrolyzable groups. Nevertheless, their stability in aqueous media is satisfactory in cosmetic products.

Safety

The mono-esters of sulfosuccinates reportedly are among the least irritating surfactants on human skin. Their innocuous nature on skin or in the eye has been documented by extensive safety tests.

E. Sulfuric Acid Esters

Surfactants belonging into the sulfuric acid ester class are the salts of monoesters of sulfuric acid. The free acids are not available commercially because they are subject to hydrolysis even by traces of water and to other decomposition reactions. Two groups of sulfuric acid esters are available. One, the alkyl sulfates, is prepared by sulfation of long-chain alkyl alcohols; the other, the alkyl ether sulfates, uses ethoxylated alcohols (alkylethers) as the starting hydrophobe.

E.1. Alkyl Ether Sulfates

Chemical properties

Alkyl ether sulfates result when the terminal OH group of an ethoxylated alcohol (IV.E.1.) is sulfated (generally with chlorosulfonic acid). The starting ethoxylated alcohol may contain one or more (repeating) ethylene glycol groupings. Ethoxylated phenols and even ethoxylated amines or amides have been converted into ether sulfates.

The alkyl ether sulfates are mixtures because the starting alcohol is rarely pure and the degree of ethoxylation is based on an average value. For example, the average range of ethoxylation in sodium laureth sulfate is from 1 to 4, but this ether sulfate may include the free alcohol or levels of ethoxylation above 4.

The starting alcohol may be derived from natural or synthetic sources. Synthetic fatty alcohols are generally derived from one of two processes. The Ziegler process yields a blend of even-number carbon atom alcohols, some of which are also found in so-called natural fatty alcohols, those obtained by the reduction of plant or animal fatty acids. The alcohols derived from the oxo process include branched-chain and odd-number carbon chain derivatives. They may also contain some secondary alcohols. The latter are considered undesirable because they undergo sulfation reaction with difficulty. In any case, the carbon chain length of the hydrophobes varies, and the degree of branching and the possible presence of secondary alcohols introduce additional variables.

The alkyl ether sulfates usually contain some inorganic salts formed during the neutralization of the excess acid after sulfation. The alkyl ether sulfates exhibit good

Generic alkyl ether sulfates

$$R(OCH_2CH_2)_nOSO_3NH_4$$

Ammonium alkyl PEG-*n* sulfate

Specific members:

Ammonium laureth sulfate
Sodium $C_{12\text{-}13}$ pareth sulfate

water solubility, and their performance is essentially unaffected by water hardness.

Another type of ether sulfate can be formed from sulfation of an ethoxylated acylamide. Still another type can be synthesized by sulfation of alkoxylated polysiloxanes.

Physical properties

The alkyl ether sulfates are available commercially as aqueous solutions (about 25 to 60% active). They foam well, but their foam density and foam volume are marginally lower than those of the alkyl sulfates. Alkyl ether sulfates possess lower cloud-points than the alkyl sulfates.

Uses

The primary use of alkyl ether sulfates as detergents is in shampoos. They are not very useful as emulsifiers but are used in skin-cleansing products. Alkyl ether sulfates can be combined with alkyl sulfates and other anionic and nonionic surfactants to achieve the desired levels and qualities of foam and detergency.

Stability

Alkyl ether sulfates possess acceptable stability in cosmetic products at the usual pHs. They are subject to hydrolysis at extreme pHs. This instability is sometimes compared with that of the alkyl sulfates and has been reported both as superior and as inferior. This issue is of no practical concern in cosmetics since the experimental data were obtained at extreme pHs that are not encountered in properly formulated consumer products.

Safety

The safety of the alkyl ether sulfates is generally rated higher than that of the alkyl sulfates. Transdermal penetration of the two types of alkyl sulfates is about the same and should not be used to confirm this reported difference. One member of this group has been reviewed by the CIR Expert Panel.

E.2. Alkyl Sulfates

Chemical properties

Alkyl sulfates are prepared by sulfation of alkyl alcohols. The preferred hydrophobe is a primary alcohol, although sulfation of secondary alcohols is possible (sulfated castor oil).

Hydrophobic alcohols shorter than about 10 carbon atoms yield sulfates that are not very useful in cosmetics. Sulfation of alcohols larger than about C18 yield products that exhibit a low cloud-point. The hydrophobic alcohols may be obtained by reduction of naturally occurring fatty acids or may be of synthetic origin. As in the case of the alkyl ether sulfates, the hydrophobe can be expected to be a blend of various alkanols.

The sulfation reaction can be carried out with a number of reagents. In the case of the alkyl ether sulfates, chlorosulfonic acid is preferred, but alkyl sulfates also can be manufactured with the aid of sulfur trioxide. The resulting mono-esters must be neutralized rapidly after contact with water in order to avoid hydrolysis.

Generic alkyl sulfates
$ROSO_3H \cdot H_2NCH_2CH_2OH$ MEA Alkylsulfate
Specific member: MEA-lauryl sulfate

The water solubility of alkyl sulfates depends on the neutralizing cation. As a rule, the sodium salts are the most insoluble.

Physical properties

Alkyl sulfates are generally available as aqueous solutions or pastes. Solid sodium alkyl sulfates are available for special application. Alkyl sulfates are good wetting agents and produce copious foam. The viscosity of aqueous solutions is variable and depends on the specific neutralizing cation and on the presence of impurities, such as salts and unsulfated alcohol.

Uses

Alkyl sulfates are useful o/w emulsifiers, wetting and dispersing agents. Their primary use is as detergents in shampoos and skin-cleansing products. The so-called lauryl sulfates, sometimes identified as dodecyl sulfates, are the most useful in light of their solubility and tendency to produce flash foam. They usually are blended with other nonionic or anionic surfactants to increase foam stability and viscosity and to decrease their tendency to defat the skin. Sodium lauryl sulfate is used as the emulsifying agent in Anionic Emulsifying Wax, Brit. Pharmacopoeia. Purified (solid) alkyl sulfates are used widely in oral hygiene products as cleansers, foamers and antimicrobial agents.

Stability

Alkyl sulfates are esters and subject to hydrolysis at extreme pH conditions. In normal cosmetic practice, alkyl sulfates are considered stable.

Safety

The safety tests conducted on alkyl sulfates are extensive. Unfortunately, many of these studies have been conducted on hydrophobe blends that were not carefully identified. The irritation potential of the lower-molecular-weight alkyl sulfates is higher than that of the longer-chain alkyl sulfates.

Alkyl sulfates are irritating at high concentration and under occlusive conditions. They tend to predispose the skin to the penetration of other substances and are believed to defat epidermal tissues. In normal cosmetic practice the alkyl sulfates are generally considered safe - especially in rinse-off products or if their aggressive properties are modified by proper formulation. Several alkyl sulfates have been reviewed by the CIR Expert Panel.

Chapter 4

Cationic Surfactants

The most important class of cationic surfactants is referred to as *quats*. Within that generic group there are four major classes:

- Alkyl quats, having three methyl groups and one long alkyl chain.
- Alkylamido quats, having a fatty amido group and two or three methyl groups.
- Imidazoline-derived quats, having been derived from a hydrolyzed imidazoline.
- Polymeric quats, commonly referred to as *polyquats*.

The exact structure will determine the properties of the quats in formulations.

The term quat is a shorthand term for *quaternary ammonium compound*. All members of this class of compounds have four alkyl groups on nitrogen. Consequently, they have a positive charge on nitrogen. The presence of this charge and its attraction to substrates that have a negatively charged surface make these products substantive to hair and skin.

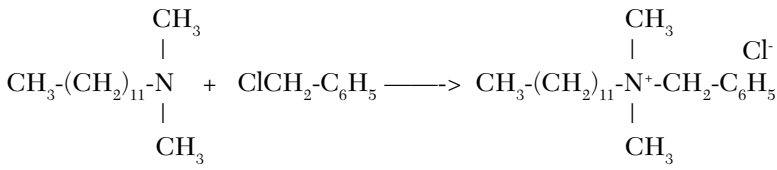
Alkyl Quats

This class of quaternary compounds finds a wide range of applications in personal care products. They are used as conditioners and softeners for hair and skin. If properly selected, alkyl dimethyl benzyl chloride-based quats are very potent antimicrobial compounds. Germicidal quats most commonly have the following substitution pattern on nitrogen:

- One group is alkyl, having a specific carbon distribution as defined shortly.
- Two methyl groups.
- A benzyl group on the nitrogen.

Reaction

One method for making alkyl quats is reacting a compound containing an organic chlorine, such as benzyl chloride, with a tertiary amine. The reaction is generally conducted in aqueous solution, but solvents like alcohol and/or glycols can be added. Inorganic chloride ion is produced as the organic chloride reacts, as shown below. C_6H_5 is the benzyl moiety.

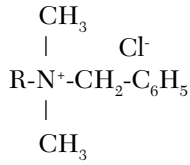


Alkyl dimethyl amine | Benzyl chloride | Benzyl chloride quat

Properties

Germicidal Quats

Germicidal quats have the following structure:



Quats used in germicidal applications need to be registered with the federal government, and the specifications are tightly controlled. In addition to specifications for the alkyl distribution, the specifications also include limits on the concentration of water, methanol, ethanol and free amine.

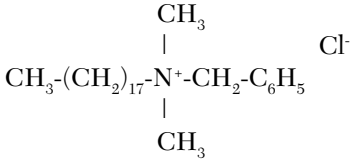
The typical alkyl group composition is:

Typical	R Group
50%	$C_{14}H_{29}$
40%	$C_{12}H_{25}$
10%	$C_{16}H_{37}$

The formulator must be careful to be sure that quats used in formulations as germicides have the proper registration. Many manufacturers of germicidal quats will help formulators with registration of formulations containing registered germicidal quats.

Conditioning Quats

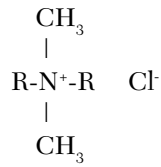
Perhaps one of the most commonly used quats is stearyl dimethyl benzyl alkonium chloride. It is an outstanding conditioner. The structure is:



The conditioning properties of this material were discovered during World War II. This quat is an excellent conditioner that provides outstanding wet-comb properties to hair. Because the quat is not clear in aqueous products even at low concentrations, it is most often used in formulated conditioners including cetyl and stearyl alcohols, an emulsifier and water. These so-called *cream rinses* have long been the workhorse of the conditioner market.

Stearalkonium chloride is a product that has some shortfalls. It has a tendency to make the hair hydrophobic, a condition that can result in a phenomenon called "gunkiness." Stearalkonium chloride is used at low concentration in personal care products because of concern for eye irritation. However, the formulation ingredients chosen for use with this quat can overcome these negative attributes.

Another group of alkyl quats is the dialkyl, dimethyl quats. These quats conform to the following structure:



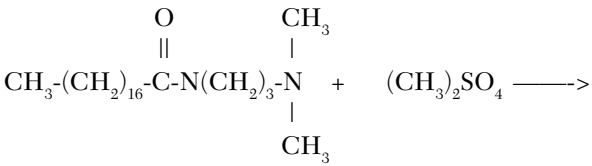
Dihydrogenated tallow dimonium chloride is one such quat. It is milder than stearalkonium chloride, presumably due to the presence of the second alkyl group. This is a very potent quat, providing outstanding conditioning at low concentrations. These kinds of quats are generally sold in alcoholic solvents to make their use in formulations more easily accomplished. They are used far more commonly in laundry softener and "softergent" products than in personal care products. The use of this kind of product will likely increase as it becomes more familiar to personal care formulators.

Alkylamido Quats

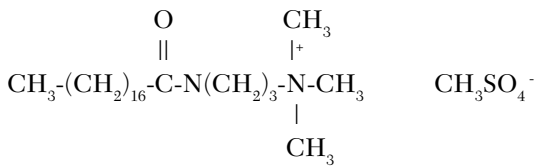
This class of quaternary compounds has an amido group in the compounds. The added amido group improves the mildness of the quat. Incorporation of an amido group into a surfactant generally will lower the irritation potential of the quat.

Reaction

One method of making alkylamido quats is reacting an alkylating agent such as dimethylsulfate with an alkylamido tertiary amine, as illustrated below.



Alkylamidoamine Dimethyl sulfate

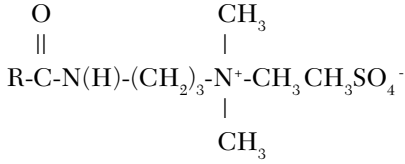


Alkylamido quat, methyl sulfate salt

Properties

The comparison of stearalkonium chloride with stearylamidopropyl dimethyl benzalkonium chloride quat offers good insights into the function of the amido group. The amido product is an outstanding conditioner, but somewhat less effective than the nonamido version. Unlike the nonamido product, the amidoamine-based product contributes luster to hair and increases body of the hair.

Another interesting amidoamine-based quat is ricinoleamidopropyl ethyldimonium ethosulfate. The material conforms to the following structure:

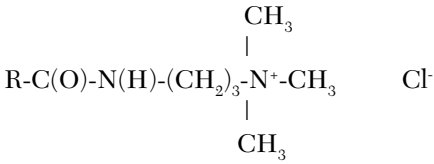


The R group is derived from castor oil. This quat is very mild from an irritation point of view and gives good conditioning and wet-comb properties. However, unlike many other alkylamido quats is a liquid as provided. In addition, unlike most other quats, this quat is water-soluble. The properties that make this product unusual appear to be related to the double-bond and hydroxyl group present in castor oil.

Mono Alkyl Quats

Monoalkyl quats of fatty acid materials having at least about 30% of at least a C-20 fatty acid component by weight are described in U.S. Patent 6,399,799. In accordance with the present invention, however, quats are made from fatty acids which are unsaturated and a content of C-20 fatty acids of greater than 30% by weight. The presence of unsaturation provides liquidity to the quat, and a high degree of conditioning.

Structure of a Typical Mono Alkyl Quat



R has greater than 30% of C-20 or above unsaturated alkyl group.

The preferred chain length for these quats is between about C-20 and about C-24. The quats are liquid at room temperature and will not require heating prior to formulation in conditioners or shampoos. The quats are liquid at room temperature and have cationic activities as high as 75%.

Di Alkyl Quats

Dialkyl quats made from long chain fatty acid constituents are disclosed in U.S. Patent 6,388,111. Surprisingly, the compounds are reported to have excellent anionic surfactant compatibility when compared to non-amidoamine based dialkyl quats. This allows them to be formulated into surfactant systems such as, for example, those present in shampoos, without the need for separate compatiblizers. Personal care products comprising a base of a shampoo, conditioner, liquid soap, facial/body wash or hair color and 0.1-10% cationic activity are easily prepared.

Generally, quats are not sold as individual compounds. Instead, they are dissolved or dispersed in a solvent or mixture of solvents. Generally, solvents can include ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol, alcohol such as ethanol, isopropyl alcohol and the like. Generally, the quats in accordance with the present invention are provided in an amount of between about 25 and 90% by weight relative to the amount of solvent. More preferably between about 25 and 80% and even more preferably between 25 and 65% by weight. In addition, fatty acids or fatty alcohols can also be used resulting in a flakable material.

Oils in accordance with the present invention include, without limitation, HEAR oil, as well as cod liver oil, herring oil, menhaden oil, mustard seed oil, pilchard oil, hear oil, salmon oil, sardine oil, and shark liver oil.

The C-20+ components of some of these oils are as follows:

Cod liver oil

8.8-14.6%	Eicosenoic acid (C20:1),
2.6-9%	Eicosapentaenoic acid (C20:5),
4.6-13.3%	Docosenoic (Erucic) acid (C22:1),
1-2%	Docosapentaenoic acid (C22:5) and
8.6-19%	Docosahexaenoic acid (C22:6);

Herring oil

1.5-19.2%	Eicosenoic acid (C20:1),
4.6-10.2%	Eicosapentaenoic acid (C20:5),
2.8-19.9%	Docosenoic (Erucic) acid (C22:1),
1-3.7%	Docosapentaenoic acid (C22:5) and
3.8-24.1%	Docosahexaenoic acid (C22:6);

Menhaden oil

0.9-2.7%	Eicosenoic acid (C20:1),
0.6-1.2%	Eicosatetraenoic acid (C20:4),
10.2-13.5%	Eicosapentaenoic acid (C20:5),
0.7-1.7%	Docosenoic (Erucic) acid (C22:1),
1.1-2.3%	Docosapentaenoic acid (C22:5) and
3.3-14%	Docosahexaenoic acid (C22:6);

Pilchard (Sardine) oil

3.2%	Eicosenoic acid (C20:1),
1.6%	Eicosatetraenoic acid (C20:4),
16.9%	Eicosapentaenoic acid (C20:5),
3.6%	Docosenoic (Erucic) acid (C22:1),
2.5%	Docosapentaenoic acid (C22:5) and 1
2.9%	Docosahexaenoic acid (C22:6);

HEAR oil

0.8-13.5%	Eicosenoic acid (C20:1),
20.1-59.4%	Docosenoic (Erucic) acid (C22:1),
0.1-1.4%	Tetrcosanoic (C24:0);

Mustard Seed oil

7%	Eicosenoic acid (C20:1),
44.2%	Docosenoic (Erucic) acid (C22:1).

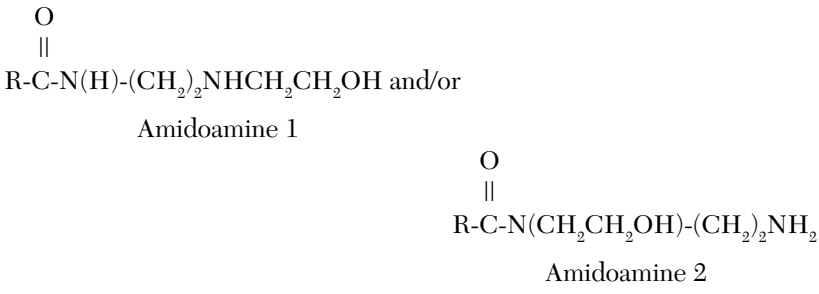
The formulations that can make use of these quats generally are conditioners, shampoos, colorings, liquid hand or body soaps, facial or body washes.

Imidazoline Quats

Quats based on imidazolines are made in a two-step process. Generally, the imidazoline is hydrolyzed under conditions of controlled pH to give the indicated amidoamine.

Chemistry

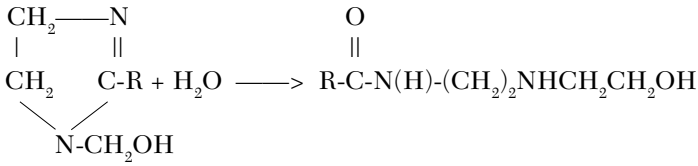
Many different specific process steps are used to make imidazoline-based quats. The specific conditions under which the imidazoline is hydrolyzed is an area of extreme interest. This is because two kinds of amidoamine compounds can be made by hydrolysis, as shown below.



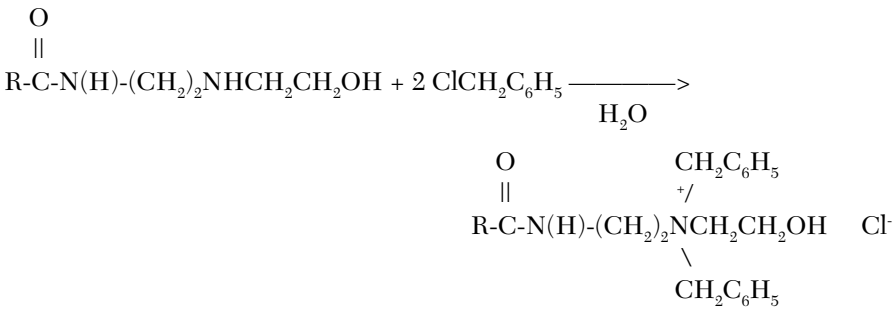
The ratio of one to the other affects viscosity, foam, performance and stability.

Reaction

Hydrolysis



Quaternization



Properties

The quats produced by the quaternization of a hydrolyzed imidazoline are similar in many ways to other alkylamido quats. They are mild to the skin and eye, provide moderate conditioning to the hair and can be formulated into highly cost-effective conditioners.

Fatty Anionic / Fatty Cationic Complexes

Anything that allows the formulator to achieve a consumer perceptible effect at a low concentration will be of interest to the consumer. One such product is an anionic / cationic complex made by combining the proper anionic and cationic material in aqueous solution.

The choice of the term complex relates to the fact that certain specific combinations of anionic and cationic materials result in a salt (or complex) that will preferentially deposit on the hair or skin to achieve the lowest free energy of the solution. Specifically, the driving force in this is the energy it takes to break hydrogen bonding in water. Oil floats on water in a two phase system that certainly is not the most random, but is the lowest energy for the very same reason; it takes energy to disrupt the hydrogen bonding that occurs in putting oil into the water.

Complexation therefore refers to the "salt" of two large molecules that disrupt more hydrogen bonding in water, and as such will be forced preferentially out of solution. This behavior produces the lowest free energy state system.

Another concept that is somewhat elusive is what happens to an aqueous solution of salts. The combination of anionic and cationic compounds in an aqueous system results in the formation of a number of salt compounds. The situation is much analogous to the blending of NaCl and KBr. The ionic species all belong to the solution, and consequently to each other. That is to say the solution contains Na^+ K^+ Br and Cl^- ions, rather than the two different salts. Generally, this is not an interesting factor, unless there is something specific of interest to one of the pairs.

Almost all cosmetic formulators have combined sodium lauryl sulfate and stearalkonium chloride. In this case the lauryl sulfate (anionic) / stearalkonium (cationic)salt is water insoluble and precipitates as a waxy mass. The remaining sodium chloride remains in solution.

It has been learned that when large molecular weight salts are made that are more water soluble than the lauryl sulfate / stearalkonium salt complex, it is possible to get a water soluble salt. The water soluble salt, by virtue of its size disrupts a lot of the water's hydrogen bonding and is energetically unfavorable. A discussion of the mathematics of these systems is described in a pioneering paper published in May 1981, by Lucasssen and Giles in the Journal of Colloid and Interface Science, Vol. 81, No. 1.

The initial work was done using a carboxy silicone and a cationic compound. The cationic compound of choice is alkyl amido quats and the complexes are disclosed in U.S. Patent 6,498,263. These complexes provide outstanding conditioning effects and skin feel in the presence of anionic surfactants at very low concentrations (as low as 0.5% by weight).

The technology has been expanded to cover non-silicone compounds.

U.S. patent 6,582,686 discloses the following:

$$R^1\text{-}O\text{-}(CH_2CH_2\text{-}O)_xCH_2\text{-}C(O)\text{-}O^- \qquad N^+\text{-}(R^2)_4$$

U.S. Patent 6,372,934 discloses compounds of the following structure:

$$R^1\text{-}O\text{-}(CH_2CH_2\text{-}O)_xC(O)\text{-}O\text{-}(R^3)\text{-}C(O)\text{-}O^- \qquad N^+\text{-}(R^2)_4$$

U.S. Patent 5,461,598 discloses the use of the compounds of 6,372,685 for conditioning hair.

These complexes are effective at very low concentrations, as low as 0.5% by weight in conditioning hair and providing conditioning and feel to skin. This approach allows for the conditioning to occur at minimal cost to the formulator, and with essentially non impact on eye and skin irritation.

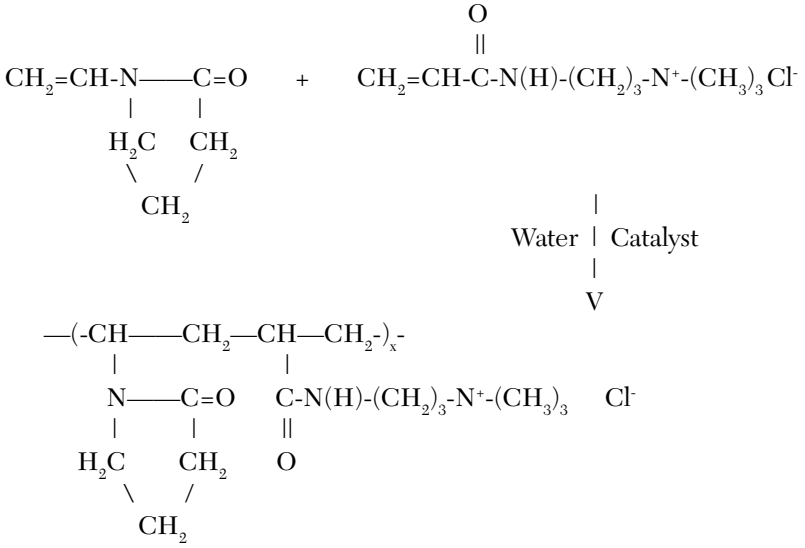
The inclusion of a high molecular weight water soluble dimethicone copolyol will improve the deposition and effectiveness of the complex.

Polymeric Quats

Quaternary compounds that have more than one cationic group are referred to as *polyquaternium compounds*. Some of the more interesting products are water-soluble. The presence of more than one cationic group on the molecule results in substantive conditioners that do not build up on the hair. The presence of the water-soluble cationic on the hair also results in a hydrophilic softness. The hair remains water-loving, rather than oil-loving, and the gunkiness encountered with the more hydrophobic conditioners is not experienced.

Reaction

Many of the polymeric quats are the result of free radical polymerization of vinyl-containing monomers in aqueous or alcoholic solutions. A typical reaction is illustrated below:



The ratio of the two monomers to each other and the exact conditions and catalysts used to make the polymer determine the functional properties and the molecular weight of the polyquaternium compound produced.

Properties

Compounds of this class are very substantive and generally durable when placed on a substrate like hair. Molecular weights of the polymers are classified as low (below 100,000 daltons), medium (100,000–800,000 daltons) and high (more than 800,000 daltons). The functionality of the polymers on a substrate is determined in part by the molecular weight. Low molecular weight products can penetrate hair to a greater extent than the middle or high molecular weight products. High molecular weight products do not penetrate. They remain on the surface of the hair, providing a somewhat greasy conditioning. Moderate molecular weight polymers have the ability to make harsh, rough hair smoother and more appealing to the touch. These quats give good wet-comb and antistatic properties.

Analysis of Cationic Surfactants

Instrumental Analysis

All cationic surfactants should be evaluated by Fourier transform infrared analysis. This instrumental technique is highly automated and when coupled with a computer analysis interface can locate small differences in products. These small differences might not be observable to the naked eye, so the use of sophisticated analytical instruments is strongly suggested. These techniques save time and money and are quite sensitive. The presence of an amido group, benzyl group and the like is significant and helpful for ensuring quality batch to batch and supplier to supplier.

Wet Analysis

The evaluation of surfactants in this class is based on the surfactants being cationic. The following analysis is recommended:

- Acid value
- Alkali value
- Zwitterionic point
- Solids
- NaCl
- Glycerin
- Bleaching agents
- Cationic activity

Information from Dr. Martin Rieger's Surfactant Encyclopedia: Cationic Surfactants

Substances are categorized as cationic if the charge on the hydrophobe is positive. Substances in which the hydrophobe carries no charge, unless the pH is lowered close to neutrality or lower, also are included in this category of cationic surfactants (for instance, alkylamines).

Cationic surfactants are further subdivided into four major classes:

A. Alkylamines
B. Alkyl imidazolines
C. Ethoxylated amines
D. Quaternaries

1. Alkylbenzyldimethylammonium salts
2. Alkyl betaines and related compounds
3. Heterocyclic ammonium salts
4. Tetraalkylammonium salts

The cationic surfactants used in cosmetics are N-derivatives. The neutralizing anion may be inorganic or organic.

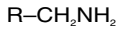
A. Alkylamines

Chemical properties

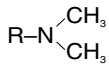
Alkylamines form a fairly large class of cosmetic surfactants. This class of cationic substances conveniently is divided into two subclasses. The (simple) alkylamines and their salts form one subclass, in which the amino function is responsible for the surface-active properties and the water solubility of the compound. Ethoxylated amines may be viewed as a second subclass. Their water solubility and utility in cosmetics depend to a large extent on the hydrophilic nature of the polyoxyethylene chain.

Primary, secondary or tertiary alkylamines, their salts, and substances with more than one basic nitrogen atom are derived from long alkyl chains and are relatively

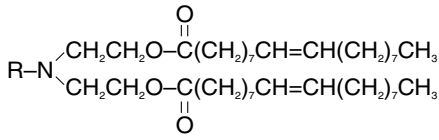
Generic alkylamines



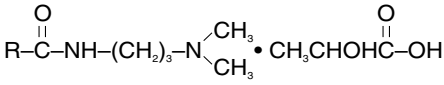
Alkylamine



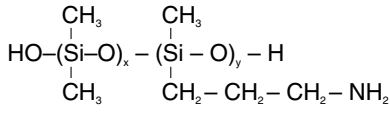
Dimethyl alkylamine



Dihydroxyethyl alkylamine dioleate



Acylamidopropyldimethylamine lactate



Amodimethicone

Selected members

Cocamidopropyl dimethylamine lactate
Dimethyl lauramine
Soyamine

hydrophobic. Their salts with inorganic and strong organic acids exhibit the type of solubility required for amphiphiles. These uninterrupted alkylamines are commonly prepared by reduction of the corresponding acylamide via the nitrile to the amine.

The synthesis of the so-called interrupted alkylamines first requires reaction of an acid chloride with one mole of a simple or substituted diamine to yield a series of substances sometimes referred to as "amido-amines." These substances are more polar than the straight-chain uninterrupted alkylamines and are more widely used in cosmetics as cationic emulsifiers.

As a rule, all these amines form precipitates with the more commonly used anionic surfactants.

Physical properties

The free amines in this group are waxy solids, while the salts and the interrupted amines exhibit higher melting points. The positive charge carried by the neutralized amines is responsible for their substantivity to negatively charged surfaces.

Uses

The amines, usually in the form of salts, are primarily used in cosmetics in combination with fairly hydrophilic surfactants. The interrupted alkylamines are compatible with a variety of other surfactants and can be used, for example, in combination with glyceryl monostearate to form emulsions with good tolerance to electrolytes. In lotion formulation, the interrupted amines prevent an increase in the viscosity upon standing. Aqueous solutions formed by the amine salts are effective hair conditioners and have antistatic properties.

Stability

The uninterrupted alkylamines are chemically stable. The interrupted amines are amides and subject to hydrolysis at extreme ranges of pH. The rate of hydrolysis is relatively slow at the lowest pH normally encountered in cosmetic products, and these amines may be considered stable at the low pH range. Their insolubility at elevated pH ranges normally precludes their use, and stability becomes a moot issue.

Safety

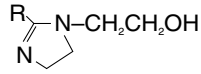
No general information on the ocular or topical safety of alkylamines is available.

B. Alkyl Imidazolines

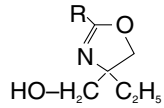
Chemical properties

The alkyl imidazolines comprise a small group of basic heterocyclic substances. They are obtained by the reaction of aminoethylethanolamine with a suitable fatty acid (derivative). During this synthesis, no linear amide is formed, but cyclization to a five-membered substituted ring occurs. The carboxyl carbon of the fatty acid becomes part of this ring. For the sake of simplicity, the nomenclature retains the name of the originally employed fatty acid, although the pendant group has been shortened by one carbon atom. Reaction of the alkyl imidazoline with an alkylating

Generic alkyl imidazolines



Alkyl hydroxyethyl imidazoline



Ethyl hydroxymethyl oleyl oxazoline

Selected member

Stearyl hydroxyethyl imidazoline

agents opens the ring and yields the amphoteric derivatives of ethylenediamine designated as class I.A. in this encyclopedia. The compounds in the group under discussion are primarily 1-hydroxyethyl-2-alkyl imidazolines.

A related product is derived from the reaction of 2-amino-2-ethyl-1.3-propanediol with a fatty acid to yield a substituted oxazoline.

Physical properties

The alkyl imidazolines are liquids and normally distributed as aqueous solutions.

Uses

These heterocyclics are used in cosmetics as oil-soluble emulsifiers to yield cationic oil-in-water emulsions. They are also used as substantive hair conditioners.

Stability

Imidazolines are subject to hydrolysis to the amide, and reformation of the cyclic structure is probably pH-dependent.

Safety

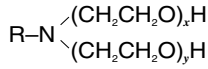
No detailed information concerning the safety of these substances has been published. They are considered irritating unless they are neutralized with a suitable acid.

C. Ethoxylated Amines

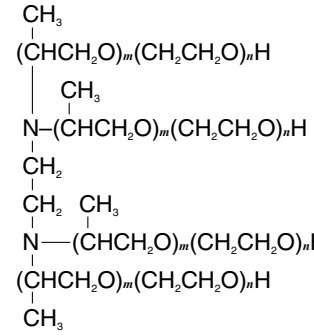
Chemical properties

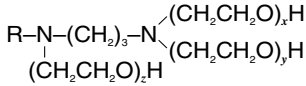
The ethoxylated amines constitute a class of nitrogen-containing surfactants in which aqueous solubility is to a large extent dependent on the degree and type

Generic ethoxylated amines



PEG-n alkylamine
(x+y has an average value of n)





PEG-n alkylaminopropylamine
(x+y+z has an average value of n)

Poloxamine

Selected members

PEG-cocopolyamine
PEG-15 tallow amine

of alkoxylation and is not always caused by salt formation. The basic nature of the amino group is not readily displayed in those substances, which carry long-chain polyoxyethylene groupings; and they are sometimes classified as nonionics.

The simple POE amines are prepared from long-chain alkylamines by ethoxylation. In some cases, the alkylamine is converted to a diamine before ethoxylation.

A more complex type of alkoxylated amine (the poloxamines) is synthesized by reaction of ethylene diamine with propylene oxide. This results in the formation of a hydrophobic tetra-substituted ethylene diamine. When this then is reacted with ethylene oxide, its hydrophobicity is decreased, depending on the ratio of hydrophobe to hydrophile. Even more complicated terminally fatty alkyl substituted alkoxylated amines have been prepared (PEG-n tallow polyamine).

Most ethoxylated amines are water-soluble and compatible with a wide variety of other surfactants, including anionics. They are relatively weak bases and do not require large amounts of acids to adjust their pH to the range normally used in cosmetics.

Physical properties

Ethoxylated amines are waxy solids that melt at relatively low temperatures.

Uses

Ethoxylated amines are used as emulsifying and hair-conditioning agents. They also can be used to aid in the dispersion of solids. Some members of this class increase product viscosity, while others are used to improve foaming.

Stability

The substances making up this class are acid- and alkali-stable and are not subject to hydrolysis.

Safety

No general information is available. As a rule, the topical and oral toxicities are quite low, while the eye irritation potential is variable and compound-dependent.

D. Quaternaries

Quaternaries comprise a large number of substances that are used extensively as surfactants and antimicrobial agents. Compounds are quaternaries only if they contain at least one nitrogen atom that is linked covalently to four alkyl or aryl substituents. This results in the formation of a positively charged nitrogen atom, and in quaternaries this positive charge is retained regardless of the environmental pH. This last requirement is a clear distinction between quaternaries, amphoterics and amine salts and is unrelated to any effect resulting from insolubility or precipitation. Lecithin, a phosphoric acid ester, is also a quaternary and meets this crucial criterion.

Quaternaries are divided into four groups: Alkyl-benzyldimethylammonium salts, betaines, heterocyclic ammonium salts and tetraalkylammonium salts.

Much synthetic expertise has been devoted to the synthesis of diverse tetraalkylammonium salts. No effort has been made to create special groups, such as hydroxyalkyl trialkylammonium salts.

Quaternaries, as a class, are known for causing ocular and topical irritation, although their potential for skin penetration is quite low. Continuous and safe use of quaternaries in cosmetics is highly dependent on the specific compound selected, its mode of use, and its concentration.

D.1. Alkylbenzyldimethylammonium Salts

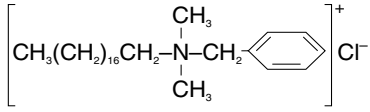
Chemical properties

This group of quaternaries represents compounds formed from the alkylation of alkyldimethylamines with benzyl chloride. The alkyldimethylamine generally is derived from a fatty alkyl group, although occasionally some more complex alkyl "chains" are used (benzethonium chloride). These substances are not compatible with anionic surfactants.

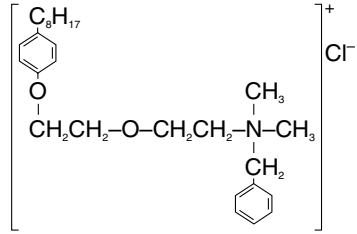
Physical properties

The members of this group are solids, but many are commercially available as aqueous suspensions or solutions.

Generic alkylbenzyldimethylammonium salts



Stearalkonium chloride



Benzethonium chloride (CIR)

Selected members

Benzalkonium chloride
Quaternium-63

Uses

Alkylbenzyldimethylammonium salts are important hair-conditioning and antimicrobial agents. Long-chain (fatty) alkyl groups are preferred for hair conditioning, and their efficacy increases with increasing alkyl chain length and resulting decrease in water solubility.

The most commonly used antimicrobial member of this class is benzalkonium chloride. This highly water-soluble material includes alkyl chains ranging from as low as C8 to as high as about C18 (stearalkonium chloride). The antimicrobial activity seems to reside predominantly in the C10 to C14 alkyl components of these commercial mixtures. The alkyl group in benzethonium chloride is derived from octoxynol-2. These quaternary substances are used as skin degerming agents and deodorants.

The alkylbenzyldimethylammonium salts can also be employed for emulsification and for formulating acid stable creams and lotions. Certain clays can react with quaternary compounds; and the resulting adducts have been found to be useful suspending agents (stearalkonium hectorite).

Stability

This group of quaternaries is stable under cosmetic-use conditions. In the presence of some anionic species, these quaternaries may form insoluble salts, depending on the ratio of anionic to quaternary. Quaternaries form the less stable hydroxides in the very high pH range, but these conditions are unlikely to occur in cosmetic use.

Safety

The general comments made in the introductory paragraph on quaternaries are applicable.

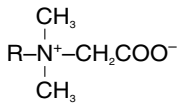
D.2. Alkyl Betaines (and related compounds)

Chemical properties

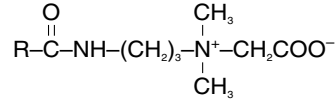
Alkyl betaines are the N-alkyl derivatives of N-dimethylglycine. They conform to the definition of quaternaries given previously. The simple alkyl betaines may be viewed as derivatives of N-di-methylalkylamines formed by alkylation with chloroacetic acid. The substituent alkyl chain may include an acyl grouping, as in the case of alkylamidopropyl betaines. The related compounds are derivatives of aminohydroxy-propyl sulfonic acid (sultaine) or of the phosphoric acid esters of hydroxypropanolamine (phostaine).

In acid solutions, the betaines exist as positively charged cations; in alkaline solutions they carry both a positive and a negative charge; finally, at intermediate pH (4 to 8) some of the positive charges may be internally compensated, and the compounds may exist partially as zwitterions.

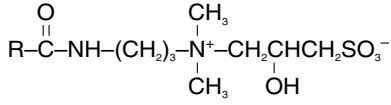
Generic alkyl betaines



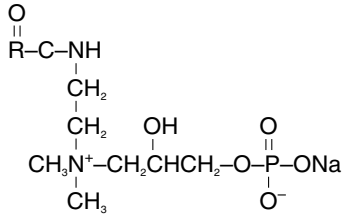
Alkyl betaine



Alkylamidopropyl hydroxysultaine



Alkylamidopropyl betaine



Sodium alkylamidopropyl hydroxyphostaine

Selected members

Oleyl betaine
Sodium lauramidopropyl hydroxyphostaine

The solubility of the betaines is unusual because they generally retain high water solubility throughout a wide pH range. This feature is, of course, related to the constant presence of the positively charged nitrogen atom.

Betaines are compatible with all types of surfactants. At or near the isoelectric point and depending on concentration, the betaines may form complexes with anionics that may interfere with a product's performance.

Physical properties

The betaines as a group are solids but are commercially available as solutions. Their solutions, especially those of the sultaines, foam well even in hard water and do not become cloudy at low temperatures.

Uses

The betaines are substantive to hair and skin proteins and provide excellent conditioning and antistatic properties. Their physical characteristics—solubility, foaming power, and cloud point—account for their wide use in shampoos in combination with anionic surfactants. As a result of their mildness, betaines are important constituents of baby shampoos. In addition, they can be used to increase the viscosity of shampoos. The same characteristics account for their utility in facial-cleansing products. They rarely are used as emulsifiers.

Stability

The betaines exhibit good stability under the conditions normally encountered in cosmetic products.

Safety

The betaines belong to a group of quaternaries that is reported to exhibit low eye-and-skin irritation potential. In fact, it has been claimed the inclusion of betaines can lower the irritation potential of anionic surfactants.

D.3. Heterocyclic Ammonium Salts

Chemical properties

The heterocyclic quaternaries form a small group of surfactants that is derived from heterocyclic aliphatic or aromatic compounds in which a ring nitrogen atom is quaternized. The original heterocyclic nitrogen atom may be part of morpholine, imidazoline, pyridine or iso-quinoline. The imidazoline-derived quaternaries may be subject to hydrolysis in aqueous media.

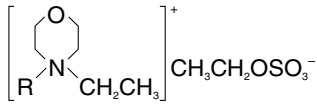
Physical properties

The heterocyclic quaternaries are water-soluble solids.

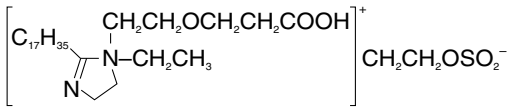
Uses

The quaternaries derived from imidazoline and morpholine are used primarily as hair-conditioning and antistatic agents. Quaternaries derived from aromatic heterocyclics have major application as antimicrobial agents. Compounds in this group generally are not used as emulsifying agents.

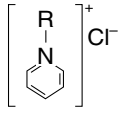
Generic heterocyclic quaternaries



Alkylethyl morpholinium ethosulfate



Isostearyl ethylimidonium ethosulfate



Alkylpyridinium chloride

Selected members

Cetylpyridinium chloride
Isostearyl ethylimidonium ethosulfate

Stability

As a group, the heterocyclic quaternaries exhibit good stability in cosmetic and pharmaceutical products.

Safety

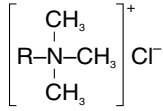
See the general comments under the heading Quaternaries.

D.4. Tetraalkylammonium Salts

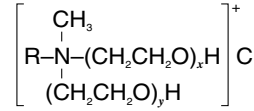
Chemical properties

The tetraalkylammonium salts possess the structure $[R^1R^2R^3R^4N^+]$ X^-, where R1, R2, R3, and R4 represent separate alkyl groups and X- represents an anion. The R groups may be identical or different and may be substituted with a variety of other functional groups such as amide or OH. One or two of the substituent alkyl groups may be of the polyoxyethylene or polyoxypropylene type. If R^1 and R^2 are both methyl and R^3 is benzyl, the resulting quaternary is classified as an alkylbenzyldimethyl derivative.

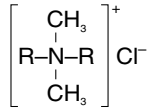
Generic tetraalkylammonium salts



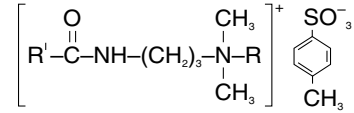
Alkyl trimonium chloride



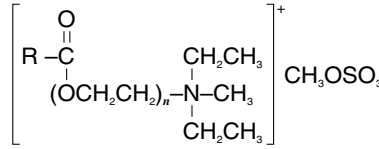
PEG-n alkylmonium chloride
(x+y has an average value of n)



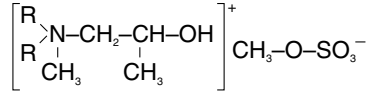
Dialkyldimonium chloride



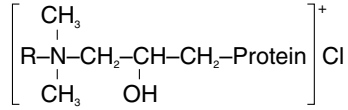
Alkylamidopropyl alkyldimonium tosylate



PEG-n Acylmethyldiethonium methosulfate



Dialkyl hydroxypropylmonium methosulfate



Alkyldimonium hydroxypropyl protein hydrolysate

Selected members

Cocamidopropyl ethyldimonium ethosulfate
Hydroxyethyl cetyldimonium chloride
Quaternium-18
Cocodimonium hydroxypropyl hydrolyzed hair keratin

Alkylene diamines form bisquaternaries and, if further substituted, can yield polyquaternaries. Some fairly complicated quaternaries result from esterification of dimethicone copolyol with an acid carrying a quaternary grouping to yield so-called silicone quaterniums.

The solubility of these quaternaries depends on the nature (polarity) of the substituent alkyl groupings. The more polar members of this class are generally water-soluble. The less polar substances, such as those with two long alkyl chains and no other hydrophilic groupings, may be oil-soluble. As a rule, these substances are incompatible with almost all anionics unless they carry long-chain polyoxyethylene groupings or multiple OH groups.

Physical properties

Tetraalkylammonium salts are solids, some of which are available as solutions or aqueous pastes. Like all quaternaries, they are adsorbed readily by negative charges on all types of surfaces. The resulting substantivity accounts for their use as conditioners, fabric softeners and antimicrobial agents.

Uses

Those members of this group that are only moderately soluble in water are used as hair and skin conditioners. The di-fatty alkyl ammonium salts (for example, distearyl dimonium chloride) are particularly powerful conditioners and are used in cream rinses for hair conditioning and as antistatics.

The more water-soluble mono-alkyl members of this group, for example cetrimonium bromide, are used as antimicrobial agents. This substance has also been used as the surfactant in several emulsifying waxes.

As a group, tetraalkylammonium salts can be used as emulsifiers in acid systems, particularly in combination with nonionic surfactants.

Stability

Tetraalkylammonium salts are considered stable under cosmetic conditions.

Safety

See general comments (Quaternaries).

Fatty Quats - Hardness of Cationic Materials*

Background

Fatty quaternaries have been known for many years. Because of their fatty nature and positive charge, these compounds find application in a variety of areas including as conditioners for hair and skin. Despite the fact these materials have been recognized as key cosmetic additives, there is little published on the structure function relationship on basic properties. For example, some quats are very insoluble when added to anionic surfactant, others have improved compatibility. The ability to select quats that have optimum compatibility with anionic systems offers the formulator flexibility in formulating heretofore unavailable. There is also much confusion related to deposition of cationic material onto hair as measured by a number of red dye uptake tests. These tests merely measure cationic on the surface of the hair. Since deposition on hair made from a solution containing cationic and anionic, contains no free cationic, no red color is observed with these tests. This does not mean however there was no deposition, it simply means the deposited material does not have an overall positive charge and consequently does not bind dye.

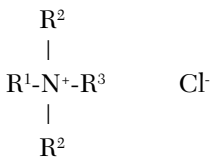
Anyone that has added stearylalkonium chloride to sodium lauryl sulfate and observed the white sticky solid that results knows anionic and cationic surfactants can be incompatible. We have begun to call anionic and cationic materials that produce a white gunky solid when mixed together *hard complexes*. As the expression implies the cationic and anionic compound possess properties which when added together form insoluble complexes (salts). We set out to determine if there are cationic materials having different structures which could be more soluble in the presence of anionic surfactants. The terms used here for quats and anionic materials are an adaptation of the work of Pearson used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases"[1]

The structural changes that can be made to cationic molecules can "soften" them, making them more compatible with anionic systems. Alternatively, there should also be the possibility of developing an anionic material that has increased compatibility with cationic surfactants, perhaps a more highly ethoxylated sulfate or a sulfosuccinate. However, this concept of modifying the anionic, is a topic for another investigation.

A study was undertaken to determine (1) compatibility of specific quats with SLS and SLES, (2) foam properties of the combinations with SLS and SLES (3) substantivity of these combinations with SLS and SLES and (4).

* This study was sponsored by Phoenix Chemical (Somerville N.J.) and SurfaTech Corporation (Dacula, Ga). It was conducted by Thomas O'Lenick (synthesis) and Tim Brockman (evaluation). Thomas O'Lenick is a senior chemistry major at Georgia Southern University and Tim is a junior Chemistry major. The applications portion of the study was directed by Steve Cochran of Phoenix Chemical.

The quats studied conform to the following structure:



The preferred definitions for the study groups are:

R^1 1. Alkyl (C12)
2. Ricinoleylamidopropyl
3. Dilinoleylamidopropyl
4. Cocamidopropyl

R^2 1. Methyl CH_3
2. 2-hydroxy ethyl CH_2CH_2OH

R^3 1. Methyl CH_3
2. Benzyl CH_2-C_6H_5
3. Glyceryl CH_2-CH(OH)-CH_2-OH

Table 1. Compounds Studied

Name	R^1	R^2	R^3	Description
AMB	Alkyl (C12)	CH_3	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C12)	CH_2CH_2OH	CH_3	Coco di-2 hydroxyethyl methyl ammonium chloride
AMG	Alkyl (C12)	CH_3	Glyceryl	Coco dimethyl glyceryl ammonium chloride
AMM	Alkyl (C12)	CH_3	CH_3	Coco tri-methyl ammonium chloride
AEB	Alkyl (C12)	CH_2CH_2OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C12)	CH_2CH_2OH	Glyceryl	Coco di-2 hydroxyethyl glyceryl ammonium chloride
CaMB	Castor Amido chloride	CH_3	Benzyl	Ricinoleylamidopropyl dimethyl benzyl ammonium
CaMG	Castor Amido	CH_3	Glyceryl	Ricinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMB	Dimer Amido chloride	CH_3	Benzyl	Dilinoleylamidopropyl dimethyl benzyl ammonium
DMG	Dimer Amido chloride	CH_3	Glyceryl	Dilinoleylamidopropyl dimethyl glyceryl ammonium
DMM	Dimer Amido	CH_3	CH_3	Dilinoleylamidopropyl trimethyl ammonium chloride
MMB	Cocamido	CH_3	Benzyl	Cocamidopropyl dimethyl benzyl ammonium chloride
MMG	Cocamido	CH_3	Glyceryl	Cocamidopropyl dimethyl glyceryl ammonium chloride
MMM	Cocamido	CH_3	CH_3	Cocamidopropyl trimethyl ammonium chloride

(A) Compatibility with anionic

A determination of compatibility of a variety of quats with two anionic surfactants, sodium lauryl sulfate and sodium laureth-3-sulfate was made. The compatibility was determined by titration. The point at which an anionic solution containing 10% anionic either became hazy formed a precipitate was determined.

PROCEDURE- Solution preparation

1. Prepare 50g of a 10% active test solution of surfactant. Record pH.

SURFACTANTS
Sodium Lauryl Sulfate
Sodium Laureth Sulfate

Ingredient	W/W
Surfactant	34.00%
Distilled Water	65.50%

Combine ingredients listed with slow to medium agitation. Mix until uniform at 20-25°C. Prepare test solutions for both SLS and SLES.
10% active SLS
10% active SLES

2. Prepare 100g of a 10% active test solution for each quat sample.

Preparation of 10% Active Quat

Ingredient	W/W
Stock Quat Solution (35% w/w)	28.50%
Distilled Water	71.50%

Combine ingredients listed with slow to medium agitation. Mix at 20-25°C until uniform.

3. Using a hot plate and stir bar set on medium agitation, slowly titrate surfactant test solution with quat solution using a 5mL disposable pipette, at a rate of one drop per second. Continue adding quat solution until a precipitate is observed. (Subjective evaluation). Solution will appear cloudy and translucent at this point. Record the amount (grams) of quat solution added at the cloud point, final pH, and the viscosity. Repeat for remaining quat solutions. Store at 20-25°C for use in part II. Observe Solutions after 24 hours. If solution remains cloudy, then titration is complete. If solution is clear, then repeat step 3. Perform titration for each quat using SLS and SLES individually.

CALCULATIONS

$$\% \text{ QUAT ADDED} = \frac{\text{GRAMS OF QUAT ADDED}}{(50 + \text{GRAMS OF QUAT ADDED})} \times 100$$

RESULTS

Table 2: Titration Data (SLS)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Final pH	Viscosity (cps)	Notes
AMB	9.75	7.6	4,400	Formed an opaque, pearlescent gel beyond the haze point
AME	6.28	7.1	<10	Did not form a gel
AMG	30.49	8.1	<10	Did not form a gel
AMM	17.63	7.8	<10	Did not form a gel
AEB	14.58	7.9	<10	Did not form a gel
AEG	29.53	7.7	<10	Did not form a gel
CaMB	25.72	7.6	1,000	Formed a gel
CaMG	44.47	7.1	1,000	Formed a gel
DMB	18.33	7.6	<10	Did not form a gel
DMG	40.25	7.6	12,000	Formed a gel
DMM	23.85	7.6	6,000	Formed a gel
MMB	15.28	7.4	14,000	Formed a
MMG	31.02	8.0	13,000	Formed a gel
MMM	21.25	8.0	13,400	Formed a gel

TABLE: 3 Titration Data (SLS)

Hard Quats – No Gel in Sodium Lauryl Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	9.75	<10	Did not form a gel
AME	6.28	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
DMB	18.33	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel

Soft Quats – Gel Formers in Sodium Lauryl Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
MMB	15.28	14,000	Formed a gel
MMM	21.25	13,400	Formed a gel
DMM	23.85	6,000	Formed a gel
CaMB	25.72	1,000	Formed a gel
MMG	31.02	19,200	Formed a gel
DMG	40.25	12,000	Formed a gel

The quats that showed the best compatibility and gellation properties with sodium lauryl sulfate were the amido quats. The only exception was the amido quat that contained an aromatic group (DMB).

Table : 4 Titration Data (SLES)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Final pH	Viscosity (cps)	Notes
AMB	18.67	6.6	<10	Did not form a gel
AME	4.47	7.0	<10	Formed a gel
AMG	25.04	7.2	1,000	Formed a gel
AMM	17.44	7.2	<10	Did not form a gel
AEB	18.35	7.2	<10	Did not form a gel
AEG	38.72	7.1	1,000	Formed a gel
CaMB	24.31	7.6	1,000	Formed a gel
CaMG	46.23	7.3	1,000	Formed a gel
DMB	11.09	7.3	<10	Did not form a gel
DMG	28.37	7.9	6,800	Formed a gel
DMM	20.00	7.0	6,200	Formed a gel
MMB	25.00	7.1	<10	Formed a gel
MMG	26.68	7.1	40,000	Formed a gel
MMM	20.23	7.3	50,000	Formed a gel

TABLE: 5 Titration Data (SLS)

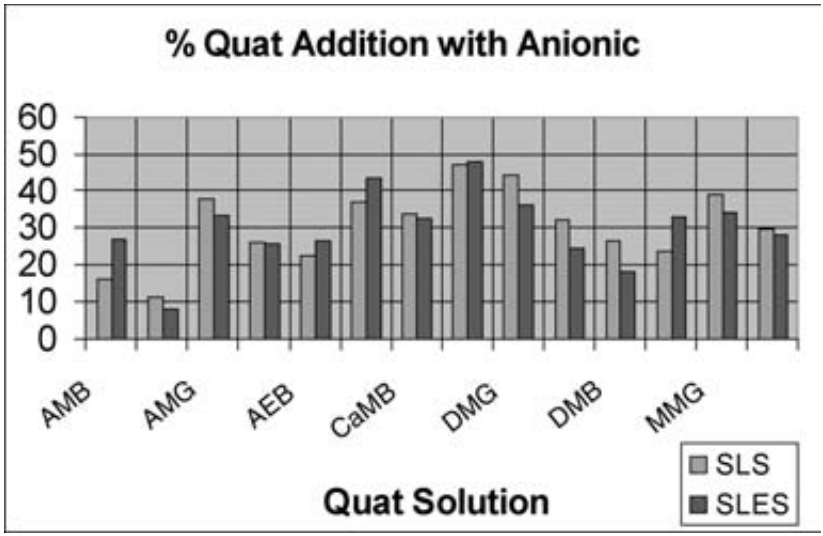
Hard Quats – No Gel in Sodium Laureth-3-Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	18.67	<10	Did not form a gel
AMM	17.44	<10	Did not form a gel
AEB	18.35	<10	Did not form a gel
DMB	11.09	<10	Did not form a gel

Soft Quats – Gel in Sodium Laureth-3-Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AME	4.47	7,000	Formed a gel
DMM	20.00	6,200	Formed a gel
MMM	20.23	50,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
AMG	25.04	1,000	Formed a gel
MMB	25.00	9,800	Formed a gel
MMG	26.68	40,000	Formed a gel
DMG	28.37	6,800	Formed a gel
AEG	38.72	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel

There was improved compatibility with sodium laureth-3-sulfate when compared to sodium lauryl sulfate. This leads to the conclusion that SLES is a softer anionic than SLES.



(B) Foam Height and Stability

It has been generally assumed that a gel made using an anionic and cationic combination would not foam. An evaluation of the gelled system was therefore undertaken to see if this is true.

PURPOSE

Determine the height and stability of foam produced from aqueous solutions of anionic surfactant containing quaternium compounds.

PROCEDURE

QUAT SOLUTIONS

TITRATED QUAT SOLUTIONS FROM PART I ABOVE

CONTROLS

INCI: Polyquaternium-10
Sodium Lauryl Sulfate
Sodium Laureth Sulfate

Name	ARL-4-84A	ARL-4-84B	ARL-4-84C	ARL-4-84D
Polyquaternium 10	1.00%	1.00%	-	-
Deionized Water	91.00%	91.00%	92.00%	92.00%
Sodium Lauryl Sulfate	8.00%	-	8.00%	-
Sodium Laureth Sulfate	-	8.00%		8.00%

1. Prepare ARL-4-84A and B by mixing polyquaternium 10 and deionized water with a prop mixer set on low speed until uniform. (1-5min, 20-25°C).

2. Add surfactant and mix with medium agitation until uniform. (1-2min 20-25°C).

3. Prepare ARL-4-84C and D by combining deionized water and surfactant. Mix with medium agitation until uniform. (1-2min 20-25°C).

RESULTS

Table : 6 Foam Heights of SLS Titrations

Quat Sample	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
AMB	-	-	-	Does not foam
AME	190	90	140	30.0
AMG	500	400	300	30.0
AMM	600	500	350	15.0
AEB	300	200	200	40.5
AEG	200	100	150	40.0
CaMB	250	150	175	95.0
CaMG	200	100	150	79.0
DMB	400	300	250	14.0
DMG	300	200	200	8.0
DMM	250	150	150	13.0
MMB	400	300	250	29.0
MMG	400	300	250	97.0
MMM	400	300	250	1440.0

Table : 7 Foam Heights of SLES Titrations

Quat Sample	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
AMB	150	50	100	141.0
AME	250	150	175	1440.0
AMG	350	250	225	240.0
AMM	200	100	150	1440.0
AEB	200	100	150	47.0
AEG	300	200	200	1440.0
CaMB	150	50	125	8.50
CaMG	150	50	125	6.0
DMB	150	50	125	5.5
DMG	200	100	150	75.0
DMM	150	50	125	9.0
MMB	200	100	150	1440.0
MMG	250	150	175	146.5
MMM	300	200	200	1440.0

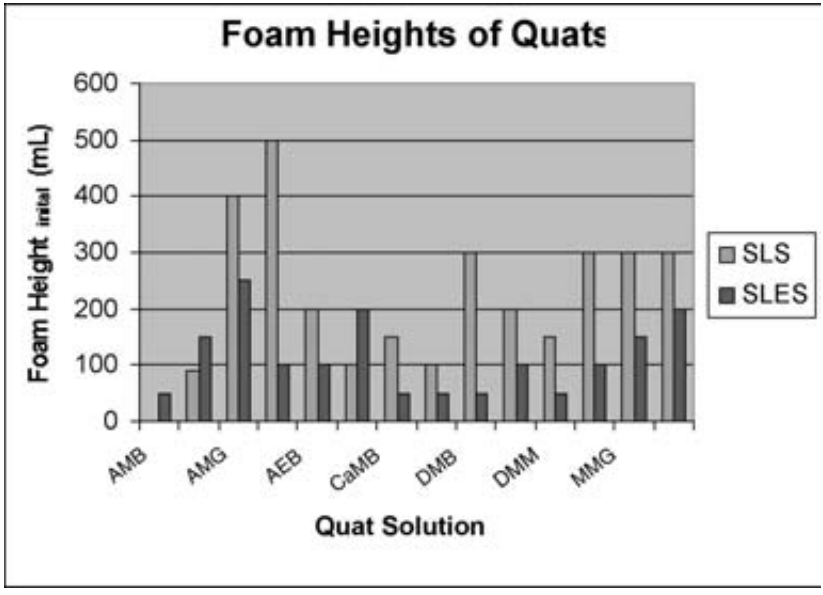


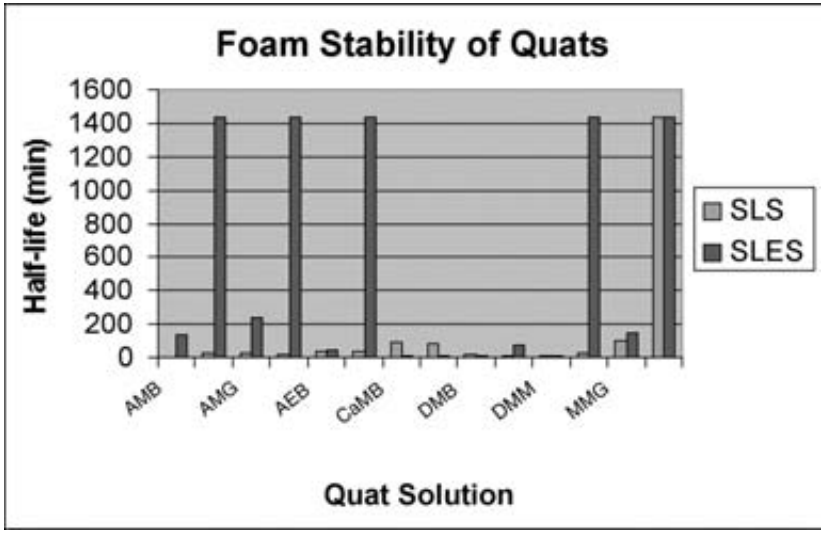
Table: 8 Foam Heights of Controls

Control	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
ARL-4-84A	200	100	100	31.0
ARL-4-84B	200	100	150	1440.0
ARL-4-84C	600	500	350	25.0
ARL-4-84D	450	350	275	180.0

Quat solutions titrated with sodium lauryl sulfate (SLS) produced higher levels of foam than those titrated with sodium laureth sulfate (SLES). However, the quat solutions that were titrated with SLES exhibited greater foam stability than those titrated with SLS. In some cases the quats titrated with SLES had a half-life greater than 24 hours (1440 minutes), including the control. After running all controls, it can be concluded that the addition of quaternium compound had a negative effect on the foaming capabilities of SLS and SLES. Stock SLS produced a foam height of 600mL, while the average foam height produced from quat/SLS was around 250mL.

Quat AMB (SLS) produced no foam. Unlike all the other quats that were titrated with SLS, which formed translucent, cloudy, gels at their respective cloud points, quat AMB produced a white, opaque paste. This is evidence that a complex is forming between this quat and SLS. This did not occur when quat AMB was titrated with SLES.

Controls for this experiment produced expected results. ARL-4-84A, which contained 1% polyquaternium 10, produced a higher foam height than ARL-4-84B, which also contained 1% polyquaternium 10, but in SLES. This also proved true for ARL-4-84C and D as well, which produced the same results. Based on



these test results, SLES produced greater foam stability than SLS, however SLS produced higher levels of foam.

Quat AMM and MMM performed superior in SLS and SLES compared to all the samples tested, including the controls. AMM showed superior foaming capabilities, by achieving the greatest foam height in SLS (500 mL), as well as having one of the best foam stabilities in SLES (over 1440 minutes). This stability was roughly ten times greater than all other quats and controls tested, with the exception of AEG, CaMB, MMG, and MMM, which all had foam stabilities of over 1440 minutes. It can be concluded that these quaternium compounds did not have a great effect on the expected foaming capabilities of SLS or SLES, with the exception of AMM and MMM. These two quat solutions increased foam stability by a factor of ten without suppressing foam height.

(C) Substantivity (Aqueous Delivery System)

PURPOSE

Determine the substantivity of quaternium compounds in an aqueous delivery system. To human hair.

PROCEDURE

TEST SOLUTION	ARL-2-73A$_1$ LOT#: 020604
STOCK SOLUTION	ARL-2-73A LOT#: 020604
	DIRECT RED 80 (ALDRICH 365548-25G, LOT#: 04927)
	GLACIAL ACETIC ACID (ALDRICH 338826-25ML, LOT #: 12405LA)

TREATMENT SOLUTIONS

Name	W/W	Formula #
35% Active Quat Solution	0.5%	ARL-4-85A-N
Deionized Water	99.5%	

CONTROL

Polyquaternium-10

RESULTS

Table: 9 Cationic Substantivity: 0.5% Quat Solutions

			RESULT	
Quat Solution	**Tress Sample**	**Treatment**	**Positive**	**Negative**
AMB	A	ARL-4-85A	Pink	-
AME	B	ARL-4-85B	Purple	-
AMG	C	ARL-4-85C	-	No Color Change
AMM	D	ARL-4-85D	Purple	-
AEB	E	ARL-4-85E	Purple	-
AEG	F	ARL-4-85F	-	No Color Change
CaMB	G	ARL-4-85G	Purple	-
CaMG	H	ARL-4-85H		No Color Change
DMB	I	ARL-4-85I	Purple	-
DMG	J	ARL-4-85J	Purple	-
DMM	K	ARL-4-85K	Purple	-
MMB	L	ARL-4-85L	Purple	-
MMG	M	ARL-4-85M	Purple	-
MMM	N	ARL-4-85N	Purple	-
- O	PositiveControl	Pink	-	
- P	Negative Control	-	No Color Change	

Hair Tresses exhibiting substantivity with 0.5% Quat Solution

Positive and Negative Controls for 0.5% Quat Solutions

Hair Tresses that Exhibit Substantivity with 0.5% Quat Solution

All quat solutions, with the exception of three, (AEG, AMG, CaMG) exhibited cationic substantivity when delivered to hair tresses in a 0.5% aqueous solution. It is likely that these quat solutions did not exhibit substantivity because of their glyceryl groups. However, quat DMG, which also contained a glyceryl group, did exhibit cationic substantivity. It is also possible that the quat group was damaged, or reacted out somewhere in the study, because they were no longer cationic.

(D) Substantivity (Anionic Surfactant System)

PURPOSE

Determine the substantivity of quaternium compounds in an anionic surfactant delivery system to human hair.

PROCEDURE – STM – PE#4

QUAT SOLUTIONS

TITRATED QUAT SOLUTIONS FROM PART 1.

INCI: Polyquaternium-10

SURFACTANTS

Sodium Lauryl Sulfate
Sodium Laureth Sulfate

Lot #	Name	ARL-4-86A	ARL-4-86B	ARL-4-86C	ARL-4-86D
565720	Polyquaternium 10	0.5%	0.5%	-	-
0321605	Sodium Lauryl Sulfate	40.00%	-	40.00%	-
04107056	Sodium Laureth Sulfate	-	40.00%	-	40.00%
062906	Deionized Water	59.50%	59.50%	60.00%	60.00%

Table:10 Substantivity of Titrated Quat Solutions in SLS

		RESULT	
Tress Sample	**Treatment**	**Positive**	**Negative**
A	Test	-	No Color Change
B	Test	-	No Color Change
C	Test	-	No Color Change
D	Test	-	No Color Change
E	Test	-	No Color Change
F	Test	-	No Color Change
G	Test	-	No Color Change
H	Test	-	No Color Change
I	Test	-	No Color Change
J	Test	-	No Color Change
K	Test	-	No Color Change
L	Test	-	No Color Change
M	Test	-	No Color Change
N	Test	-	No Color Change
O	Positive Control	-	No Color Change
P	Negative Control	-	No Color Change

Table: 11 Substantivity of Titrated Quat Solutions in SLES

		RESULT	
Tress Sample	**Treatment**	**Positive**	**Negative**
A	Test	-	No Color Change
B	Test	-	No Color Change
C	Test	-	No Color Change
D	Test	-	No Color Change
E	Test	-	No Color Change
F	Test	-	No Color Change
G	Test	-	No Color Change
H	Test	-	No Color Change
I	Test	-	No Color Change
J	Test	-	No Color Change
K	Test	-	No Color Change
L	Test	-	No Color Change
M	Test	-	No Color Change
N	Test	-	No Color Change
O	Positive Control	-	No Color Change
P	Negative Control	-	No Color Change

No substantivity was observed when quat solutions were delivered from a 10% active, anionic solution of surfactant. (SLS and SLES). The test measures cationic deposition as opposed to deposition of a compound of any nature. Since the quat and anionic form a complex, the deposited material is not cationic and consequently does not provide a color when tested with the dye test. More representative of the deposition is combing force.

(E) Instrumental Analysis of Combing Force

PURPOSE

Determine the force needed to comb wet and dry hair tresses treated with 0.5% active quaternium compound by instrumental analysis.

PROCEDURE

TREAT HAIR TRESSES

1. Treat hair tresses by soaking them in 10-15mL of 0.5% active quat solution for two minutes at 20-25°C.
2. Rinse hair tresses under running tap water (2.0-2.5 gallons/min, 35-40°C), for one minute. Allow hair tresses to air dry for 24 hours at 20-25oC and 40-50% relative humidity.

RESULTS

Table: 12 Measured Combing Force (grams)

Subject A	1st Combing	2nd Combing	3rd Combing	Average
Blue	10.0	15.0	13.0	12.6
Yellow	25.0	19.0	15.0	19.6
Red	30.0	13.0	13.0	18.6
Green	40.0	38.0	30.0	36.0
Black	12.0	13.0	15.0	13.3
Subject B	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	25.0	13.0	15.0	17.6
Yellow	29.0	20.0	10.0	19.6
Red	30.0	28.0	20.0	26.0
Green	45.0	40.0	35.0	40.0
Black	25.0	15.0	10.0	16.6
Subject C	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	10.0	12.0	10.0	10.6
Yellow	15.0	10.0	10.0	11.6
Red	15.0	25.0	20.0	20.0
Green	22.0	24.0	25.0	23.6
Black	30.0	23.0	30.0	27.6

Subject D	1st Combing	2nd Combing	3rd Combing	Average
Blue	10.0	10.0	12.0	10.6
Yellow	35.0	22.0	25.0	27.3
Red	15.0	15.0	10.0	13.3
Green	43.0	40.0	35.0	39.3
Black	20.0	10.0	13.0	14.3
Subject E	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	27.0	16.0	10.0	15.0
Yellow	40.0	20.0	20.0	26.6
Red	20.0	20.0	12.0	17.3
Green	38.0	40.0	45.0	41.0
Black	23.0	20.0	15.0	19.3

Table:13 Average Values of Combing Force (grams)

Tress Color	Total Score
Blue	13.20
Yellow	17.02
Red	19.04
Green	35.98
Black	18.22

The instrumental analysis of 0.5% active quat compounds showed that Blue (MMM), performed the best followed by yellow (MMG), black (deionized water), and red (Polyquaternium 10). This confirms the test results that were obtained in part five of this study.

Conclusions

Quaternium compounds can be classified as hard or soft by their ability to form gelled systems with anionic systems. Cationic systems that form a gel at near stoichiometric amounts are classified as "soft", those that form precipitates of haze without appreciable viscosity build are classified as "hard" quats. "Soft quats" can produce foam in the systems they gel, albeit at levels below the volume of foam generated by the anionic per se.

Quaternium compounds titrated with sodium laureth sulfate (SLES) produced greater viscosities with amido quats. The exception was amido quats containing a benzyl group, which exhibited a low viscosity in SLES.

Compounds that contained a benzyl group, or were a alkyl rather than amido, (i.e. AMB, AME, AMG, AMM, AEB, AEG), precipitated at lower levels of titration and are consequently classified as "hard quats".

Overall, all quat/anionic solutions tested had less foam than when the anionic itself was tested. This was true for both SLS and SLES.

With the exception of quats AEG, AMG, and CaMG, and the negative control, all 0.5% active, aqueous solutions of quaternium compounds produced positive results for cationic substantivity, when evaluated per se.

In aqueous solutions of anionic surfactants, all quat solutions, including the positive control (polyquaternium 10), produced negative results. This is thought to be due to the fact that there is no net positive charge of the hair, due to the fact that the anionic and cationic in combination have a new zero charge. This is not to be confused with no deposition. Instrumental dry combing analysis of human hair tresses treated with aqueous quat solutions confirmed conditioning, showing that quat MMM indeed performed the best, followed closely by MMG, polyquaternium 10, and the negative control. Again, quat DMG did not show any improvement in performance.

Quat AMB concluded to be the poorest performer yielding opaque surfactant mixtures in part one at low levels. Foam height and stability was dramatically suppressed in part two. Although AMB was substantive to human hair when delivered from an aqueous solution, no substantivity was observed from an anionic mixture.

Quat MMM concluded to be the best performer, yielding a thick, translucent gel with a viscosity well over 10,000 cps for both SLS and SLES titrations. MMM/Anionic Solutions produced an above average foam height without suppression and extended foam stability well over 24 hours or, ten times greater than SLS and SLES, controls, and positive controls (polyquaternium 10 and SLS/SLES). MMM performed equally as well in substantivity tests when delivered from an aqueous system. Like all other quat solutions, no substantivity was observed when delivered from an anionic mixture. Because of its performance, MMM was chosen for subjective and combing analysis. Like quats DMG and MMG, quat MMM performed poorly in the wet combing test of part V. However, it did perform slightly better in the dry combing test. Quat MMM turned out to perform the best in the instrumental analysis of combing force, part VI. The average performance of quat MMM was superior to all quats in this study, including the positive control, polyquaternium 10.

References

1.R.G. Pearson, *J Am Chem Soc*, **85**, 335 (1963).

Chapter 5
Nonionic Surfactants

Alkanolamids

Alkanolamids are a major class of nonionic surfactants used in the personal care market. They are used to boost and stabilize foam and, depending on the kind, provide conditioning effects on hair and skin.

Raw Materials

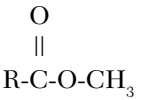
Alkanolamids can be made using a variety of reactants. The commonality between the reactants is that one reactant is a fatty acid, ester or triglyceride and the other is an alkanolamine, most commonly diethanol amine and monoethanol amine, as illustrated below.

Amines

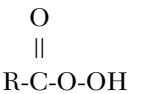
$HN\text{-}(CH_2CH_2OH)_2$ Diethanolamine

$H_2N\text{-}CH_2CH_2OH$ Monoethanolamine

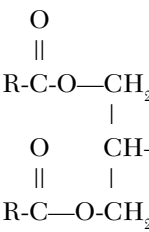
Fatty Sources



Fatty Methyl Ester



Fatty Acid



Fatty Triglyceride

Alkanolamids are varied by molecular manipulation to give molecules with a wide range of functional properties, making alkanolamids a class of compounds that are a true multi-application chemical specialty. Alkanolamids perform a variety of functions, including viscosity enhancement, foam stabilization, emulsification

and detergency. The practical question facing formulators of a high performance product is "Which alkanolamid is best for my application?" The answer isn't a simple one and involves selection of a number of structural variables that produce the desired functionality. These variables include:

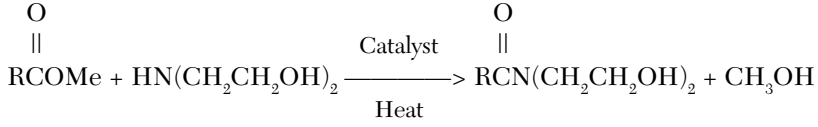
- Fatty source.
- By-products and impurities.
- Chain length of hydrophobe.
- Alkanolamine type.

Reaction

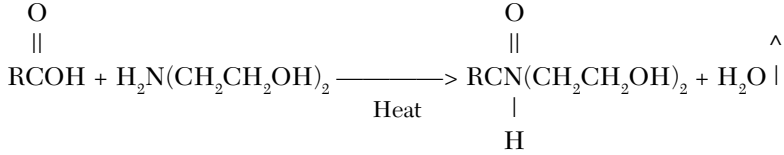
Chemically, alkanolamids are the reaction product of an alkanolamine and a fatty material. The reaction sequence for the most commonly used fatty materials in commercial alkanolamid manufacture is shown below.

The sources of the fatty materials include coconut, peanut, soybean, meadowfoam and rapeseed oils, fractionated and non-fractionated fatty methyl esters, and acids of almost any carbon length. The selection of the proper fatty raw material is perhaps the single most important step in selection of the alkanolamid. The fatty source makes up most of the product by weight and can vary considerably in cost.

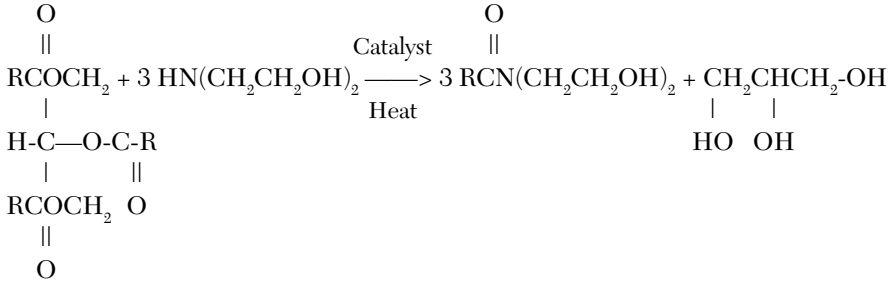
Methyl Ester-Derived



Fatty Acid-Derived



Triglyceride-Derived



Properties

The source of the fatty material and the carbon chain length distribution affects the performance of an alkanolamid. In addition, the presence and concentration of reaction by-products will influence functional properties. Glycerin, for example, formed when triglycerides are used as the raw material fatty source, can be a desirable component in an alkanolamid. It serves as a diluent, reduces the melting point of the amid and contributes some humectant properties. It also can have the potentially undesirable property of giving lower viscosity in some formulated products.

Incorporation of additives unrelated to the reaction process can have a profound and unpredictable effect on the formulation. Additives can include glycols, polyethylene glycols, alkanolamids with different carbon chain length distributions, oxidation or reduction agents added for color control, and a number of other materials. The addition of these materials in low concentrations can affect product performance from manufacturer to manufacturer or even batch to batch.

Effect on Viscosity

The effect on viscosity of alkanolamids is demonstrated with the following simple formula:

Material	%
Water	45.0
Sodium lauryl sulfate (28%)	50.0
Diethanolamid	5.0

A 0.1 percent blend of the formulation was evaluated for foam at one-, five- and 10-minute intervals using a blender foam test. The results are illustrated in the table below.

Foam Evaluation

	Alkanolamid Type				
Time (min)	A	B	C	D	E
1	80 ml	130 ml	150 ml	170 ml	155 ml
5	70 ml	120 ml	145ml	160 ml	140 ml
10	60 ml	110 ml	135 ml	155 ml	125 ml

Alkanolamid Evaluated

A is no amid

B is cocamid diethanolamine (glyceride-derived)

C is cocamid diethanolamine (methyl ester-derived)

D is 70 percent lauramid diethanolamine (methyl ester-derived)

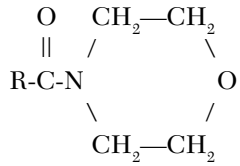
E is 90 percent lauramid diethanolamine (methyl ester-derived)

As shown, highest most stable foam is observed with the lauric alkanolamids. The highest initial foam and the most persistent foam is observed with the 70/30 lauric myristic alkanolamid in this simple formulation.

Several by-products may be found to different extents in commercial alkanolamids. Their concentration depends on the process used, the purity of raw materials and other factors.

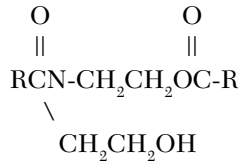
Heterocyclic by-product

This by-product is formed by the reaction of the hydroxyl groups in diethanolamine to form a heterocycle and water, as shown on the next page.



Amid ester by-product

Amid ester forms from the reaction of the fatty source with the hydroxyl group in diethanolamine, as shown below. The concentration of this by-product drops with time for liquid alkanolamids. However, if overheated, the content of amid ester can increase.



Perhaps the most dramatic functional variation that can be made in alkanolamids is the number of carbon atoms in the fatty source. Short chain fatty materials result in alkanolamids that are useful as humectants and hair anti-tangle agents. These products are based on fatty esters having fewer than eight carbon atoms in the hydrophobe. Alkanolamids having eight to 10 carbon atoms in the hydrophobe exhibit foam stability but contribute little as thickeners. The medium range alkanolamids having 12 to 14 carbon atoms are the best foam boosters; they also show good viscosity-building properties. Lauric-myristic diethanolamid is a common ingredient in formulations of high-foaming products such as bubble bath and hair shampoo. They also contribute emollient and conditioning effects on skin and hair in many formulations. This is why the lauric-myristic alkanolamids have become the workhorses of the cosmetics industry.

The use of higher molecular weight unsaturated fatty alkanolamids reduces foam and foam stabilization but produces good viscosity. The optimum performance in

a formulation is often obtained when formulators employ blends of alkanolamids having different carbon chain lengths. This can result in the desired properties of both materials. Oleic and linoleic alkanolamids are excellent viscosity builders at low concentration in most shampoos and are of particular interest in formulations that contain surfactants that are difficult to thicken. Such surfactant components are based on alpha olefin sulfonates, some amphoterics and 60 percent ether sulfates having ethyl alcohol present as a hydrotropic solvent. These higher molecular weight unsaturated products also are excellent hair conditioners and fatting agents. The unsaturated systems can suffer from oxidative instability and may interfere with the top note of some perfumes. Isostearamid diethanolamine is excellent when this problem is encountered.

Diethanolamids with 18 or more carbon atoms in the fatty part of the molecule have found utility in the thickening of hair colorant formulations and as lubricants. The following graphic illustrates the functional properties of alkanolamids.

Alkanolamid Functional Properties

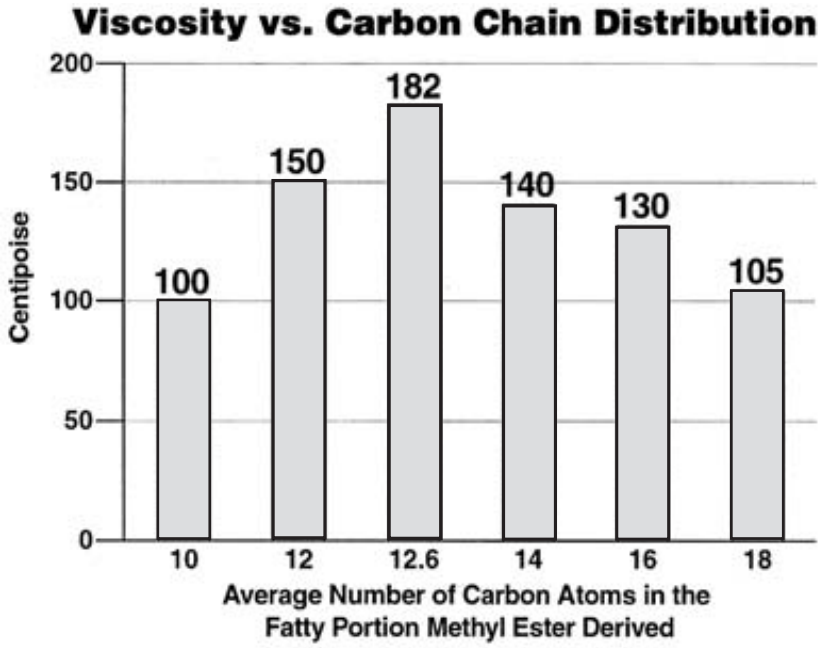
Carbon Atoms Present	Application
8 to 10	Good foam stability Little viscosity improvement
12 to 16	Good foam boosters Good viscosity building
Lauric/Myristic	Good foam stability Some emollient properties Some conditioning
18 +	Reduced foam stabilization Good viscosity builders Some emollient properties

Carbon Chain Length Distribution vs. Viscosity Performance

The effect of the carbon chain length distribution on the viscosity of formulations can be demonstrated using the following simple formulation:

Material	%
Water	45.0
Sodium lauryl sulfate	50.0
Diethanolamid	5.0

As the carbon chain length in the diethanolamid hydrophobe increases, the viscosity of the formulation increases to a maximum of about 12.6 carbons. This value is achieved using a hydrophobe that is 70 percent C-12 (lauric) and 30 percent C-14 (myristic). The viscosity of the formulation then drops off as the number of carbon atoms in the amid increases, as the following chart illustrates.



2:1 Alkanolamids

Alkanolamids discussed until this point are the so-called superamids. The other kind of alkanolamids, the so-called 2:1 *alkanolamids*, are actually older. The now famous Kritchevsky class of alkanolamids was first patented in August 1937. The patent describes the reaction of fatty acids and diethanolamine. The 2:1 alkanolamids were so named because of their reactant molar ratio, two moles of ethanolamine to one mole of fatty acid. Kritchevsky's alkanolamids differ chemically and functionally from superamids.

By-products are present in higher concentrations in the Kritchevsky products, due in part to the higher processing temperatures used for their manufacture. These by-products can affect product quality and, if present in sufficiently high concentrations, can cause performance differences.

Kritchevsky alkanolamids and superamids differ in the following ways:

- Superamids have less soap than Kritchevsky alkanolamids.
- Superamids have higher concentration of alkanolamid.
- Superamids contain less free ethanolamine and less "ester amid."

The choice of the class of products to be used depends on the application. For example, in hard surface cleaning applications and liquid laundry applications, soap is desirable for detergency. Viscosity build is generally less important in these formulations. Consequently, Kritchevsky amids are preferred. Because most shampoo formulations are based on fatty alcohol sulfates or fatty alcohol ether sulfates, viscosity and foam enhancement are critical functional properties for the alkanolamid.

Here, superamids are generally employed. Kritchevsky products may be used in some shampoos for their detergency and perfume oil solubilization properties.The graphic below ranks the various properties of Kritchevsky amids and superamids.

Relative Ranking of Properties

Type	Detergency	Foam	Foam Stability	Viscosity	Cost
Kritchevsky amids	++	+	+	+	+
Superamids	+	++	++	++	++

Alkanolamids vary in composition as a result of the raw material used to make them. This variability for 1:1 amids is shown as follows:

Components of Triglyceride vs. Methyl Ester-Derived 1:1 Alkanolamids

Component	Glyceride	Methyl Ester
Diethanolamid	>81%	>92%
Free Diethanolamine	> 7%	> 5%
Amine Soap	> 1%	> 1%
Alkyl Metal Soap	> 1%	> 1%
Residual Esters	> 1%	> 1%
Glyceride	9%	-

Alkanolamids have come under increasing scrutiny in the last few years due to the formation of nitrosoamines. Nitrosoamines now are generally accepted as carcinogens. As a result, many producers of personal care products are seeking replacements for alkanolamids. This is most interesting because this class of products has been a workhorse of the cosmetics industry for many years.

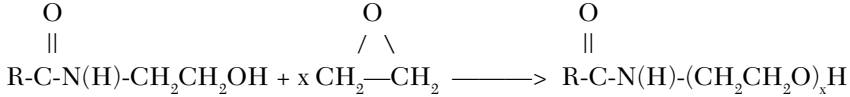
There has been some success in addressing the problem, but most of the approaches try to minimize diethanolamine content by reacting it to make new compounds. The concept is that no nitroso-diethanolamine will form. This approach has two potential shortfalls. The first has to do with the practical levels of residual diethanolamine that are achievable and those needed to overcome the problem. Most organic reactions are simply not effective enough to obtain residual levels of reactants in the parts-per-million range. The second problem is that many of the products that modified diethanolamine produces may themselves be inclined to form nitroso compounds, which are also undesirable and can introduce other undesirable by-products into the products. It remains very difficult to obtain a cost-effective substitute for this class of products.

Ethoxylated Amids

Ethoxylated amids are members of a class of nonionic surfactants. They are used primarily as emulsifiers in systems that are formulated at very low or high pH. These materials are of interest in antiperspirant formulations. This is due to their stability at extremes of pH. Some work has been done to use ethoxylated amids as replacements for standard alkanolamids, hoping that the ethoxylation process will lower the concentration of diethanolamine present in the final product. This approach needs to be evaluated carefully because there is always some free level of diethanolamine present. The nitrosamine is of concern in the parts-per-million level because of the indications that it is a potent carcinogen in animal models. Care must be exercised to make sure that no diethanolamine remains.

Reaction

Ethoxylated amids are made by the reaction of an alkanolamid with ethylene oxide. The reaction is conducted using alkaline catalyst. The result is an oligomer distribution of ethoxylates. The reaction is shown below:



Properties

Ethoxylated amids find application more commonly in industrial rather than personal care applications. Industrial usage of these materials is based on their good lime soap dispersing properties.

Propoxylated Alkanolamid

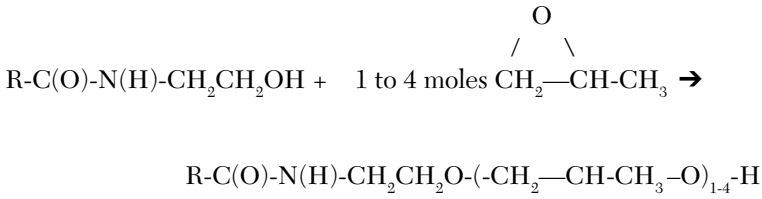
There has been a continuing significant attempt to replace DEA based alkanolamids with DEA free products. This is because of concern over nitrosoamines, specifically the nitrosamine of DEA. While this has been an industry wide goal, there has not been any molecular approach that has worked. There have been some formulated products that are claimed to replace alkanolamids.

In March 2003, U.S. Patent 6,531,443 reports a series of products based upon the reaction of a triglyceride-based alkanolamids that is reacted in a post step with 1 to 4 moles of propylene oxide or butylene oxide. This approach overcomes the need to use a solid MEA based product. Since the products are liquid at ambient temperatures or lower. These propoxylated products are said to exhibit surfactant properties substantially the same as those exhibited by diethanolamids such as foam stabilization and viscosity building as well as other desirable characteristics.

The patent states that "up to now, monoalkanolamids have not been available in liquid form which has limited their use in many applications. In recent years, because of regulatory concerns and restrictions, formulation trends have been shifting toward greater usage of monoalkanolamids; such products being solids,

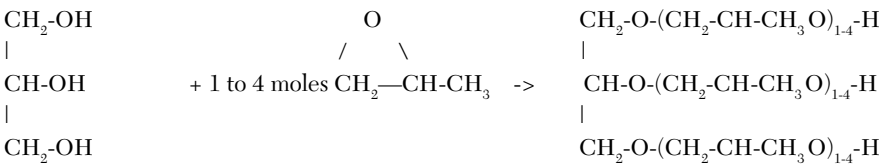
are more difficult to handle and are inconvenient to use in large scale production processes. Accordingly, it would be highly advantageous to be able to combine the performance characteristics of monoethanolamids with products having liquid physical characteristics at below ambient conditions."

The chemistry is as follows;



It is interesting to note that the patent covering this technology applies to triglyceride based products only. The novelty relates to the co-propoxylation of glycerin present in the starting MEA product to act to improve the liquidity of the amid. The reason for the choice of propylene oxide over ethylene oxide for the post reaction is the fact that the polyoxypropylene moiety with its methyl group will be more liquid than will products made with linear polyoxethylene.

The co-reaction is the propoxylation of glycerin present from the starting MEA amid and is as follows:



The patent states "other components in such mixtures, are alkoxylated glycerin, glycerin and nonalkoxylated monoethanolamid the total amount of which generally ranges from 10% to about 55% by weight, the relative concentration of each of such additional components depending on the degree of alkoxylation of the reaction mixture and the monoethanolamid composition mixture from which the modified monoethanolamid composition mixture of the invention is prepared". The effect of added glycerin or glycerin propoxylates on the pour point of a triglyceride-derived caprylic/capric monethanolamid modified with 1 mole of propylene oxide results in increased liquidity which the authors say is achieved by increased concentrations of the same glycerin and propoxylated glycerin.

Table one shows the differences in the composition of the propoxylated and non-propoxylated products. Even with only one mole of propylene oxide added, there is a dramatic reduction in free glycerin.

Composition of Modified Monethanolamids
% By Weight

	Caprylic/Capric MEA Amide-1PO		Coconut MEA Amide-2PO		Soya MEA MEA Amide-3PO	
Component	**Theory**	**Found**	**Theory**	**Found**	**Theory**	**Found**
Propoxylated Amid	44.6	46.9	77.7	68.9	77.7	75.5
Non-Propoxylated Amid	34.4	32.1	0.0	8.8	0.0	2.2
Propoxylated Glycerin	21.0	18.7	22.3	20.7	22.3	22.3
Glycerin	0.0	2.3	0.0	1.6	0.0	0.0

More recently, products have become available that do not have the propoxylated glycerin present. They are likewise claimed to be replacements for DEA alkanolamids and since they do not have glycerin or propoxylated glycerin present, are claimed to have somewhat higher melting points, but also to provide higher viscosity formulations with less salt.

Mixed n-butyl and iso-propyl phthalamide

U.S. Patent 6,306,373 discloses the use of a specific eutectic mixture of lower alkyl phthalamide that is surprisingly effective in solubilizing 4-(1,1-dimethylethyl)-4'-methoxydibenzoylmethane. Such concentrates solutions can be used to formulate a more effective sunscreen, having a surprisingly increased sunscreen protection factor (SPF) and such that the 4-(1,1-dimethylethyl)-4'-methoxydibenzoylmethane is more effective over a longer period of time so that the sunscreen composition need not be applied to the skin as frequently.

The material is a mixture of butyl isopropyl alkyl groups. By making the specified mixtures of the alkyl groups, most importantly normal butyl and isopropyl, a so-called eutectic mixture results. This mixture is a liquid having a very low melting point and remains liquid over a wide range of temperatures. We have found that the increased solubilization of the sunscreen compounds in the mixture occurs only within the so-called eutectic range. Within the eutectic rang, a mixture of the compounds has a lower melting point than either of the two pure components in the mixture. We have discovered that this phenomenon is critically important in developing compounds that can solubilize high levels of sunscreening agents.

Grams of solvents necessary to solublize 1 gram of avobenzone

Material	**Grams of Solvent**	**% Avobenzone Solution**
Mixed n-butyl and iso-propyl phthalamide	1.5	40.0

Esters

Fatty acid esters are a class of compounds that find applications in many diverse segments of the cosmetics industry.

Reaction

Simplistically, fatty esters are prepared by reacting an alcohol, generally a fatty one, and a fatty acid or equivalent, usually under elevated temperature and in most instances under reduced pressures, as shown below:

Ester Synthesis (from methyl ester)

$$CH_3\text{-}(CH_2)_{10}\text{-}\overset{\overset{O}{\|}}{C}OCH_3 + CH_3\text{-}(CH_2)_{11}\text{-}OH \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3\text{-}(CH_2)_{10}\text{-}\overset{\overset{O}{\|}}{C}O(CH_2)_{11}\text{-}CH_3 + CH_3OH$$

As with any commercial product, the simplistic reaction sequence outlined above glosses over a number of issues that may affect product consistency, quality and performance.

Direct Esterification Methods

Esters made using a fatty acid as the raw material are said to be made by the *direct esterification process.* As the reaction sequence below illustrates, the by-product is water, which is removed by temperature and vacuum. The acid value of the resulting product tends to be higher than the esters made by the transesterification process.

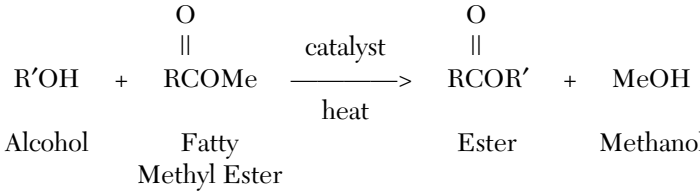
Fatty Acid-Derived

$$\underset{\text{Alcohol}}{R'OH} + \underset{\text{Fatty Acid}}{\overset{\overset{O}{\|}}{R}COH} \xrightarrow{\text{heat}} \underset{\text{Ester}}{\overset{\overset{O}{\|}}{R}COR'} + \underset{\text{Water}}{HOH}$$

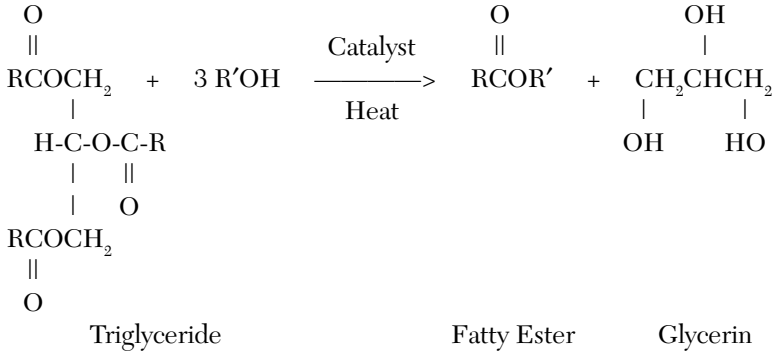
Transesterification Methods

Esters made using another ester as a raw material are said to be made by the *transesterification process*. These esters include methyl esters in which methanol is the by-product and triglycerides in which monoglycerides, diglycerides and/or glycerin are produced, as illustrated on the next page. Because the raw material ester has no appreciable acid value and its own saponification value, the analysis of esters made by this process is somewhat more complicated.

Methyl Ester-Derived

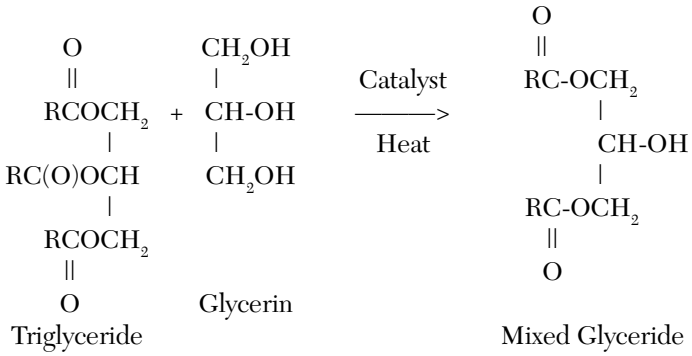


Glyceride (Oil)-Derived



Reconstituted Glycerides

The reaction of a triglyceride with an alcohol is a major transesterification process, which can result in so-called *reconstituted glycerides*. For example, as illustrated below, glycerin can be reacted with an equivalent of a triglyceride to give a product that is a mixture of monoglyceride, diglyceride and triglyceride. The new glyceride is less hydrophobic and has different functional attributes.



A major concern is the source of the fatty acid and fatty alcohol chosen. Fatty alcohols, as shown in Chapter 1, can come from a variety of sources and have differing amounts of branching and differing numbers of carbon atoms present. All of these factors affect ester performance.

Fatty acid materials are a class of compounds that include fatty carboxylic acids, fatty methyl esters and fatty triglycerides.

Fatty Alcohol Source

"Simple" Fatty Alcohols

The "simple" fatty alcohols used to prepare fatty esters can be classified by the process used for their manufacture and are most commonly selected from oxo, Ziegler and natural alcohols. There are inherent differences in the branching patterns, as discussed in Chapter 1. In addition, most alcohols are not pure compounds and have varying amounts of products from C10 to C18.

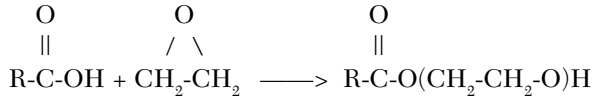
Polyfunctional Alcohols

The most commonly encountered alcohols in this group are glycerin, ethylene glycol and pentaerythritol. These alcohols have low equivalent weight and as such lead to a molecule that is predominantly fatty acid by weight. An example is pentaerythritol tetrastearate, which is more than 90 percent stearic acid by weight. The degree of substitution of a polyfunctional alcohol is also an issue. There is a potential for any mole ratio of acid to alcohol, from one-to-one to one-to-four equivalents. The hydrophobicity of such esters, their melting points and functional attributes would differ significantly.

Fatty Ester Types

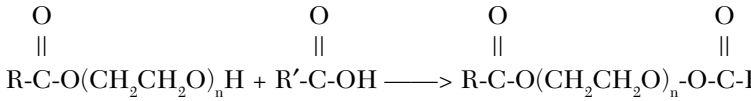
Fatty Alkoxylate Esters

Monoesters. This class of compounds is divided into three subclasses, depending on the oxide used. The chemistry is essentially identical in each case. The difference lies in the use of propylene oxide, ethylene oxide or mixed alkoxide. The generalized reaction is as follows:



The particular polyethylene glycol can be made and subsequently reacted with the acid of choice to give a product with a very similar composition. Products made by ethoxylation should be carefully compared in the candidate formulation with those made by esterification before a substitution is approved. In most instances, the materials can be substituted with little difficulty.

Diesters. This class of materials is derived from the esterification of a monoester derived by alkoxylation of a fatty acid, or from the direct esterification of the polyethylene glycol with two equivalents of acid. The generalized reaction is as follows:



Examples of Alkoxylate Esters

Alkoxylated esters are a group of compounds that include polyethylene glycol monoesters, such as PEG-600 monostearate, and diesters of polyoxyalkylene glycol, such as PEG-600 distearate.

Complex Fatty Esters

Complex fatty esters are the result of the reaction of one polyfunctional reactant with a monofunctional reactant. According to this definition, pentaerythritol reactions with monofunctional acids are complex esters. Among the common complex fatty esters are:

- Pentaerythritol esters (diesters, triesters and tetraesters).
- Glyceryl esters (monoesters, diesters and triesters).
- Citrate esters (monoesters, diesters and triesters).

Many other complex esters find applications in household and personal care areas and in a host of industrial applications. Dimer acid also can be reacted to give a complex ester.

Properties

Esters function in several important ways in cosmetics formulations. If they contain water-loving groups, like polyoxyethylene groups from ethylene oxide, or free hydroxyl groups, they function primarily as emulsifiers. If no polar groups exist, the ester will function as a wax or oil and provide emmoliency, lubrication and gloss. The data that follow illustrate the properties of esters, showing structure/function relationships.

Simple Esters. The structure of the ester has a dramatic effect on skin feel, spreadability and melting point. Esters made with linear saturated alcohols and acids are generally solids if they contain more than 32 total carbon atoms. These esters are waxy and are used as emmolients. The term "dry time" is commonly used to indicate the amount of time it takes for 0.5 ml of an ester to feel dry on the skin (back of the hand) when rubbed in with the index finger. The lower the number, the drier the ester. The opposite of "dry" is "cushion." Esters with cushion are said to have a long "play time." The table below shows the dry times of four simple and two di-Guerbet esters.

Guerbet Branching. Introduction of Guerbet branching into the ester makes the product liquid and provides a dry feel on the skin. Improved liquidity is seen by introduction of a Guerbet branch. The liquidity improvement occurs if either the acid or alcohol has the Guerbet branch. But, if the Guerbet branch is in the acid side, the improved liquidity is enhanced.

Simple Esters

Material	Description Alcohol : Acid	Melting Point (°C)	Dry Time
Hexyldecyl palmitate	C16(G):C16	50	48 sec
Octyldodecyl eicosanoate	C20(G):C20	48	56 sec
Cetyl hexyldeconate	C16:C16(G)	9	15 sec
Eicosanyl octyldodecanate	C20:C20(G)	34	22 sec

Di-Guerbet Esters

Material	Description Alcohol : Acid	Melting Point (°C)	Dry Time
Hexyldecyl hexyldecanonate	C16(G):C16(G)	<0	11 sec
Octyldodecyl octyldodecanate	C20(G):C20	<0	10 sec

Glycerol Esters. Glyceryl esters are used primarily as emulsifiers. The number of fatty groups in these esters determines the hydrophobe lipophile balance of the resultant esters, as shown below. The esters bring the additional properties of opacification and emmoliency to personal care formulations.

Material	Hydrophobe Lipophile Balance	Melting Point
1. Glyceryl monooleate	3.7	- 5°C
2. Glyceryl dioleate	2.8	0°C
3. Glyceryl monolaurate	4.8	45°C
4. Glyceryl dilaurate	4.0	30°C

The presence of the polar hydroxyl group in the molecule contributes the water-loving portion of the molecule and makes these materials emulsifiers. The hydrophobe lipophile balance values are quite low, favoring water-in-oil emulsions.

Polyoxyethylene Glycol Esters. The esters of polyoxyethylene glycol function as emulsifiers over a wide range of hydrophobe lipophile balance values. This is because the molecular weight of the polyoxyethylene glycol can be altered, which changes the percentage of the water-loving portion of the emulsifier. In addition to being outstanding emulsifiers, the polyoxyethylene glycol esters are good emmolients and solubilizers of fragrance oils.

The data below show the hydrophobe lipophile balance and melting points of the lauric acid esters of different polyoxyethylene glycols.

Monoesters

Product	Alkyl	Hydrophobe Lipophile Balance	Melting Point (°C)
PEG-200 monolaurate	C12	9.3	5°C
PEG-300 monolaurate	C12	11.4	8°C
PEG-400 monolaurate	C12	13.0	13°C
PEG-600 monolaurate	C12	14.6	23°C
PEG1000 monolaurate	C12	16.6	40°C
PEG1540 monolaurate	C12	17.5	46°C
PEG-4000 monolaurate	C12	19.0	55°C

Diesters

Product	Alkyl	Hydrophobe Lipophile Balance	Melting Point (°C)
PEG-200 dilaurate	C12	5.9	9°C
PEG-300 dilaurate	C12	7.9	12°C
PEG-400 dilaurate	C12	9.7	18°C
PEG-600 monolaurate	C12	11.9	21°C
PEG-1000 dilaurate	C12	14.2	38°C
PEG-1540 dilaurate	C12	15.8	42°C
PEG-4000 dilaurate	C12	18.1	52°C

The next set of data presents the effect of various alkyl groups on PEG-600.

Diesters (Saturated)

Product	Alkyl	Hydrophobe Lipophile Balance	Melting Point (°C)
PEG-600 dilaurate	C12	11.9	21°C
PEG-600 dipalmitate	C16	10.9	31°C
PEG-600 distearate	C18	10.2	36°C
PEG-600 diarachidate	C20	9.8	40°C
PEG-600 dibehenate	C22	9.3	44°C

Diesters (Unsaturated)

Product	Alkyl	Hydrophobe Lipophile Balance	Melting Point (°C)
PEG-600 dioleate	C18:1	10.2	10°C
PEG-600 dieurcate	C20:1	9.8	14°C

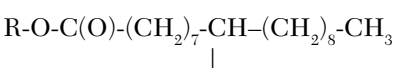
Diesters (Guerbet)			
Product	Alkyl	Hydrophobe Lipophile Balance	Melting Point (°C)
PEG-600 dibutyloctonate	C12:G	11.9	-9°C
PEG-600 dihexyldecanonate	C16:G	10.9	-7°C
PEG-600 dioctyldecanoate	C18:G	10.2	-5°C
PEG-600 dioctyldodeaconate	C20:G	9.8	-2°C

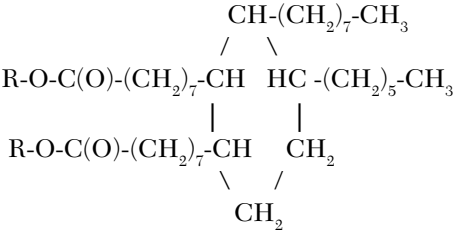
The structure of the ester affects both the hydrophobe lipophile balance and melting point. Several products with the same or similar hydrophobe lipophile balance values have vast differences in their physical properties *per se* and produce different properties in formulations. Enlightened selection by formulators is key to obtaining the optimum formulation.

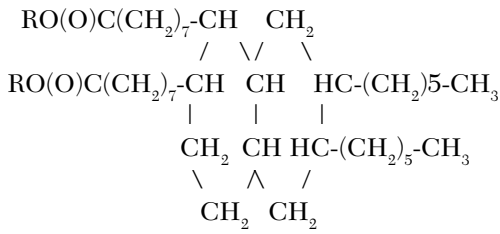
Hydrolytically Stable Esters

One of the problems encountered with esters is their inherent instability to hydrolysis. Some esters hydrolyze faster than others. The hydrolysis rate is generally faster for water soluble esters and decreases as the ester becomes more hydrophobic. Generally, esters are not recommended for use at a pH of below 5 or above 10. There has recently been described a series of esters that do not hydrolyse to an appreciable extent over the entire pH range. This type of ester is useful in a variety of applications where very high pH is encountered (relaxers for example) or very low pH is encountered (alpha hydroxy products for example). The esters derived from a specific 36 carbon diol and fatty acids including Guerbet acids. They are the topic of U.S. Patent 6,537,531 issued March 25, 2003. The basis for the patent is the esters are surprisingly stable to hydrolysis and consequently of interest in high and low pH applications.

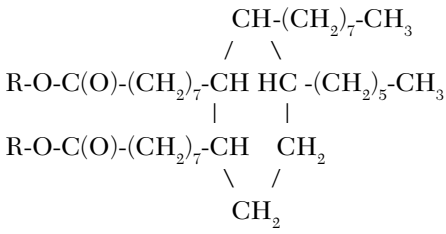
The esters conform to the following formulae;





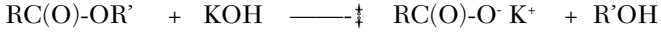


and



The products show an extraordinary resistance to hydrolysis both on the acidic and alkaline pH values. This is most easily seen when one attempts to run a saponification value. Saponification value is an analytical technique, which allows one to determine the molecular weight of an ester, by breaking down the ester with base (KOH). In standard esters, the amount of KOH consumed in the analysis is measured and is stiochiometric with the molecular weight of the ester. Surprisingly, the esters of the present invention do not have the expected saponification value. They have essentially no saponification value, since the ester must hydrolyze to provide the saponification value.

Saponification Analysis



The analysis is run with excess KOH and the difference between the starting amount of KOH and the residual KOH is titrated with standardized acid. The amount of KOH consumed is stiochiometric and the saponification value is reported as mg KOH/gram of sample tested.

Saponification Value Method

This method is applicable to all fats and oils, as well as products derived from them such as esters and fatty acids. The saponification value is the amount of alkali necessary to saponify a definite quantity of the sample. It is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of the sample. A sample is refluxed in 0.5N methanolic KOH for 1.5 hours and titrated using 0.5N HCl.

Materials needed are:
1. Potassium hydroxide (KOH), ethanolic 0.5N
2. Hydrochloric acid (HCl), 0.5N
3. Phenolphthalein indicator solution, 0.1% in ethanol.

Procedure:
1. Melt the sample, if not a liquid, and mix thoroughly to ensure homogeneity. Using Table 1 as a guide, weigh the appropriate amount of sample into an Erlenmeyer flask. Record the weight.
2. Pipette 50 mL of 0.5N KOH into the flask, add some boiling stones, and reflux for 1.5 hours. Make sure that there is cold water going through the condensers so as to aid in the condensing of the sample back into the Erlenmeyer flasks.
3. Prepare and run a blank simultaneously with the samples by pipetting 50 ml of 0.5N KOH into an empty flask, adding some boiling stones, and refluxing along side the samples.
4. After 1.5 hours of refluxing, rinse the inside of the condensers with about 25 mL of deionized water and catch the rinsings in the Erlenmeyer flasks. Remove the flasks from the condensers and allow the sample solutions to cool to room temperature.
5. To each flask, add 3 to 5 drops of phenolphthalein indicator and a stir bar. Titrate, while mixing, with 0.5N HCl until the pink color just disappears. Record the respective titration volumes used to reach each endpoint.
6. Using Equation 1 in the Calculations section of this method, calculate the SAP value of the samples analyzed. Report the results to one decimal place.
7. The ester value of a product can be determined using Equation 2, if the acid value is also known.

Calculations:
Equation 1

$$\text{SAP value} = \frac{(\text{mL Blank} - \text{mL Sample})(\text{N of HCl})(56.1)}{(\text{wt. of sample})}$$

Equation 2
Ester value = Saponification value – Acid value

Precision:
The relative standard deviation for saponification value determinations has been determined to be ±0.5% when one sample was analyzed 36 times by different chemists on different days within the same laboratory. This relative standard deviation was determined on a sample with an average saponification value of 336.0.

Reference:
A.O.C.S. Official Method Cd 3c-91.

HYDROLYTIC STABILITY OF DIMER ESTERS	
Product	**% Hydrolyzed**
Stearyl Ester	5.0%
Oleyl Ester	3.3%
Ricinoleic Ester	5.3%
Stearyl Stearate	00.0 %

Polyesters

Castor Polyesters

Castor polyesters have been developed and patented per se in U.S. patent 6,342,527 and as cationic derivatives in U.S. patent 6,521,220. These products are said to provide topical benefits to the skin, including gloss, decreasing transepidermal water loss (TEWL), lubrication, conditioning, emoliency and pigment wetting based upon a raw material that has been around for a thousand years. Castor oil has been given a chemical "twist", namely incorporation into a polyester.

Castor oil is a unique triglyceride, derived from Ricinus communis L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor Oil is a clear, viscous, light colored fluid that is nondrying and quite stable. The Purity of Castor Oil (89%)occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

Castor Oil (Ricinus communis)

Castor oil is a unique triglyceride. It is derived from Ricinus communis L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor oil contains a large content of hydroxy containing compounds that are unsaturated.

This versatile material is a clear, viscous, light colored, freely flowing fluid that is nondrying and quite stable. The purity of composition of Castor Oil occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

Carbon Distribution

Component	Typical % Weight
C16:0	1
C18:0	1
C18:1-OH	89
C18:1	3
C18:2	6

CAS Number: 8001-79-4 ; EINECS Number: 232-293-8; Titer Point 2 ° C; Iodine Value: 85

The chemical structure of castor oil shows why it is so important to making a suitable polymer. The molecule is a triglyceride that has three reactive hydroxyl groups. If these groups are reacted with a multi-functional acid, polyesters result. These polymers have unique properties, both per se and in derivatives. In addition, unlike many polymeric materials are made by the free radical polymerization of vinyl containing monomers to form high molecular weight polymers. These polymers of times have desirable properties, and contain residual unreacted monomer. By making polyesters of castor oil, products that contain no free vinyl monomers are achieved! These polymers are based upon the naturally occurring products castor oil and succinic acid. The polymers can be made to varying molecular weights, allowing for the custom selection of viscosity, playtime on the skin and penetration of the skin. Finally, by placing functional groups on the polymer, a variety of properties like gloss, conditioning, and hardness can be affected.

Castor Succinate Polyester

FEATURE	BENEFIT
1. 100% active	1. High total performance product. Fully functional.
2. Pigment wetter.	2. Improves color brightness.
3. Versatile.	3. Hair, skin, sun and color applications.
4. Natural organic ingredients.	4. No petroleum base or phenyl groups. Biodegradable
5. High molecular weight .	5. Gives high substantivity and gloss. Little penetration of the skin.
6. High oxidative solubility.	6. Retards dicoloration in finished formula.
7. Known ingredient (castor oil and succinic acid).	7.Easy to formulate product.

USES / APPLICATIONS

Shampoos	Eyeliner pencils	Conditioner
2-in-1 Shampoos	Leave-in conditioner	Lip-gloss stick
Lipsticks	Liquid makeup remover	Lip-gloss pots
Makeup pencils	Makeup remover spray	Sun tan oils
Hair gloss sprays	Hair pomades	Hair colorant with shine

Alkoxylated Alcohols

Raw Materials

Ethylene Oxide

Ethylene oxide is a colorless, low-boiling gas. It boils at 10.4°C and can easily form explosive mixtures with air. Ethylene oxide is soluble in water, alcohol, ether and most polar solvents.

Ethylene oxide reacts in an extremely exothermic manner with compounds having a labile hydrogen. Alkaline and acidic catalysts accelerate these reactions. Compounds that react with ethylene oxide include water, alcohol, amines, carboxylic acids, phosphate acid esters, and other similar materials.

Addition of ethylene oxide to these materials introduces a 2-hydroxy ethyl group into the molecule, which increases water solubility.

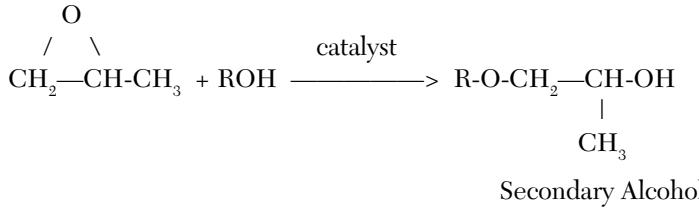
Propylene Oxide

Propylene oxide also is a colorless, low-boiling liquid. Unlike ethylene oxide, however, it is insoluble in water. Propylene oxide, although still quite reactive, is not as reactive as ethylene oxide. However, it does react in an extremely exothermic manner with compounds having a labile hydrogen. Alkaline and acidic catalysts accelerate these reactions.

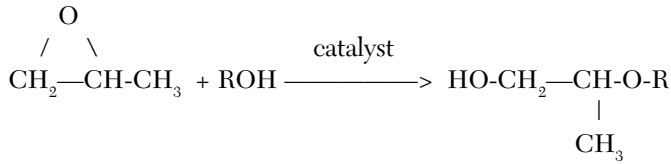
Propylene oxide, unlike ethylene oxide, has a methyl group on one of the oxirane carbons. This makes the molecule asymmetrical. It exists in two optical isomers, with the commercial product being the racemic mixture. Because of this asymmetry, two possible sites of nucleophilic attack exist, resulting in a primary and a secondary alcohol, as shown in the two reaction sequences below. By far, the predominant reaction results in nucleophilic attack at the less-hindered carbon and a secondary alcohol.

Secondary alcohols are less easily reacted in subsequent steps, such esterification. This is why it is easier to make polyoxyethylene glycol esters than polyoxypropylene glycol esters.

Reaction Sequence 1 (Primary Reaction)
(Nucleophilic attack at the less-hindered carbon)



Reaction Sequence 2 (Minor Product)
(Nucleophilic attack at the more-hindered carbon)



Primary Alcohol

Compounds that react with propylene oxide include water, alcohol, amines, carboxylic acids, phosphate acid esters, and other similar materials.

The presence of the methyl group in the alkoxylate has profound effects on the performance of the surfactant. A look at polyoxyethylene glycol and polyoxypropylene glycol compounds *per se* reveals the differences. Polyoxyethylene glycol, having a molecular weight from 200 to 8,000, is water-soluble at both 1 percent and 10 percent by weight. Polyoxypropylene glycol, however, is water-soluble at a molecular weight of 425 at both 1 percent and 10 percent, but it is insoluble at molecular weights of between 1,000 and 4,000 at both 1 percent and 10 percent by weight.

The location of the polyoxypropylene group in a surfactant will have a dramatic effect on the properties. These include alkali stability, water solubility and liquidity.

Fatty Alcohol Alkoxylates

This kind of nonionic surfactant is based on the reaction of ethylene oxide and/or propylene oxide with a suitable hydrophobic material.

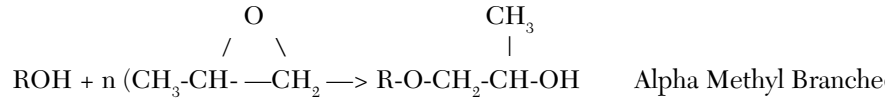
Surfactants from this class represent a wide range of alkoxylates processed from various fatty alcohol hydrophobes. These extremely stable products are excellent detergents, wetting agents and emulsifiers; they are used as dispersants, solubilizers and coupling agents.

This class of surfactants can be divided into three subclasses, depending on the oxide used. The chemistry is essentially identical in each case. The difference lies in the use of ethylene oxide, propylene oxide or combinations of the two. The generalized reactions are as follows:

Ethoxylation

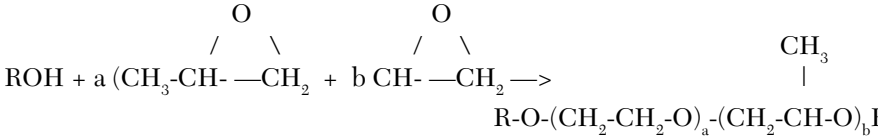
n is the number of moles of ethylene oxide used.

Propoxylation



n is the number of moles of ethylene oxide used.

Mixed Ethoxylation/Propoxylation



where a is the number of moles of ethylene oxide and b is the number of moles of propylene oxide. In reactions where the ethylene oxide and propylene oxide are premixed, a random polymer is obtained.

Homopolymers of polyoxypropylene are not as water-soluble as homopolymers of polyoxyethylene. In fact, once one reaches a molecular weight of about 1,200 the polyoxypropylene glycol is no longer water-soluble.

Liquid esters are of interest in the formulation of personal care products for use as emmolients, moisturizers and conditioners. The ability to control melting point is useful in formulating skin-care products. The options to make liquid products in the past were principally accomplished by incorporation of unsaturation or branching into the molecule. One particular branch type, the Guerbet branch, is effective for liquidity but very expensive. Incorporation of propylene oxide into a molecule significantly alters the material's melting point.

Melting Point

For a material to be a crystalline solid, the particles must be arranged in a regular, symmetrical manner to make up the repeating unit of the crystal. Liquid materials, on the other hand, are random in their order and move about freely. Melting is the change from orderly arrangement of a solid into a random liquid form. If the forces that lead to an ordered system are destroyed, the melting point of a material decreases. Stated another way, the amount of energy necessary to disrupt the organized structure of a solid and make it a liquid (i.e., melt it) decreases for those molecules that have structural features that tend to disrupt the crystalline structure. This is the precise reason that branching lowers melting point. The branched molecule rotates more rapidly as the temperature increases until the crystalline structure is destroyed. A particularly striking example of the effect of symmetry on melting point is seen by comparing the melt point of benzene with that of toluene. The presence of the methyl group in the toluene lowers the melting point from 50°C to -95°C. With this in mind a study was undertaken to see if the introduction of a methyl branch via propoxylation of stearyl alcohol could dramatically reduce melting point of the resultant compounds.

Propoxylation of Stearyl Alcohol

The propoxylation reaction is carried out by reacting propylene oxide with stearyl alcohol under base catalyst. The product that results is a methyl branched alcohol having three more carbon atoms, an additional oxygen atom and a new ether linkage. Equally important, the new molecule has a secondary hydroxyl group (-CH-(CH_3)OH), rather than the primary one (-CH_2OH) that previously was present. The presence of the methyl group and the number of moles of propylene oxide added (the "n" value) will determine in large degree the melting point of the ester

produced by reacting the propoxylated alcohol with various fatty acids. An analysis of propoxylated stearyl alcohol appears in the following table.

Analysis of Propoxylated Stearyl Alcohol

	O	A	B	C
Color (Gardner)	1	1	1	1
Appearance 50°C	Clear	Clear	Clear	Clear
pH 1% Aqueous	7.0	7.0	6.9	6.8
Acid Value	0.0	0.06	0.05	0.03
Hydroxyl Value	208.7	181.2	161.2	139.3
Moisture (%)	0.1	0.1	0.1	0.1
Titer point (°C)	49	38	31	27
Moles of propylene oxide Added	0	0.7	1.5	2.2

The titer point drops from 49°C to 27°C with the addition of 2.2 moles of propylene oxide.

Stearate Esters of Propoxylated Stearyl Alcohol

The lower melting point is also seen with stearate esters of the propoxylated stearyl alcohol, as seen in the following table.

Analysis of Propoxylated Stearyl Stearate

	S-O	S-A	S-B	S-C
Color (Gardner)	5	4	3	3
Appearance 5°C	Clear	Clear	Clear	Clear
Acid Value	2.0	3.1	2.9	3.8
Hydroxyl Value	7.6	6.8	8.0	7.0
Saponification Value	104.5	97.2	89.7	84.0
Titer point (°C)	51	41	38	29
Moles of propylene oxide Added	0	0.7	1.5	2.2

The use of propylene oxide as a melt-point modifier is a major application of alkoxylation.

Fatty Alcohol Ethoxylation

Fatty alcohols react with ethylene oxide at the hydroxyl group to give an ether linkage and a new hydroxyl group. Although the reaction is simple conceptually, in reality the reaction product is a complex mixture of oligomeric products that are a series of compounds that contain different amounts of ethylene oxide. Relatively wide distributions of species, which have varying amounts of oxide reaction products present on the base hydrophobe, are produced by the reaction.

Analyses of the products that are produced when one mole of ethylene oxide is reacted with one mole of stearyl and coco alcohol are shown below. The analysis was done via gas liquid chromatography as described in Chapter 7.

As shown below, when one mole of ethylene oxide is reacted with one mole of fatty alcohol, adducts having no added ethylene oxide are the predominant material in the mixture, making up 60.3 percent of the mixture. The other adducts, ranging from one to eight moles of ethylene oxide, make up the remainder.

By the law of mass balance, the total amount of ethylene oxide added to the reaction must be maintained. The total amount of ethylene oxide added (in this case one mole) can be calculated by multiplying the number of moles of ethylene oxide added to each adduct by the percentage of that adduct present in the composition and taking the sum. This is shown in the following table. This calculation accounts for 0.978 moles out of 1.0 added on a theoretical basis. The difference between the observed 0.978 moles and the 1.0 added is primarily due to polyoxyalkylene glycol formation.

Ethoxylation of Stearyl Alcohol with One Mole Ethylene Oxide

DESIGNATION	MOLES OF ETHYLENE OXIDE (Value A)	AREA % (Value B)	ETHYLENE OXIDE CONTRIBUTION (Value (A)x(B)
18-0	0	60.3	0.000
18-1	1	13.6	0.136
18-2	2	8.8	0.176
18-3	3	7.9	0.237
18-4	4	5.9	0.236
18-5	5	2.2	0.110
18-6	6	0.9	0.054
18-7	7	0.3	0.021
18-8	8	0.1	0.008
		Total	100.0%
	TOTAL CALCULATED MOLES ADDED		0.978

When one mole of ethylene oxide is reacted with one mole of coco fatty alcohol, adducts having no added ethylene oxide are the predominant material in the mixture, making up 54.8 percent of the mixture. The other adducts ranging from one to eight moles of ethylene oxide make up the remainder. If the amount of ethylene oxide found on each adduct is multiplied by the percentage of that adduct, the ethylene oxide contribution is calculated. The difference between the observed 0.993 moles and the 1.0 added represents primarily polyoxyalkylene glycol formation.

Ethoxylation of Coco Alcohol with One Mole Ethylene Oxide			
DESIGNATION	MOLES OF ETHYLENE OXIDE (Value A)	AREA % (Value B)	ETHYLENE OXIDE CONTRIBUTION (Value (A)x(B)
NO EO	0	54.8	0.000
EO 1	1	19.6	0.196
EO 2	2	10.2	0.204
EO 3	3	6.8	0.204
EO 4	4	5.5	0.220
EO 5	5	2.1	0.105
EO 6	6	0.7	0.042
EO 7	7	0.2	0.014
EO 8	8	0.1	0.008
		Total	100.0%
	TOTAL CALCULATED MOLES ADDED		0.978

Much work has been done in recent years to "peak" ethoxylates. Catalysts chosen to produce peaked ethoxylates have a narrower distribution of ethoxylated oligomers.

The ethoxylation of alcoholic hydroxyl groups is a complicated reaction for two reasons. First, the products of the reaction sequence are complex mixtures, and, second, the reaction begins immediately; there is no induction period before the start of the reaction. Induction time is a salient property of fatty acid ethoxylation.

The reaction of fatty acids with ethylene oxide is significantly different than the reaction of fatty alcohols with ethylene oxide. Significant differences exist in the kinetics of ethoxylation comparing fatty acid ethoxylation and fatty alcohol ethoxylation. The differences are most dramatic in the initial stages of the reaction.

Unlike the kinetics observed with the ethoxylation of fatty alcohols, the base-catalyzed reaction of ethylene oxide with fatty acids is divided into two stages. In the first stage, negligible product forms. Slowly, the reaction of the acid and ethylene oxide begins after an induction period to give mostly ethylene glycol monoester. In the second stage, after the addition of about one mole of ethylene oxide per mole of acid, the reaction rate increases. Clearly then, the existence of an induction period in the ethoxylation process indicates that the reaction is one of a fatty acid and ethylene oxide, rather than a fatty alcohol and ethylene oxide.

The ethoxylation of fatty alcohols will not occur appreciably without catalyst. Catalyst can be either acidic or, more typically, alkaline. Alkaline catalysts generally produce fewer by-products.

One of the by-products, which are made in the ethoxylation of fatty alcohols, is polyethylene glycol. Having water present in the fatty material before ethoxylation increases this by-product concentration.

The concentration of polyethylene glycol is as follows:

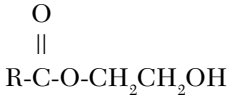
Hydrophobe	NaOH Catalyst	Moles Ethylene Oxide	Ethoxylate	Polyethylene Glycol
Cetyl/Stearyl Alcohol	1.0	5.0	96.0%	4.0%
Lauryl Alcohol	1.0	10.0	93.3%	6.7%
Lauryl Alcohol	1.0	20.0	91.8%	8.2%
Lauryl Alcohol	1.0	50.0	88.5%	11.5%

Fatty Acid Ethoxylation

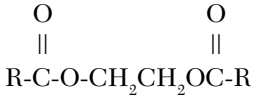
When reacted with ethylene oxide, fatty acids produce complex mixtures of hydroxy-esters. Unlike the ether products formed by the ethoxylation of fatty alcohols, esters are formed when ethylene oxide is reacted with fatty acids. In addition to the oligomeric species that form during the reaction of a fatty acid with ethylene oxide, an added complication arises — the formation of diester, as shown below.

Ester Products

Monoester



Diester



The ratio of monoester to diester is as follows:

Hydrophobe	Moles Ethylene Oxide	Monoester	Diester	Polyoxyethylene Glycol
Stearic Acid	9.0	38.9	41.1	20.0
Oleic Acid	13.6	59.7	26.8	13.5

The salient difference between fatty acid ethoxylation and fatty alcohol ethoxylation under base catalysis is that fatty acid ethoxylation has an induction period. During this early stage of the reaction, there is a period in which negligible amounts of product are formed. After that initial induction period, the reaction rate increases to about that of the fatty alcohol. Increasing the amount of alkaline catalyst shortens the induction period but does not eliminate it.

The ethoxylation of fatty acids, like that of fatty alcohols, will not occur without catalyst. Catalyst can be either acidic or, more typically, alkaline. Alkaline catalysts generally produce fewer by-products.

Ethoxylation Rate

The amount of ethylene oxide that may be added to a particular hydrophobe in a given amount of time varies by the kind of hydroxyl or carboxyl group present. Fatty acids, having a carboxyl group, ethoxylate significantly slower than alcohols because of their induction period.

The data below indicate the number of moles of ethylene oxide that react with the specified compound for the specified amount of time. Stearyl alcohol, castor oil and 12-hydroxystearic acid all exhibit about the same rate of ethoxylation. Nonylphenol ethoxylates react most rapidly.

Moles of Ethylene Oxide Added vs. Time at Reaction Conditions

	0.1 KOH				
Time (Hrs)	Nonyl Phenol	Stearyl Alcohol	Castor Oil	12-hydroxy Istearic Acid	Stearic Acid
0	0	0	0	0	0
1.0	4.9	1.1	1.4	1.0	0.5
1.5	7.5	2.5	3.3	2.2	0.6
2.0	9.5	4.2	6.1	4.0	0.8
2.5	11.1	7.0	8.2	6.0	3.0

The amount of ethylene oxide added to various hydrophobes using 0.1 percent KOH catalyst per unit of time is shown above. Stearyl alcohol has added 4.2 moles of ethylene oxide in two hours, and nonylphenol has added 9.5 moles in the same time.

Mixed Alkoxylation

The mixed alkoxylation reaction makes use of ethylene oxide and propylene oxide to give a mixed polyoxyethylene and polyoxypropylene backbone, as shown below.

$$ROH + n\,(PO) \text{ and } y\,(EO) \longrightarrow RO((EO)_y\text{-}(PO)n)H$$

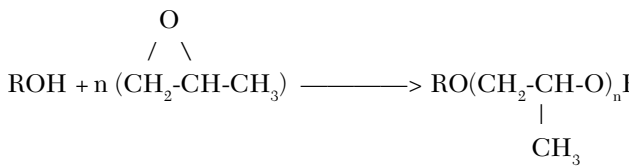
n is the number of moles of propylene oxide used,
and y is the number of moles of ethylene oxide used.

The ethylene oxide and propylene oxide can be randomly added or blocked into units depending on the application desired. Process variables have dramatic effects on final product functionality. Specifically, cloud point, alkaline stability, foam properties and viscosity can be altered by changing the temperature of alkoxylation, catalyst type/concentration, and method of blending or blocking. This means that hydroxyl determinations may be of little help in ensuring product quality.

Ethylene oxide/propylene oxide-blocked nonionic surfactants based on a linear alcohol hydrophobe offer the advantages of increased fluidity over alkoxylates containing only ethylene oxide or only propylene oxide. In addition, they tend not to gel when added to water. They also can be modified to be low-foaming and have increased alkaline stability.

Propoxylation

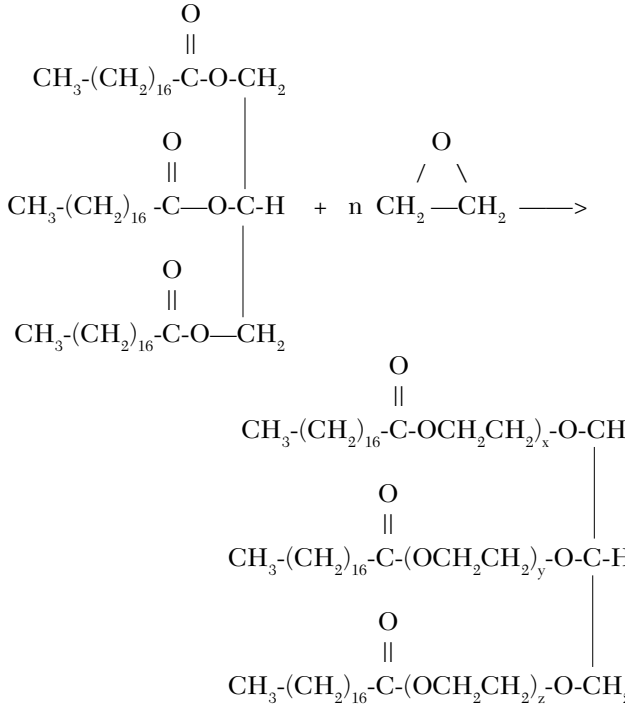
The propoxylation reaction introduces a branched, three-carbon atom polyoxypropylene group onto the hydrophobe. The products that result are almost exclusively those in which the methyl group is on the alpha carbon. The result, therefore, is a secondary alcohol.



n is the number of moles of propylene oxide used.

Alkoxylated Triglycerides

Triglycerides will react with ethylene oxide under base catalyst by a process called *ethenification*. The process can be demonstrated by the following reaction sequence:



n = x + y + z
Addition to x+y+z is the result of ethenification.

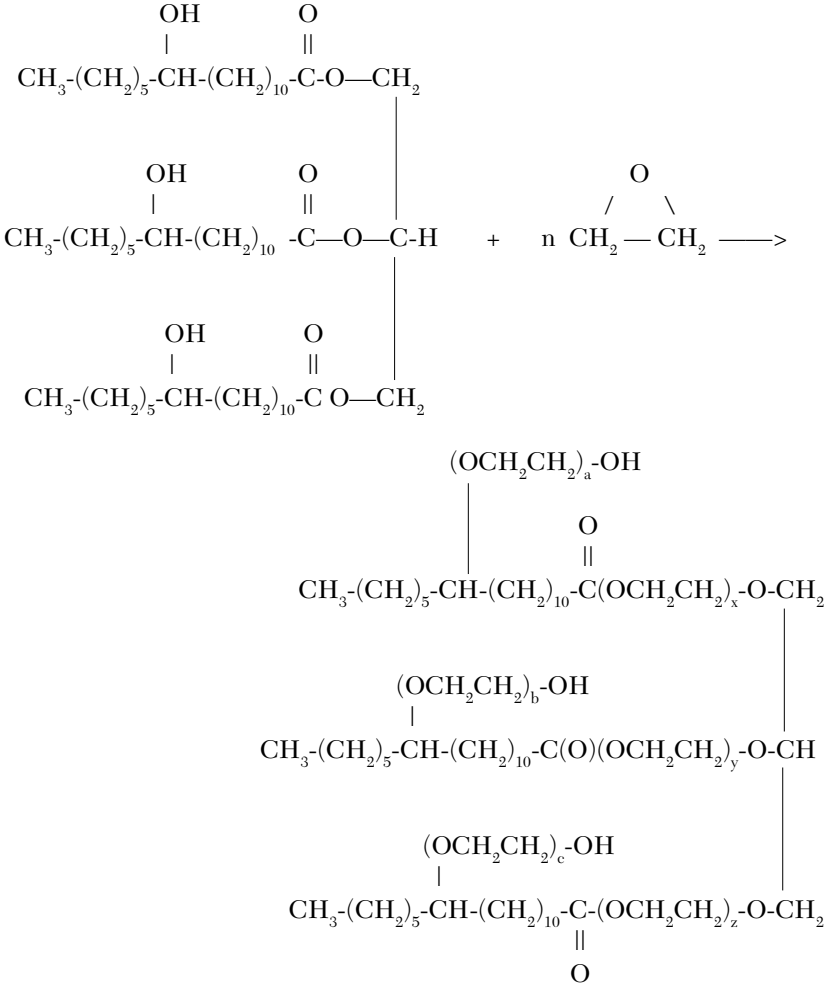
Hydrogenated castor oil has the ester functionality and the hydroxyl functionality present in one molecule. It offers a unique possibility to study the relative rates of ethoxylation of the hydroxyl group and the ethenification of the ester.

Hydrogenated castor oil is principally 12-hydroxystearic triglyceride. Hydrogenated castor ethoxylates are items of commerce and are commonly used in several applications, including textile and personal care applications. It was originally thought that they ethoxylated almost exclusively on the hydroxyl group. It is now

understood that this material ethoxylates unusually. The ethylene oxide is added to the ester group and the hydroxyl group. Therefore, it is possible to evaluate the relative amount of ethylene oxide that adds to each functionality.

In short, there is a group selectivity or preference for ethoxylation. This group selectivity can be classified as strong, intermediate or weak, depending on the results obtained with the ethoxylation.

The reaction of hydrogenated castor oil can occur at two different sites or both sites to differing extents. The reaction sequence that follows shows reaction at both sites.



n = a + b + c + x + y + z

Addition to x+y+z is the result of ethenification.

Addition to a+b+c is the result of ethoxylation.

When one mole of ethylene oxide is reacted with one mole equivalent of hydrogenated castor oil using 0.1 percent KOH as catalyst, the product gave 58 percent insertion reaction (ethenification), 29 percent hydroxyl group ethoxylation and 13 percent polyethylene glycol formation.

Alkylpolyglucosides

Alkylpolyglucosides are a class of nonionic surfactants that have been known for quite some time. However, improved process technology and formulation expertise necessary to make commercial use of these materials have been fairly recent developments.

An interesting aspect of the chemistry of alkylpolyglucoside surfactants is that their synthesis does not depend on the use of ethylene oxide to make the fatty alcohol into a surfactant. Instead, the chemistry uses naturally available raw materials, sugar and fatty alcohol, to make this class of surfactants.

Reaction

Alkylpolyglucosides are synthesized by the reaction of cornstarch glucose with a fatty alcohol, as shown below. The number of moles of glucose that react is limited by the choice of catalyst and processing conditions.

Properties

Alkylpolyglucosides, like most surfactants, lower surface tension effectively. They are naturally derived products that are very mild when compared with traditional anionic surfactants such as sodium lauryl sulfate. These two factors make the class of materials exciting to cosmetics formulators.

The choice of the alcohol chosen to prepare the alkylpolyglucoside has a dramatic effect on its properties. The lauryl range products act as thickeners in anionic systems and build foam stability. In this regard, they act like alkanolamids. The decyl range products provide detergency, foam and surfactant properties as the primary surfactant. Alkylpolyglucosides will almost certainly grow in significance in the personal care area as the various manufacturers introduce more custom-tailored products.

Alkyl Polyglucoside - new trends

APG compounds have become a major area of interest in the formulation of personal care products. As is often the case, they are more commonly used in Europe. The desire to make APG compounds more formulator friendly has been a quest for many suppliers. Indeed, the first edition of this book published in 1999, had very little information on this class of materials. This is because the class of compounds hade very little commercial use in the cosmetic arena. Over the intervening five years this has changed.

One approach to overcome some of the limitations of these materials is to make blends with traditional surfactants. These blends have gained acceptance in many formulations. Another approach is to functionalize the APG molecule itself. The latter seems to me to have the greatest chance of success.

Alkyl Polyglucoside Derivatives

It is very difficult to find a comprehensive study of APG's (Alkyl Poly Glycosides), and yet, this class of fatty alcohol derivatives is gaining tremendous momentum as both a finished product and a more recently, a very desirable raw material. Here then a discussion of where these APG's have come from and where the author thinks they are going. This chapter will, of course, not be the complete story as new developments are blossoming every day.

For many years the Alkyl Glycosides, as they were called, were a pretty well known laboratory curiosity. Emil Fischer, the famous carbohydrate chemist, synthesized these products on the lab bench over 100 years ago. Sixty years ago came the first patent application describing the use of alkyl glycosides in detergents. It took another 40 to 60 years before the production of APG's was seriously examined. The initial solutions to the technical problems were sought by Rohm & Haas. The product as they emerged were reactions of glucose with alcohols having alkyl chain lengths of C_8 through C_{16}. These were a little afield from Fischer's efforts with mostly low molecular weight alcohols such as methanol and ethanol. The result was the 1st offering of commercial products by Rohm & Haas in the late 70's. BASF and Seppic soon followed suit. These first candidates were based on the C_8/C_{10} carbon chain length. The good news, here was an emerging technology based on renewable resources, namely glucose, corn oil and coconut oil. The bad news was that the products from the shorter chain fatty alcohols were poor in quality, dark in color, and short on performance. They did find some applications in limited quantities in industrial and institutional markets.

As the early 80's unfolded, efforts were made by two companies to produce longer alkyl chain length products in the C_{12} to C_{16} range. The Horizon Division of AE Staley was one and Henkel (Germany) the other. Henkel subsequently acquired the Horizon Division of Staley and has since become the giant in the APG industry. Henkel began their production efforts with a 10 mm lb. pilot plant unit in Crosby, Texas in 1988 and 1989. This unit, built on the combined background experience of Staley and Henkel, was designed to solve the rather complex mechanics of APG production with an eye towards increasing plant size. This next crucial step was accomplished by Henkel in 1992 when they announced the construction of a 50 mm lb. plant in North America. This was followed by the subsequent announcement of another 50 mm lb. plant slated for construction in Germany in 1995. With these two plants up and running, Henkel, now Cognis emerged as the top gun in the APG industry. Others in more secondary roles are, first Seppic, then Soliance in France and finally another player in our country, Akzo Nobel.

A very brief examination of the chemistries that have emerged would highlight the water- soluble types in the C_8 to C_{14} range and the insoluble products made from APG's with carbon chain lengths of C_{18} and up. Our concern in this chapter

is with the relatively water-soluble types represented in the market place by Cognis' Glucopon 220 and Glucopon 625 and Seppic's Sunalsol SL-8 and SL-10. The products mentioned all have degrees of polymerization that range from 1.2 to 1.8. Several classical surfactant routes emerged initially to produce these products. However, enzymatic and or microbial procedures, because they are selective could have easily replaced the complicated chemical protection and deprotection steps that create the regioselective formulation of the glycoside. The problems inherent in this route were never worked out and the emerging technology settled on the Fisher glycosylation. Production process must satisfy process economics and performance properties of the finished products. The product properties must then lead themselves to market requirements. Adaptations of the Fisher process have accomplished these goals. Another advantage of the Fisher adaptation is that the degree of polymerization of the products can be precisely controlled. This allows relevant performance properties of the finished products, i.e. hydrophilicity, to be positioned to meet requirements.

The hydrophilic portion of these molecules is obtained from coconut or palm kernel feed stocks for the C12-14 ranges and tallow, palm or rapeseed oil from the C16-19 fatty alcohols. The hydrophilic part of the desired alkyl poly glycosides is derived from a carbohydrate. Usually a starch based on corn, wheat or potatoes. It is the poly functionality of the carbohydrate partner that through the acid-catalyzed Fisher reaction yields an oligomer mixture in which an average more than one glycose unit is attached to an alcohol molecule. The average number of glycose units linked to an alcohol group is described as the average degree of polymerization. The molecules of concern to the average formulators are those that have a carbon chain length from C4 to C16 have a degree of polymerization lying between 1.2 and 1.6.

APG compounds are generating a lot of interesting and useful benefits to the cosmetic formulator. They include;

- good detergency
- synergy with anionic surfactants
- good lime soap dispersing properties
- fast rinse on hard surfaces
- high electrolyte tolerance
- mild on the skin
- greatly reduce filming and streaking on hard surfaces
- good for concentrates and blends
- don't gel when diluted
- compatible with cationic surfactants
- derived from renewable resources
- readily biodegradable
- very mild to skin and eyes
- "Eco Friendly"

The inherent drawbacks do the APG have that have kept them mostly in the industrial arena and out of the cosmetic arena for the most part are;

- some odor problems
- dark color
- unacceptable foam
- moderate irritation profile for longer chain lengths
- not soluble enough in some anionic formulations

Surfactants Based Upon Alkyl Polyglucoside

The use of alkyl polyglucoside in personal care products has been limited. The growth has been in the industrial markets, with hard surface cleaners being a major finished product area. One approach to making cosmetically acceptable, easily formulated products is to combine them with other surfactants. Such blends include alkyl polyglucoside with sulfated fatty alcohols, sulfated fatty alcohol ethoxylates and combinations of other surfactants.

There have been a series of new molecules developed that are surfactants made from alkyl polyglucoside covered by U.S. Patent 6,627,621. These derivatives are available in anionic, cationic and non-ionic surfactants that offer advantages to the formulator over traditional alkyl polyglucoside. Unlike derivatives, these products are not made from the direct reaction of alkyl polyglucoside with reagents like P_2O_5, SO_3, and other aggressive reagents. These products are made with mild reagents in aqueous systems; hence color, odor and cosmetic acceptability are improved.

The compounds of interest are derivatives of APG that conform to the following structure;

$$APG\text{-}O\text{-}CH_2CH(OH)CH_2\text{-}R$$

APG is alkyl polyglucoside that has been functionalized on one or more of the hydroxyl groups. This functionality can have a (-) charge making them anionic, a (+) charge making them cationic or no charge making them non-ionic.

Anionic	
Type	**Structure**
Phosphates	$APG\text{-}CH_2CH(OH)CH_2\text{-}O\text{-}P(O)\text{-}(OH)_2$
Sulfates	$APG\text{-}CH_2CH(OH)CH_2\text{-}SO_4\,Na$
Sulfonates	$APG\text{-}CH_2CH(OH)CH_2\text{-}SO_3\,Na$
Carboxylates	$APG\text{-}\,CH_2C(O)\text{-}OH$

Cationic	
Type	**Structure**
Alkyl quats	APG-$CH_2CH(OH)CH_2$-N^+(-CH_3)(-CH_3)-R
Alkylamido quats	APG-$CH_2CH(OH)CH_2$-N^+(-CH_3)(-CH_3)-$(CH_2)_3$-N(H)-C(O)-R

These products are the topic of several patents now issued and now pending.

APG Quats

The best known compounds in the above series are the quaternary compounds. They are mild to skin and eyes, compatible with anioinic surfactants over a wide range of concentrations, antimicrobial, and high foaming surfactants. This profile makes these compounds of interest in many personal care applications.

Alkyl Polyglucoside Derived Quats - Commercial Offerings	
Designation	**Proposed CTFA/INCI Names**
SugaQuat L-1010	(Lauryl Dimethyl Ammonium Hydroxy Propyl) Decyl Polyglucosides Chloride
SugaQuat L1210	Lauryl Dimethyl Ammonium Hydroxy Propyl) Lauryl Polyglucosides Chloride
SugaQuat S1010	(Stearyl Dimethyl Ammonium Hydroxy Propyl) Decyl Polyglucosides Chloride
SugaQuat S1210	(Stearyl Dimethyl Ammonium Hydroxy Propyl) Lauryl Polyglucosides Chloride

The sugar or alkyl glycoside backbone is cationic. This process yields products that are high in molecular weight, naturally derived, and cationic in character. They provide hydrophilic conditioning, anti microbial properties, high foam and are compatible with anionic surfactants.

As highly substantive materials, they provide lubricity and detangling to wet hair while at the same time effectively building volume. Fly-away hair is controlled by the humectant nature of the materials. In addition, they also impart an elegant feel to the skin.

Their compatibility with anionic surfactants like lauryl sulfate and lauryl ether sulfate at almost any concentration allowing the formulator to build desired conditioning properties, from light to extreme, into conditioning or all-in-one shampoo formulations, concentrates, and body washes.

BENEFITS	
• Sugar derived	• Soft after feel
• Non-Irritating	• No greasy build-up
• Excellent wet comb properties	• Controls fly-away hair
• Biodegradable	• Formulates in the presence of anionics
• Builds foam in shampoo formulations	• Supports viscosity in shampoos
• Can be formulated as MEA/DEA Replacements	• Cationic emulsifier for water in oil emulsions

TYPICAL PROPERTIES OF COMMERCIAL PRODUCTS

	L-1010	L-1210	S-1010	S-1210
Physical Appearance	Clear liquid	Clear liquid	Clear liquid	Clear, viscous liquid
Ionic Nature	Cationic	Cationic	Cationic	Cationic
Color (Gardner)	2	2	2	2
Solids (%)	30	30	30	30
pH (10% aqueous)	7.0	7.0	7.0	7.0
Viscosity, cps (25°C)	25	98	22	9800

Properties of other Materials

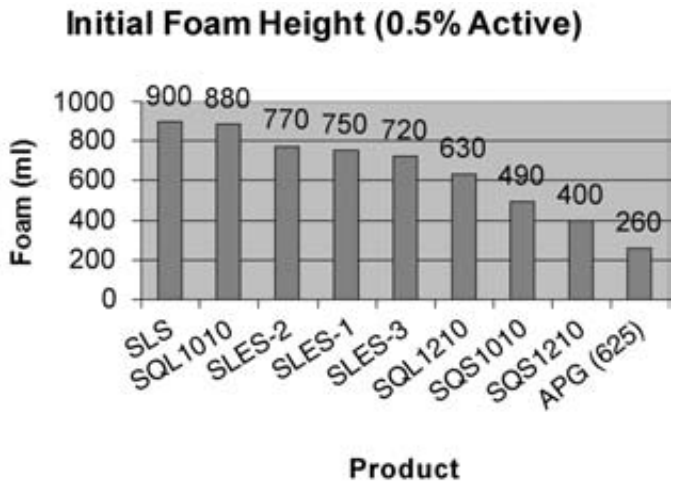
The products are listed below using a combination of digits and numbers. The numbers relate to the alkyl group on the APG, and the letters the alkyl group on the quat.

Designation	Alkyl Group on APG
04	Butyl
08	2-ETHYL Hexyl
86	C8-C16
10	C8-C10
12	C12–C16

Designation	Quat Alkyl
S	Stearyl
L	Lauryl
TM	Methyl

Table of Properties								
Quat Subst:	Methyl			Lauryl			Stearyl	
B-0410	**B-1212**	**B-8610**	**L-1010**	**L-1210**	**L-8610**	**S-1010**	**S-1210**	
Color	7	1+	1	1	1	1	1	1
Activity	30.0	30.5	30.6	30.8	29.7	30.2	29.1	30.5
Viscosity	12.5	272		16	106	11	21.5	9800
Odor								
pH 10%	7.2	7.8	7.7	6.7	7	6.45	6.76	7.12
App 10%	Clear	Cloudy	Clear	Clear	Clear	Clear	Clear	Clear
Foam 1%								
Initial	54	78		250	238	250	186	230
30 sec	50	78		250	238	250	186	230
60 sec	50	78		250	238	250	180	230
120 sec	50	78		250	238	250	180	230
Draves Wet (1% active)	>200	35		4	9	5	15	15
Solubility								
50% NaOH	S	S		Cloudy	Cloudy	Cloudy	Soluble	Cloudy
25% NaOH	S	S		Clear			Soluble	
25% H2SO4	S	Cloudy		Clear	Soluble	Soluble	Soluble	Cloudy

Two important reasons for one to use surfactants are foam and wetting properties. These properties are reported below.

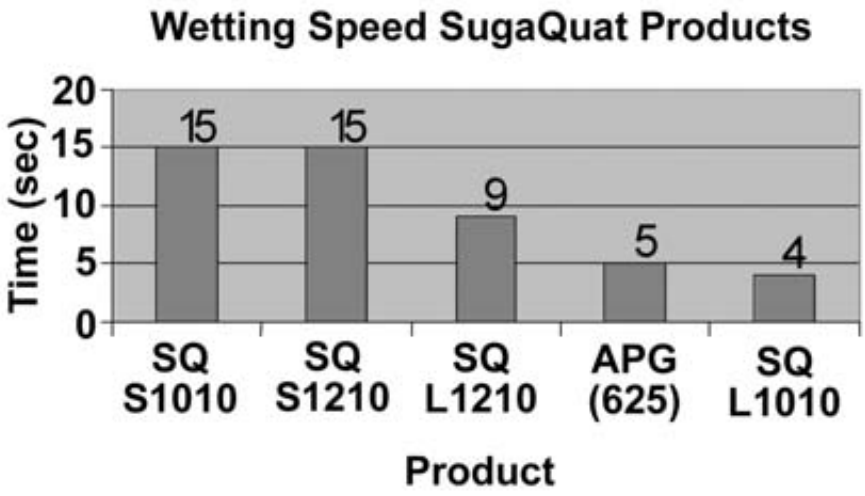


Foam data

The APG quats are all better foaming than the starting APG and surprisingly somewhat better than SLES and somewhat lower than SLS.

Wetting Data

APG is a good wetter per se. The quats are either comparable or worse depending upon the specific structure chosen.



Toxicological Propierties

The evaluation of these materials as an eye irritant was performed using the chorioallantoic membrane technique. This test utilizes the inner membrane of a hen's egg to gauge the irritation potential of a compound by visual observation of injurious changes in the membrane. They were rated to be as mild as a leading brand of baby shampoo.

Typical Applications

These products are ideal components in a wide variety of hair and skin care applications, including conditioning shampoos, hair conditioners, hairsprays, styling aids,moisturizing hair finishes, creams, lotions, and shower gels.

Shampoo Performance- Salt Curves

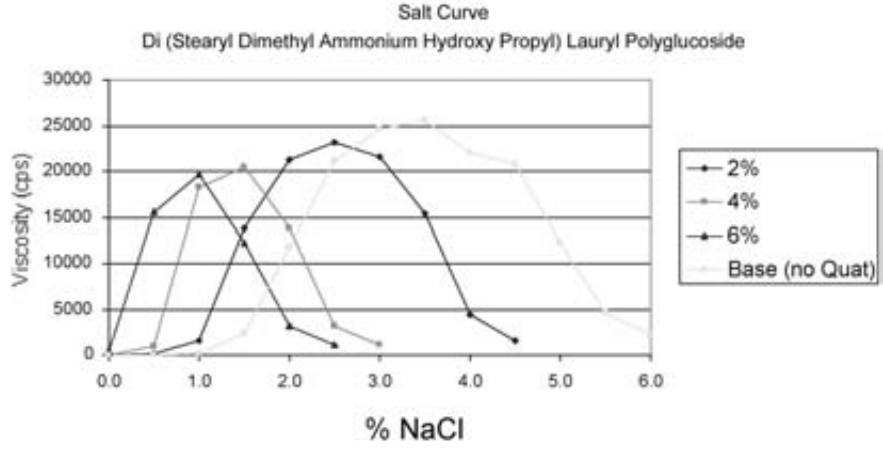
A basic shampoo blend was prepared containing 10% active surfactants. The blend was based on an 80/20 ratio of anionic to amphoteric, with the anionic surfactants at a 50/50 SLS / SLES ratio. Water was added to a total of 94 parts.

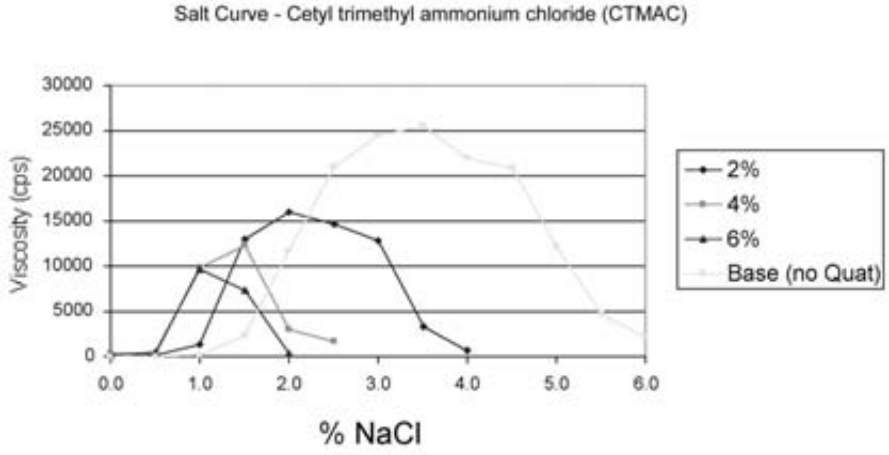
Stearyl di ammonium hydroxy lauryl glucosides chloride was then added at levels of 2, 4 and 6%; water was added to bring the total to 100 parts.

The salt curve performance of stearyl di ammonium hydroxy propyl lauryl glycosides chloride was compared with cetyl trimethyl ammonium chloride (CTMAC).

Conclusion - Effect Upon Shampoo Viscosity

Note that the addition of SugaQuats to a typical shampoo blend in the absence of amide, results in a significant retention of viscosity while the CTMAC drastically reduces viscosity to the point of being insoluble.





Cationic Emulsifier

SUGAQUATS have application in water-in-oil emulsions as a secondary emulsifier. High viscosity creams and lotions have been formulated using SUGAQUATS in combination with cetyl-dimethyl copolyol.

Rubine Dye Test

Evaluation by the Rubine Dye Test indicates that the SugaQuats have comparable substantivity as CTMAC on a substrate. This combination of efficacy, mildness, and substantive nature make the SugaQuats unique in the industry.

Antimicrobial Properties

The antimicrobial properties of several APG quats were assessed by an outside laboratory in Zone Inhibition studies. The results are below:

Zone Inhibition Study

Purpose:

To determine the antimicrobial capability of three (3) SugaQuat (alkylpolyglucoside) variations utilizing the zone inhibition technique. The test materials were evaluated for gross antimicrobial activity against a series of four (4) test organisms: *Pseudomonas aeruginosa* (Gram negative bacteria); *Staphylococcus aureus* (Gram positive bacteria); *Candida albicans* (yeast) and *Aspergillus niger* (mold) utilizing the zone inhibition technique. Results of the assays are presented below.

Test Samples:

1) SugaQuat L-0810 (1.0%, 0.50% and 0.25% concentration).
2) SugaQuat L-1210 (1.0%, 0.50% and 0.25% concentration).
3) SugaQuat S-1210 (1.0%, 0.50% and 0.25% concentration).

Combined Activity Summary

SCORING:
1 = Excellent; 2 = Very Good; 3 = Good ;
4 = OK (moderate); 6 = Poor; 8 = No Activity

SAMPLE	Sa	Psa	Ca	An	Score	Comments
1. SugaQuat L-0810	1	2	3	8	14	Good B & Y; No M Activity
2. SugaQuat L-1210	2	8	3	6	19	Good Sa & Y; Psa & M
3. SugaQuat S-1210	1	2	1	2	6	Excellent Activity

B = bacteria; Y = yeast; M = Mold
NOTE: The lower the score, the greater the activity.

Individual Sample Results

SAMPLE/%	Sa		Psa		Ca		An		Average Score
	mm	clarity	mm	clarity	mm	clarity	mm	clarity	
SugaQuat L-0810									
1.00%	13	4+	10	4+	9	3+	0	0	
0.50%	12	4+	8	3+	8	1+	0	0	14
0.25%	10	4+	8	3+	8	0	0	0	
SugaQuat L-1210									
1.00%	11	4+	0	0	8	3+	8	1+	
0.50%	9	3+	0	0	8	3+	0	0	19
0.25%	8	3+	0	0	8	2+	0	0	
SugaQuat S-1210									
1.00%	12	4+	10	4+	9	4+	9	4+	
0.50%	12	4+	8	3+	9	4+	8	3+	6
0.25%	12	4+	8	3+	9	4+	8	3+	

NOTES: 4+ = Excellent Activity; 0 = No Activity; mm = Zone Size.

Comments:

- SugaQuat S-1210 demonstrated exceptional antimicrobial activity against all four of the test organisms employed. This material compares favorably to the general antimicrobial profile than phospholipids.
- SugaQuat L-0810 displayed very good activity against the bacteria and acceptable activity against the yeast. There was, however, no apparent activity against the mold, Aspergillus niger
- SugaQuat L-1210 showed good activity against Sa and Ca only.

Conclusion

The development of new derivatives of APG compounds offers the best opportunity to make this class of compounds that are more formulator friendly. They can provide multi-functional properties to the cosmetic formulator, making them both useful and cost effective. Sulfonates have already been developed that provide the foam of sodium lauryl sulfate, that are low irritation, and environmentally friendly.

If the standard SLS and SLES compounds are in their old age in personal care products, APG compounds are in their childhood, the derivatives are newly born. We expect many important developments in the derivative arena in the near future.

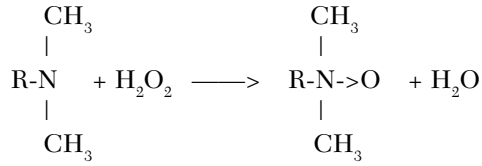
Amine Oxides

Members of the amine oxide class of surfactants are prepared by the oxidation of a tertiary amine with aqueous hydrogen peroxide.

Alkyl Dimethyl Amine Oxides

Reaction

If an alkyl dimethyl amine is reacted with aqueous hydrogen peroxide, the resulting amine oxide is an alkyl dimethyl amine oxide, as shown below.



Properties

Amine oxides provide copious, dense foam to formulations. They are good detergents and have antistatic and some transient conditioning properties when applied to hair.

Amine oxides as a class contain varying amounts of unreacted amine in them. Because the peroxide oxidation is not quantitative and free peroxide is not desirable, the reaction is normally run with a slight excess of amine.

Alkyl amine oxides are one of the few kinds of compounds that are stable in bleach. This explains their use in tile cleaners and hair bleaches. Alkyl amine oxides do not contain the amido function that can minimize effectiveness of the surfactant at the extremes of pH. Bleach not only has an effect on the stability of the product per se but also has a pH of about 13.

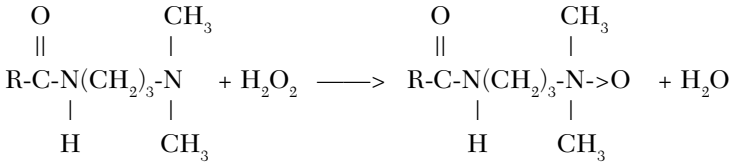
One interesting variant on the alkyl amine oxide theme is oleyl amine oxide. The high molecular weight of the product coupled with the presence of the double-bond results in a product that produces a high viscosity aqueous solution at low concentrations. For example, 3 percent of oleyl amine oxide in water produces a gel. This material gives outstanding conditioning to hair and has good stability in alkali and bleach systems.

Alkylamidopropyl Amine Oxides

As is generally the case with surfactants, the introduction of the amido group into an amine oxide molecule results in a milder surfactant that gives more copious, more stable foam. The presence of the amidopropyl group results in a lowering of detergency properties and resistance to the effects of extremes of pH relative to the amino oxide that does not contain the amido group.

Reaction

Alkylamidopropyl amine oxides are made by the aqueous oxidation of an amido-amine with peroxide, as shown below.



Properties

Cocamidopropyl amine oxide has been used in shampoo systems and conditioners. It provides a high level of tight foam and has a good feel on the skin. In addition, it provides thickening to many anionic systems.

Sorbitan Esters and Alkoxylates

Sorbitol is sugar that contains six carbon atoms. The sorbitol of commerce is 70 percent sorbitol in water. To prepare surfactants from sorbitol, three steps must occur. They are:

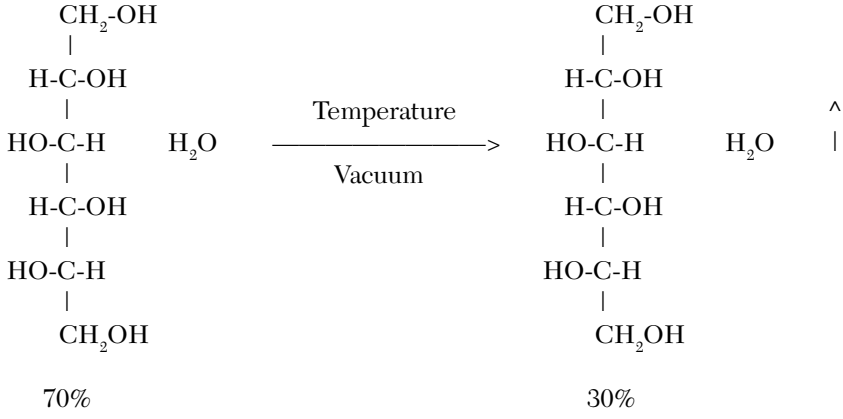
- Removal of the water present with the sorbitol.
- Cyclization of linear sorbitol molecule to form a ring structure.
- Reaction with a fatty acid with a remaining hydroxyl group.

The reaction with the fatty acid introduces the fatty portion of the molecule, which is necessary to obtain a surfactant. The result of the three steps is a surfactant that is water-insoluble. The three steps are conducted differently by different companies. Some manufacturers conduct them in one process by selecting the proper catalysts and proper conditions of temperature and pressure. Older methods use three distinct steps, each having different conditions and catalysts. The exact distribution of species and, consequently, functionality is affected by the selection of processes, catalysts and temperatures.

For simplicity and clarity, the process for the preparation of sorbitan esters using the three-distinct-step process follows.

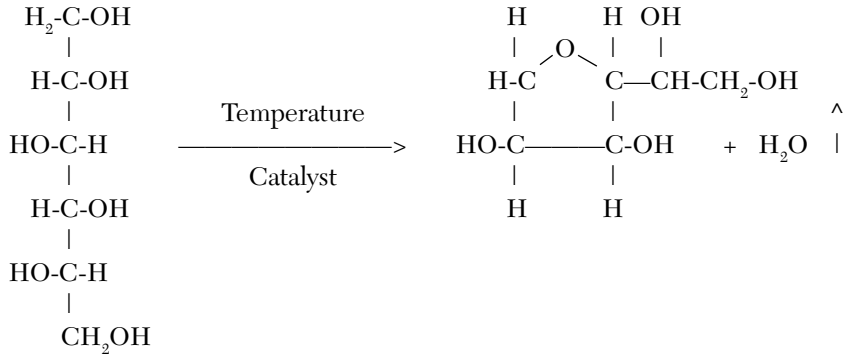
Step 1 (Dehydration)

In this step, water is removed using heat and vacuum, as shown below.



Step 2 (Cyclization)

The second step in the reaction sequence is cyclization, which gives a cyclic product. The cyclization is conducted with catalyst at elevated temperatures. Care must be exercised not to over react the material in this stage because a polycondensation can occur, giving polysorbide. Although some early patents specify that this material is desirable, the content relative to the monocyclized product needs to be controlled
in the process from lot to lot and supplier to supplier.

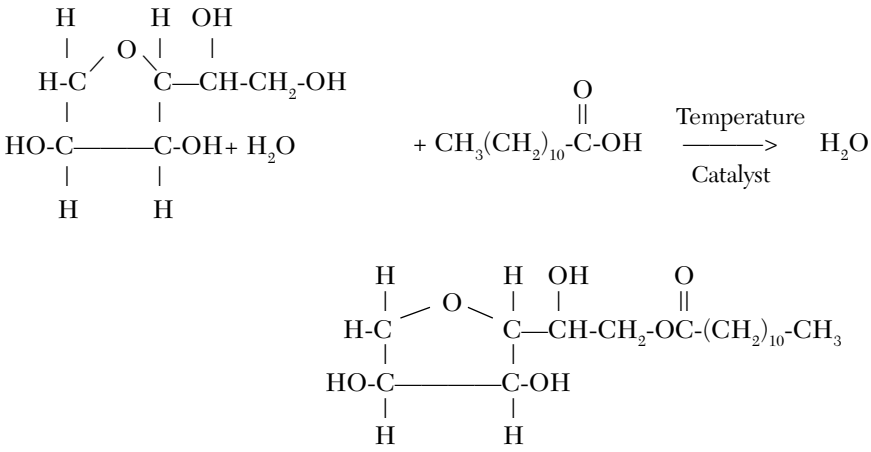


Step 3 (Esterification)

The introduction of the fatty group occurs by the esterification of a hydroxyl group with a fatty acid, as the reaction sequence below illustrates. This step is likewise conducted at high temperature, albeit with a different catalyst. It is important to note that once this step is complete the resulting product is a sorbitan ester. After this stage, the water-soluble groups needed for preparation of oil-in-water emulsifiers have not yet been introduced. These groups are introduced by reaction of the sorbitol ester with ethylene oxide in a subsequent step.

The sorbitan ester produced using the three steps outlined is a water-in-oil emulsifier and is generally a relatively dark caramel-smelling organic phase. The reason for the color is the necessity of exposing the compound to high temperature for protracted amounts of time. Some manufacturers bleach the ester quite extensively, but it is suggested that bleaching be avoided.

The adoption of a process in which all three steps can be run nearly simultaneously has resulted in lighter-color, lower-odor products that are better suited to personal care applications. The difficulty with these processes is that when three processes occur at nearly the same time control of catalysts and temperatures is critical to product reproducibility. However, once the details of the process are worked out, the process becomes quite reproducible, and the resulting products are quite acceptable for cosmetic applications.

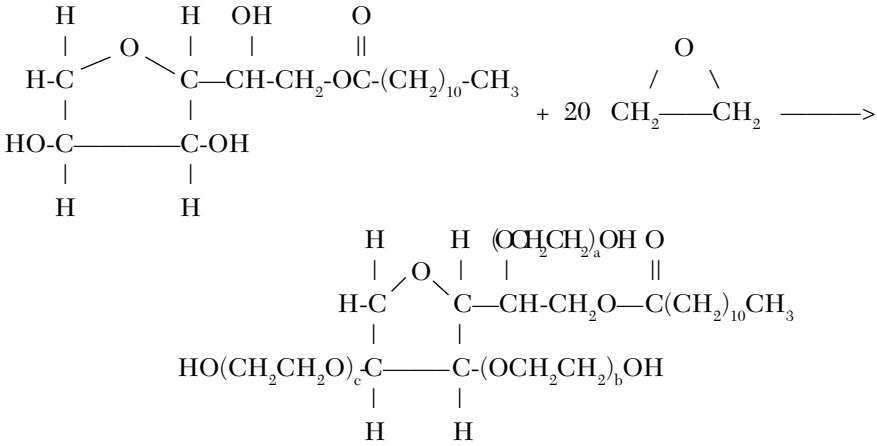


Ethoxylated Sorbitan Esters

To obtain emulsifiers that are more water-soluble, the sorbitan ester is reacted with ethylene oxide in varying concentrations. This allows for the manufacturer to make a wide range of emulsifiers that are useful over a range of hydrophobe lipophile balance values. It is no coincidence that the company which pioneered the hydrophobe lipophile balance system, Imperial Chemical Inc., is also one of the premiere manufacturers of these surfactants.

Reaction Sequence: Ethoxylation of Sorbitan Esters

The hydroxyl groups of the sorbitan ester react with ethylene oxide under catalytic conditions, as shown below.



Note: a + b + c =20

It must be clearly understood that the values of a, b and c are not a single number but a series of different numbers that make up an oligomeric distribution. If one looks independently at the values of a, b and c, each will range from zero to 20, with the maximum at about seven. It also must be understood that the distribution of the values of a, b and c will be affected by the catalyst system chosen. Refer to the section on alcohol ethoxylates on pages 81-84 for a more in-depth discussion, including the section on "peaking" and the resulting oligomer distribution.

With this broad range of potential variability, the ethoxylated sorbitan esters are some of the most complicated surfactants to analyze and represent a class of materials that can have much variability from supplier to supplier.

The number of moles of ethylene oxide reacted with a sorbitan ester determines the water solubility of the ethoxylate. Consequently, a series of products based on a common sorbitan ester having a wide range of solubilities can be prepared. The following table shows such a series based on SMO-sorbitan mono-oleate.

	Moles		Solubility @ 10% Weight			
Description	EO	Hydrophobe Lipophile Balance	Water	Mineral Oil	Mineral Spirits	Toluene
SMO	0	4.6	Insol	Sol	Sol	Sol
PSMO-5	5	10.0	Disp	Disp	Disp	Sol
PSMO-20	20	15.0	Sol	Disp	Insol	Disp

Disp = dispersible; Insol = insoluble; Sol = Soluble

Description	Moles EO	Hydrophobe Lipophile Balance	Type of Emulsion
SMO	0	4.6	Water in Oil
PSMO-5	5	10.0	Either
PSMO-20	20	15.0	Oil in Water

The sorbitan esters are a class of compounds that can be modified to provide a wide range of emulsifiers useful in the personal care market.

Analysis of Nonionic Surfactants

Instrumental Analysis

All nonionic surfactants should be evaluated by Fourier transform infrared spectroscopy (FTIR). This instrumental technique is highly automated and when coupled with a computer analysis interface can locate small differences in products. These small differences might not be observable to the naked eye, so the use of sophisticated analytical instruments is strongly suggested. These techniques save time and money and are quite sensitive. The nonionic class is made up of materials that have very salient groups, esters, amids, ethers etc. FTIR is a very important analytical technique for this class of compounds.

Wet Analysis

The wet analysis of surfactants in this class is primarily accomplished by looking for the levels of unreacted raw materials. The following analysis is recommended:

- Acid value
- Alkali value
- Hydroxyl value
- Solids
- Saponification value
- Bleaching agents

Information from Dr. Martin Rieger's Surfactant Encyclopedia: Nonionic Surfactants

Substances are categorized as nonionic whenever the hydrophobe carries no charge at the pH at which the amphiphile is normally used in cosmetic products.

Various levels of ethoxylation or propoxylation are common characteristics of many surfactants. Alkoxylated compounds could thus be placed into simple groups of ethers or alcohols. For example, PEG-n acylate could be classified as a (poly)ether to recognize the POE chain; it could also be classified as an alcohol to recognize the terminal OH grouping; finally, it could be classified as an ester to recognize this functional grouping. Instead, such restrictive chemical functionalities are rarely used in the following classification scheme. Nonionic amphiphiles can be chemically subdivided into five major classes and a number of subclasses:

A. Alcohols
B. Alkanolamides
1. Alkanolamine-derived amides
2. Ethoxylated amides
C. Amine oxides
D. Esters
1. Ethoxylated carboxylic acids
2. Ethoxylated glycerides
3. Glycol esters (and derivatives)
4. Monoglycerides
5. Polyglyceryl esters
6. Polyhydric alcohol esters and ethers
7. Sorbitan/sorbitol esters
8. Triesters of phosphoric acid
E. Ethers
1. Ethoxylated alcohols
2. Ethoxylated lanolin
3. Ethoxylated polysiloxanes
4. Propoxylated POE ethers
5. Alkylpolyglycosides

A. Alcohols

Chemical properties

Surfactants of the alcohol class are the hydroxyl derivatives of long-chain alkane hydrocarbons. These alcohols exhibit the classic surface and interfacial alignment behavior of surfactants, but their essential water insolubility prompts many investigators to consider them primarily as co-emulsifiers in cosmetic products. They are included in this encyclopedia in light of their wide use as surfactants in many cosmetic products.

Only primary alcohols having carbon chains ranging from about 8 to 18 exhibit useful surfactant properties. The presence of a second hydroxyl group, such as in lanolin alcohols, enhances the alcohol's cosmetic utility.

Originally, most surfactant alcohols were obtained by hydrogenation of the corresponding natural fatty acids and, therefore, contained an even number of carbon atoms. In recent years, alcohols have been prepared by various synthetic processes. The Ziegler process yields even-numbered straight-chain alcohols. The oxo process yields even- and odd-numbered alcohols that may exhibit some branching and presence of secondary alcohols. The properties of these alcohols differ, and their further use in the manufacture of surfactant raw materials makes this distinction significant.

A third type of synthetic primary alcohols is a large group of Guerbet alcohols that exhibit alkyl branching. These substances are rarely used as surfactants in cosmetics.

Most commercially available alcohols are mixtures of homologues. The alcohols are chemically inert and do not undergo reactions during the preparation of cosmetic products.

Physical properties

The alkanols comprising this class are generally waxy solids or liquids, depending on their purity. They tend to crystallize in finished emulsions unless the products are carefully formulated.

Generic alcohols
$R–CH_2–OH$
Alkanol
Selected members
Cetearyl alcohol (CIR) Hydrogenated tallow alcohol Lanolin alcohols (CIR)IV.B. Alkanolamides

Uses

As noted already, alcohols perform their surfactant function primarily in the presence of a second surfactant, for example, in emulsifying waxes. Depending on the concentration employed, they can be emulsion stabilizers, opacifiers, viscosity in-creasing agents and foam boosters.

Stability

Alcohols are chemically stable in cosmetic products.

Safety

Alcohols of the surfactant type are regarded as safe for use in cosmetics. Members of this group have been reviewed by the CIR expert panel.

B. Alkanolamides

Alkanolamides are a diverse class of compounds, all of which contain at least one alkoxyl or one POE grouping. The former group comprises alkanolamine derivatives of alkanoic acids that — in pure form — are water-insoluble. The water solubility of the latter group, the ethoxylated amides, depends on the size and number of POE substituents.

In light of their diversity, the alkanolamides are divided into two major groups, alkanolamine-derived and ethoxylated amides.

B.1. Alkanolamine-derived amides

Chemical properties

This important group of nonionic surfactants is derived from the reaction of an alkanolamine (such as, monoethanolamine) with an alkanoic acid or a derivative (such as, a methyl alkanoate). The nature of the product depends on the alkanolamine used, the alkanoic acid, the ratio of the two reactants, and the reaction conditions.

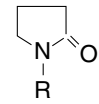
The reaction of monoethanolamine with lauric acid in a 1:1 molar ratio at about 150°C produces a so-called "superamide," in this case primarily N-lauroylmonoethanolamide. This essentially water-insoluble material is accompanied by some impurities, such as the ester RCO-$OCH_2CH_2NH_2$ and the ester amide RCO-OCH_2CH_2NH-COR. The comparable reaction with diethanolamine may produce yet another impurity, the diester amide (RCO-OCH_2CH_2)2N-COR.

A similar type of reaction occurs when two moles of alkanolamine are reacted with one mole of acid. The resulting Kritchevsky condensates contain the same types of compounds as the 1:1 condensates. In addition, they also may contain some alkanolamine soaps, a number of derivatives of morpholine and of piperazine, and free alkanolamine. These mixtures are essentially water-soluble. The presence of the soap as an impurity does not warrant the inclusion of these substances among the anionics.

The current INCI nomenclature does not differentiate these amides on the basis of their total composition or method of manufacture. Instead, these substances are identified by their predominant readily identifiable chemical constituent, the amide.

Generic alkanolamine-derived amides

Acylamide DEA



N-Alkyl pyrrolidone

Selected members

Palmamide MEA
Peanutamide MIPA

Presumably, purer alkanolamine derivatives could be prepared by reacting a simple amide with controlled amounts of ethylene oxide. Lauramide might then yield a blend of lauramide MEA, lauramide DEA, and possibly some PEG-n lauramide.

Alkylation of the cyclic amide pyrrolidone yields a fairly novel class of surfactants. They are formed from the reaction of butyrolactone and an alkylamine (C8 to about C14) to yield a hydroxybutyramide that is finally cyclized by heating.

Physical properties

Alkanolamine-derived amides are waxy or soft solids, depending on the starting materials. Their color varies widely.

Uses

In cosmetics, most of these alkanolamine derivatives are used as foam boosters and viscosity-increasing agents, especially in shampoos. The 1:1 condensates are not useful as primary emulsifiers. The Kritchevsky condensates occasionally are used as emulsifiers or hair conditioners.

The alkylpyrrolidones help to depress surface tension in the presence of others surfactants and increase wetting. They also tend to increase the viscosity of typical anionics, such as the alkyl sulfates, used in shampoos.

Stability

These amides and their ester impurities are subject to hydrolysis at extreme pH conditions. In normal cosmetic use, these substances are quite stable, although they tend to discolor on exposure to air and light.

Safety

These raw materials do not cause adverse reactions under normal use conditions. Some of the members of this group have been reviewed by the CIR expert review panel.

Alkanolamine derivatives containing free diethanol-amine are reported to form a carcinogenic nitroso compound by an unknown mechanism.

B.2. Ethoxylated Amides

Chemical properties

Ethoxylated amides are produced by reacting an alkyl amide or an alkanolamine-derived amide with ethylene oxide. The reaction is generally believed to result in the replacement of only one hydrogen atom on the nitrogen, although replacement of both hydrogens is a distinct possibility. Most of the ethoxylated amides, especially those containing large amounts of POE, are water-soluble or at least water-dispersible. Like most amides, they exhibit better stability in moderately acidic media than in alkaline media.

Physical properties

The ethoxylated amides are waxy solids. They do not foam well.

Uses

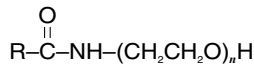
The relatively good stability of these substances in acid systems makes them useful emulsifiers at low pH. They are used sometimes in antiperspirants and acidic permanent wave neutralizers. These amides can be used as lime soap dispersants.

Stability

Ethoxylated amides possess adequate stability for use in cosmetic products.

Safety

Ethoxylated amides appear to be safe as used in cosmetics.

Generic ethoxylated amides

PEG-n acylamide
Selected member
PEG-50 tallow amide

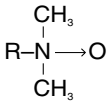
C. Amine Oxides

Chemical properties

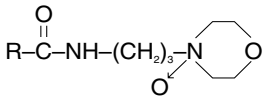
Amine oxides are a fairly large class of synthetic surfactants prepared by the hydrogen peroxide oxidation of tertiary aliphatic amines. The amine may be linear or heterocyclic. Amine oxides are nonionic surfactants. It has been claimed that they can accept protons at low pH ranges, which would make them perform similarly to N-alkylamines.

Commercial amine oxides are contaminated with significant amounts of unoxidized tertiary amines, and that may account for some of the cationic behavior of commercial products at low pH. An alternate explanation depending on the formation of a hydroxylammonium ion (R^3NOH+) has been offered.

Generic amine oxides



Alkylamine oxide



Acylamidopropyl morpholine oxide

Selected members

Cocamidopropylamine oxide
Lauramine oxideV.D. Esters

Amine oxides are compatible with all classes of surfactants and are water-soluble. They are effective detergents.

Physical properties

Amine oxides are available commercially as 30% to 50% aqueous solutions or dispersions.

Uses

Amine oxides are used as antistatics and hair-conditioning agents and are useful in hair-coloring products. They are effective foam boosters in shampoos and behave as lime soap dispersants. Their ability to increase and stabilize foam in the presence of typical anionic detergents is reportedly better than that of the alkanolamides. It also has been asserted that amine oxides help reduce the skin-irritant characteristics generally attributed to anionic surfactants.

Stability

Amine oxides have acceptable stability in cosmetic preparations.

Safety

Amine oxides evidently are well tolerated in cosmetics as long as free hydrogen peroxide or unneutralized amines are absent.

D. Esters

A wide variety of esters has found use as cosmetic surfactants. Most are derivatives of alkanoic acids formed by reaction with ethylene oxide, glycerin, sorbitan, or other alcohols. Like all esters, they are subject to hydrolysis by acids and bases. Thus, their use generally is restricted to pH ranges from about 5 to about 9. An

additional level of instability is introduced whenever unsaturated acids form part of the molecule because oxidative attack may affect the odor or color of a product.

On a strictly chemical basis, the ester class of surfactants may be subdivided into eight groups:

1. Ethoxylated carboxylic acids
2. Ethoxylated glycerides
3. Glycol esters (and derivatives)
4. Monoglycerides
5. Polyglyceryl esters
6. Polyhydric alcohol esters and ethers
7. Sorbitan/sorbitol esters
8. Triesters of phosphoric acid

D.1. Ethoxylated Carboxylic Acids

Chemical properties

Ethoxylated carboxylic acids, commonly called polyethyleneglycol esters, form a large group of important cosmetic surfactants. As a rule, they are prepared by the reaction of a hydrophobic alkanoic acid with ethylene oxide. This leads to the formation of POE monoesters. These compounds are multifunctional and may be viewed as alcohols, ethers or esters. Alternately, these monoesters can be prepared by esterification of acids with preformed polyoxyethylene. This reaction generally leads to the formation of some of the diester. The diesters are prepared normally by condensing two moles of the acid with one mole of POE.

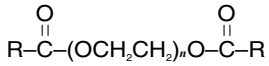
As a generalization, the esters containing fewer than about 6 to 8 ethylene oxide units are not water-soluble but only water-dispersible. When the POE chain is lengthened beyond about 8 ethylene oxide units, the esters become water-soluble. Obviously, longer POE chains are required to provide water-soluble diesters.

The self-emulsifying forms of the short-chain POE monoesters are blends with a water-soluble surfactant, such as a soap.

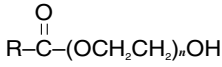
Physical properties

The esters making up this group may be mobile liquids or fairly hard solids, depending on their chemical structures.

Generic ethoxylated carboxylic acids



PEG-n diacylate



PEG-n acylate

Selected members

PEG-8 dilaurate
PEG-8 laurate

Uses

The HLB of the ethoxylated carboxylic acids covers a wide range, and most of these substances are useful emulsifiers. Others can be employed as solubilizers. The most commonly used members have POE chains ranging from about 8 to 12. The tendency of these substances to impart viscosity to lotions and cremes increases with the chain length of the alkanoic acid and decreases with the length of the POE chain.

Stability

See the general comments concerning esters.

Safety

The majority of the members of this group have a long history of safe use in cosmetics. The safety of a number of ethoxylated carboxylic acids has been reviewed by the CIR expert panel.

D.2. Ethoxylated Glycerides

Chemical properties

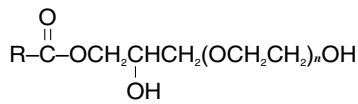
The ethoxylated glycerides comprise three chemically diverse groups of substances, all of which are derived from various acyl glycerides.

One group of these substances is obtained by ethoxylation of a monoglyceride. Thus, PEG-20 glyceryl oleate, for example, is obtained by the ethoxylation of glyceryl (mono) oleate. The latter contains two OH groups, each of which may react with ethylene oxide until the total level of POE equals 20.

A second group is derived from the OH-group containing glycerides, which includes glyceryl ricinoleate, castor oil and trihydroxy stearin. The ethylene oxide addition then can occur on any available hydroxyl grouping. In addition, some reactions may occur that resemble those postulated for the third type.

The third type of ethoxylated glyceride results when a natural triglyceride is allowed to react with ethylene oxide. The nature of this reaction is not clear. One may assume that the reaction system is not anhydrous and that some reaction is initiated by the presence of trace amounts of water to generate some ethylene

Generic ethoxylated glycerides



PEG-n glyceryl acylate

Selected members

PEG-4 castor oil
PEG-120 glyceryl stearate
Triolein PEG-6 esters

glycol or polyoxyethylene. In the presence of the usual ethoxylation catalyst, these alcohols undergo some transesterification reactions that can result in the formation of a complex mixture of end products.

The water-solubility and HLB characteristics of the substances in these three subgroups depend on the starting glyceride and the level of ethoxylation.

Physical properties

The members of this group may be solids or liquids. They do not foam well, and some of them retain the lipid characteristics of the starting glyceride.

Uses

Some ethoxylated glycerides are useful emulsifying agents and can be used as suspending and solubilizing agents. Other ethoxylated glycerides have been used as skin conditioners or emollients.

Stability

See the general comments on esters.

Safety

Ethoxylated glycerides have been used widely in cosmetic products and are considered safe.

D.3. Glycol Esters (and derivatives)

Chemical properties

Surfactants of the glycol ester group are monoesters of either ethylene or propylene glycol. The diesters are extremely hydrophobic and not useful as surfactants. Because the simple glycol esters possess one unesterified hydroxyl group, they can be ethoxylated to increase their hydrophilic characteristics.

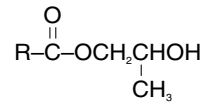
The self-emulsifying grades are formed by adding some soap or other hydrophilic surfactant to the standard grades of glycol esters.

Physical properties

Most of the glycol esters are waxy solids.

Generic structures

Glycol acylate



Propylene glycol acylate

Selected members

Glycol stearate SE (CIR)
Propylene glycol ricinoleate

Uses

Glycol esters as a group are quite hydrophobic. Their low HLB (about 3) makes them useful as w/o emulsifiers. They have a tendency to thicken and opacify all types of formulations. They must be used in combination with other, more effective emulsifiers.

By contrast, the self-emulsifying grades can be used as the primary (or even the only) emulsifier in creams and lotions.

Stability

The relative water-insolubility of the glycol esters makes them somewhat more stable against hydrolysis than related, more hydrophilic esters. Use at extreme pH conditions should be avoided.

Safety

Glycol esters have been used safely in cosmetic products for many years. Some members of this group have been reviewed by the CIR expert panel.

D.4. Monoglycerides

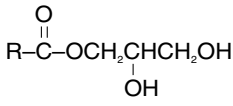
Chemical properties

The surface-active agents belonging to the group of monoglycerides are used widely in cosmetic products. Monoglycerides may be prepared by chemical treatment (transesterification) of a triglyceride with glycerin. They also can be prepared by more direct synthetic methods, such as the treatment of a methyl alkanoate (or similar ester) with glycerin.

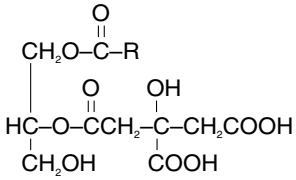
The commercially available monoglycerides are mixtures of a- and b-monoglycerides and generally contain some 1,2- and 1,3-diglyceride.

During storage of the raw material (anhydrous) and of finished products, b-to-a conversion may take place as well as other equilibration reactions leading to the formation of diglycerides from monoglycerides.

Generic monoglycerides



Glyceryl acylate



Glyceryl acylate citrate

Selected members

Glyceryl myristate
Glyceryl palmitate lactate

The monoester content of the commonly distributed monoglycerides is about 40% to 50%, while the diester content is generally in excess of 50%. The efficacy of monoglycerides as emulsifiers increases with their monoester content. Grades containing 90% monoester are more powerful w/o emulsifiers than the standard grades.

Self-emulsifying grades of monoglycerides may contain soap, ethoxylated carboxylic acids, or quaternaries to make them effective primary emulsifiers. Both the self-emulsifying and the regular grades of monoglycerides are insoluble in water.

The unesterified OH groups on the glycerin portion of the monoglyceride molecules can be reacted further with other low-molecular-weight carboxylic acids, such as citric or lactic acid. The resulting substances exhibit surfactant properties different from those of the starting monoglyceride and are used widely as food emulsifiers.

Physical properties

Glyceryl esters may be liquids or waxy or hard solids. They have been shown to lower the interfacial tension between water and various lipids at elevated temperatures. Their efficacy as o/w or w/o emulsifiers is only partially related to their effect on interfacial or surface tension. It is known that monoglycerides orient themselves on the surface of the dispersed phase of emulsions to provide viscoelastic surface films or to form liquid crystals.

Uses

The monoglycerides are commonly used as emulsifiers in combination with other, more hydrophilic surfactants in all types of products. They can be formulated into anionic and cationic systems. Glyceryl stearate is probably one of the most widely used cosmetic raw materials. As a group, monoglycerides increase the viscosity and the opacity of finished products. The selection of both the primary emulsifier used and the monoglyceride must take into consideration the nature of other ingredients of the product and pH.

Stability

The monoglycerides are esters and cannot be used in products at extreme pH ranges. Their stability is adequate for use in antiperspirants (about pH 4 to 5) with a nonionic or cationic surfactant, or in peroxide hair bleaches (about pH 9 to 10) with a nonionic or anionic emulsifier.

Safety

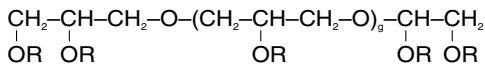
Monoglycerides have been used safely in cosmetics, food and drugs for many years. Some monoglycerides have been reviewed by the CIR expert panel. Many of them are GRAS food additives.

D.5. Polyglyceryl Esters

Chemical properties

Polyglyceryl esters comprise a group of alkanoic acid esters of polyglycerol. Polyglycerol can be prepared by the alkaline polymerization (dehydration) of glycerin. In another approach, the hydrophile of the polyglyceryl esters is derived

Generic polyglyceryl esters



Polyglyceryl-*n* acylate or
Polyglyceryl-*n* alkyl ether
(where g+2 equals n and where R may be Acyl, H, or Alkyl)

Selected members

Polyglyceryl-6 distearate
Polyglyceryl-4 oleyl ether

from glycidol. This can be polymerized and then acylated with food-grade or other fatty acids. In a third method, the acid can be reacted with glycidol; the resulting ester can be further reacted with glycidol.

The commonly provided structure of polyglycerol as a linear polyether, as shown in the generic structure, is a gross oversimplification. There is no justification for assuming that only the a- and g-hydroxyl groups of glycerin can react to form ether linkages. Reaction of the b-hydroxy group leads to branching and potential cross-linking.

In addition, dehydration reactions can lead to cyclization to substituted dioxanes and macrocyclic compounds. Regardless of the synthetic route, these substances are exceedingly complex mixtures since the hydrophile may contain various ethers.

The location of the acyl substituents is essentially unknown, and polyglyceryl esters are best classified as complex mixtures of compounds.

The water-solubility or dispersibility of these substances varies with their hydrophilicity, which depends on the degree of substitution and the ratio of alkanoic acid to glyceryl polymer.

The rather unusual group of polyglyceryl ethers is included in this group as a matter of convenience.

Physical properties

The reactions leading to the formation of polyglyceryl esters are quite harsh, and the end products are deeply colored, viscous and tacky liquids.

Uses

Polyglyceryl esters are useful o/w and w/o emulsifiers. The more lipophilic members of this group (such as polyglyceryl-10 decaoleate) are reported to produce stable w/o emulsions.

Stability

The general comments on the stability of esters are applicable to this group of substances. The ether derivatives of polyglycerol can be expected to exhibit good stability in cosmetic products.

Safety

Polyglyceryl esters have been used with no reported adverse effects in cosmetics. Some of them are approved food additives.

D.6. Polyhydric Alcohol Esters and Ethers

Chemical properties

Polyhydric alcohol esters and ethers form a small group of cosmetic surfactants, most of which are acylated carbohydrates.

The acylation of sucrose yields a range of mono-, di-, and tri-esters, depending on the ratio of the starting materials.

A second type of ester is derived from methyl glucose, or more specifically, from the 2:1 blend of the a-b acetal. The hydrophilicity of these substances then is controlled further by reaction with ethylene oxide.

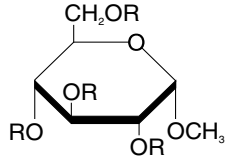
Physical properties

The commercially available polyhydric alcohol esters are viscous fluids.

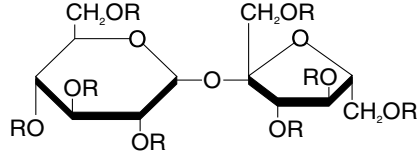
Uses

Polyhydric alcohol esters are used as emulsifiers and have been claimed to provide some skin conditioning. The alkyl ethers of glucose or glucose oligomers are described later (Alkylglucosides).

Generic polyhydric alcohol esters and ethers



PEG-n methyl glucose acylate
(where R may be Acyl, POE, or H)



Sucrose acylate
(where R may be Acyl or H)

Selected members

Methyl gluceth-20 sesquistearate
Sucrose distearate

Stability

The ester grouping in these substances is subject to hydrolysis at extreme pH ranges. These substances also may contain some acetal linkages, which appear to be stable under the conditions of use in cosmetics.

Safety

The substances in this group are generally believed to be safe in cosmetic products.

D.7. Sorbitan/Sorbitol Esters

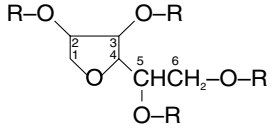
Chemical properties

The sorbitan/sorbitol esters form an important group of cosmetic, pharmaceutical and edible surfactants. They are obtained by acylation of sorbitan or sorbitol and may be further modified by ethoxylation. The nomenclature and identification of the members of this group are incomplete, and esters of sorbitol are sometimes identified as esters of sorbitan and vice versa.

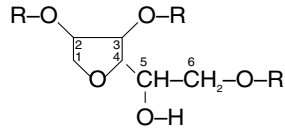
Sugar alcohols form internal ethers by dehydration under the influence of heat or acidic reagents. In the case of sorbitol, the initial product is identified as 1,4-sorbitan, which then is dehydrated further to yield isosorbide, a bicyclic ether. The formation of 1,5-sorbitan and of 2,5-sorbitan also has been reported.

The surfactants of interest are generally identified chemically as esters of 1,4-sorbitan in which the terminal hydroxymethyl group is esterified (sorbitan acylate). Such monoesters can be obtained by reacting preformed sorbitan with an alkanoic acid (derivative). Such esters also are formed during the reaction of sorbitol with an alkanoic acid using various esterification procedures. The preparation of a true sorbitol acylate is possible only under carefully controlled reaction conditions.

Generic sorbitan/sorbitol esters



POE-sorbitan acylate
(where R may be Acyl, POE, $(CH_2CH_2O)_nC$–R, or H)



1,4-Sorbitan acylate
(Where R may be Acyl or H)

Selected members

Polysorbate-60 (CIR)
Sorbitan sequiisostearate

Isosorbide mono- and di-acylates can be formed directly from sorbitol and the alkanoic acid in the presence of sulfuric acid at about 70°C and from sorbitol and a triglyceride (by transesterification) at about 270°C.

None of the reactions outlined here goes to completion, and the sorbitol/sorbitan esters — even in the absence of subsequent ethoxylation — are complex mixtures in which composition varies from process to process.

Sorbitan acylates contain free OH groups that can react with ethylene oxide. During this reaction, acyl groups attached to the sorbitan moiety generally migrate (via transesterification) to the ends of any POE chains. In the case of monoacylates, attachment at position 6 is generally accepted (see structure of POE sorbitan acylate). Further ethoxylation and/or acylation can lead to still more highly substituted sorbitan derivatives, such as PEG-60 sorbitan tetraoleate.

Some of the esters in this group are extremely hydrophilic and water-soluble due to the presence of polyoxyethylene chains. Others are so hydrophobic that they cannot be dispersed in water.

Physical properties

The sorbitan/sorbitol esters are beige to tan liquids, or waxy solids. They lower interfacial tension significantly but do not yield stable foams.

Uses

These esters, singly or in combination, are widely used emulsifying agents. Depending on the HLB selected, they are capable of forming w/o or o/w emulsions. The more highly ethoxylated derivatives also find use as solubilizers.

Stability

This group of compounds has been used in cosmetics, drugs and foods under a variety of conditions, and their stability in these types of products is well documented.

Safety

The wide use of these sorbitan/sorbitol esters in diverse consumer product applications attests to their safety. Some of these surfactants have been reviewed by the CIR expert panel.

D.8. Triesters of Phosphoric Acid

Chemical properties

The triesters in this group exhibit surfactant properties only if the esterifying alcohol is hydrophilic. Trialkyl phosphates derived from hydrophobic alcohols are not classified as surfactants. The phosphoric acid esters of ethoxylated alcohols are best prepared from the POE-alcohol and phosphorous oxychloride ($POCl_3$). They exhibit some solubility in lipid materials as well as in water.

Physical properties

The triesters of phosphoric acid are liquids.

Generic triesters of phosphoric acid

$$\left[R{-}(OCH_2CH_2)_nO\right]_3P{=}O$$

Trialkyl phosphate

Selected members

Trideceth-3 phosphate
Trioleth-8 phosphate

Uses

These triesters are quite hydrophobic and are used primarily as o/w and w/o emulsifiers.

Stability

Phosphoric acid esters are subject to hydrolysis, and use in acid media probably should be avoided.

Safety

Only limited information on the safety of these products in cosmetics is available.

E. Ethers

Ethers are distributed widely among cosmetic surfactants. Any POE derivative is, in effect, an ether. In the ethers discussed here, this wide range of ethers is narrowed by limitation to nonionics and by the intent of including only substances that possess no functional grouping other than the terminal OH group of the POE chain. As a matter of convenience, ethoxylated lanolin derivatives are included, even though the source, lanolin, is best described as a blend of hydroxy esters.

The nonionic ethers, therefore, are divided into five groups:

1. Ethoxylated alcohols
2. Ethoxylated lanolin
3. Ethoxylated polysiloxanes
4. Propoxylated POE ethers
5. Alkyl polyglycosides

E.1. Ethoxylated Alcohols

Chemical properties

Ethoxylated alcohols are the ethylene oxide derivatives of alcohols. With very few exceptions, most of the starting alcohols are monofunctional primary alcohols or phenols.

Hydrophobic alcohols are used in the ethoxylation reaction. Other alcohols for

ethoxylation include sterols and three types of phenols, two with single alkyl chains and one with a dual alkyl substituent. Octyl phenol is obtained from the Friedel Crafts reaction of diisobutylene with phenol to yield a monosubstituted derivative. The production of nonylphenol requires alkylation with a blend of nonenes prepared from propylene. Dual alkylation with nonenes yields a dinonylphenol.

The ethoxylation of alkanols or alkylphenols by ethylene oxide is carried out under pressure and heat with alkalies as the catalysts. As a rule, the catalyst is not removed but merely neutralized before the end product is drummed.

The mixture of ethoxylated alcohols from such a reaction contains a broad range of products differing in the POE chain length. Free alcohol or phenol is a common contaminant. The n value represents an average, and no single entity is present in commercial products as the major component. Thus, laureth-8 may contain ethylene oxide oligomers ranging from 0 to about 20. The oligomer in which n is specifically 8 probably represents only a small fraction (10% to 20%) of the total and may not even be the predominant species.

In light of this, the differentiation between commercial grades of similar homologues, such as laureth-7, -8 and -9, is not very significant. The water solubility of these surfactants depends on the degree of ethoxylation.

Physical properties

Ethoxylated alcohols may be mobile liquids or unctuous solids, depending on the starting alcohol and the degree of ethoxylation. The HLB of these substances ranges from as low as about 3 to as high as about 18. These substances are generally considered to foam poorly, although they develop significant foam in standard, in vitro foaming tests.

Uses

The surfactants in this group are emulsifiers for o/w and w/o preparations. It is customary to use blends of these ethers because these combinations yield more

Generic ethoxylated alcohols

$$R(OCH_2CH_2)_nOH$$

Ethoxylated alcohol

$$R\text{–}O\underset{\underset{CH_3}{|}}{C}HCH_2\text{–}(OCH_2CH)_nOH$$

Propylene glycol alkyl POE-*n* ether

Selected members

Ceteareth-10
Nonoxynol-9

stable emulsions. The ethoxylated alcohols are effective detergents, but their poor foaming qualities make them unattractive in cosmetics requiring foam. On the other hand, the more hydrophilic members of this group are commonly used stabilizers in numerous cosmetic applications.

Stability

Ethoxylated alcohols are generally believed to be inert and exhibit good stability in all types of cosmetic products.

Safety

Ethoxylated alcohols have been used safely in cosmetic preparations for many years. The incidence of reported adverse reactions is low. A few members of this group of surfactants have been reviewed by the CIR expert panel.

E.2. Ethoxylated Lanolin

Chemical properties

The hydroxyl groups present in lanolin, its hydrogenation product and its physically separated fractions can be ethoxylated with ethylene oxide. The resulting surfactants are complex mixtures of ethoxylated sterols, lanolin alcohols, lanolin fatty acids and unaltered lanolin. Formation of these mixtures is a result of the presence of water in lanolin and of transesterification during reaction with ethylene oxide. Most members of this group possess levels of ethoxylation that render them water-soluble.

Physical properties

Most of the ethoxylated lanolin derivatives are beige-colored waxy solids.

Uses

Ethoxylated lanolin derivatives are intended to provide the benefits of lanolin in finished cosmetic products without imparting the unctuous characteristics of lanolin. These products can be used as emulsifiers, suspending agents and solubilizers.

Stability

This group of lanolin-derived surfactants is believed to exhibit acceptable stability in cosmetic products.

Generic ethoxylated lanolin
No structural formula can be provided for these complex mixtures.
Selected members
PEG-20 lanolin (CIR) PPG-12-PEG-65 lanolin oil

Safety

The ethoxylated lanolin derivatives meet the safety requirements of raw materials used in the cosmetic industry. Selected members of this group have been reviewed by the CIR expert panel.

E.3. Ethoxylated Polysiloxanes

Chemical properties

Ethoxylated polysiloxanes are ethylene oxide derivatives of polysiloxanes. The synthetic routes leading to these substances are essentially proprietary. The starting products for these surfactants are, as a rule, medium-to-low molecular weight dimethyl polysiloxanes endcapped with a functional silane such as, a silanol, identified by R in one of the accompanying structures. Such a compound then can be further reacted with ethylene oxide or occasionally with propylene oxide to yield the end products. As a group, they are identified as dimethicone copolyols.

INCI nomenclature does not specify the levels of ethoylation and or propoxylation. In order to provide water solubility, ethoxylated polysiloxanes as a rule contain no less than about 75% by weight of POE. The terminal OH group(s) of these compounds can be esterified with various acids to create additional surfactants.

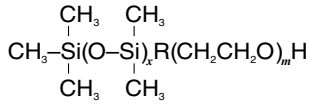
Physical properties

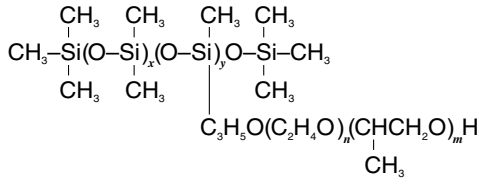
Ethoxylated polysiloxanes are mobile liquids at room temperature and exhibit molecular weights in excess of about 1,200.

Uses

Many members of this group are used as emulsifiers especially for silicones, while others have recently achieved popularity as water-in-oil emulsifiers. If the terminal OH group in the polymer has been further reacted, the resulting material serves in a function that depends on the nature of the added substituent.

Generic ethoxylated polysiloxanes





Selected member

Dimethicone copolyol

Stability

Ethoxylated polysiloxanes are quite inert and exhibit good stability in cosmetic products.

Safety

Cosmetic use of these substances has been found to be acceptable.

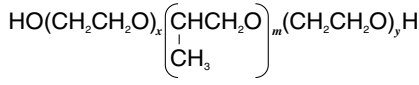
E.4. Propoxylated POE Ethers

Chemical properties

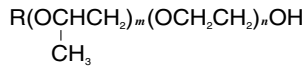
The term propoxylated POE ethers is used here to describe a wide range of block polymer products prepared by slightly different chemical reactions. As a rule, the hydrophobe is an (alkyl) polyoxypropylene (alkyl polypropylene glycol or PPG). The self-condensation of propylene oxide is conducted at high pressure and temperature in the presence of an alkali catalyst. Propylene oxide will not react with itself unless an "initiator" is added. If the initiator is a monohydroxyl derivative (for instance, butanol), a propoxylated butyl ether with one terminal hydroxyl group is formed. This hydrophobe then can be reacted with ethylene oxide to yield an ethoxylated PPG-n alkyl ether, such as PPG-7-buteth-10.

If propylene glycol is used as the initiator, a hydrophobic PPG is formed that possesses two terminal hydroxyl groups. In order to be hydrophobic, the molecular weight of the PPG polymer should be no less than about 1,000. This hydrophobe then is ethoxylated on both hydroxyl groups to yield poloxamers.

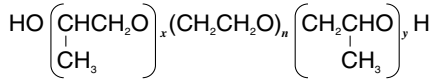
Generic propoxylated POE ethers



Ethoxylated PPG-m ether
(where x generally equals y)



Ethoxylated PPG-*m* alkyl ether



Propoxylated POE-*n* ether
(where x commonly equals y)

Selected members

Meroxapol 314
Poloxamer 122
PPG-5-ceteth-20

For the sake of conserving space, the reverse polymers, which contain a central block of POE and two pendant PPG chains, are included. In order to create the bifunctional POE starting material, ethylene oxide polymerization is initiated with ethylene glycol. Subsequent propoxylation yields the propoxylated POE-n ethers (meroxapols).

The HLB of these ethers can be controlled by the chain length of the various PPG and POE chains.

As ethers, they are chemically inert except as noted in the introduction.

Physical properties

The propoxylated POE ethers are essentially colorless liquids, or soft or hard solids. Some of them foam well, while others tend to gel in the presence of water. They reduce surface and interfacial tension.

Uses

The diverse properties of these ethers and their compatibility with all types of other surfactants account for their use in a variety of applications. In addition, their high molecular weight is believed to be responsible for their general mildness in skin products. Their HLB covers a range from as low as 1 to as high as about 30. They are powerful wetting and dispersing agents and act as emulsifiers and solubilizers. They also can be used as spreading agents and lime soap dispersants.

Stability

Except for their susceptibility to peroxide formation, this group of ethers is considered stable in cosmetic applications.

Safety

These propoxylated POE ethers are considered safe for cosmetic use. Several of them can be used in food stuffs, and some have been used in drug applications on open wounds.

E.5. Alkylpolyglycosides

Chemical properties

The alkylpolyglycosides represent a small but growing group of surfactants prepared by the reaction of hydrophobic alcohols with glucose. Commercially, oxo or fatty alcohols are reacted with glucose to yield a blend of alkylated mono- and oligoglycosides. The average degree of polymerization is about 1.4. The alkylpolyglycosides foam copiously and are compatible with all types of surfactants. Their current popularity is due to their reported mildness and biodegradability.

Physical properties

The alkylpolyglycosides are supplied as viscous aqueous solutions.

Uses

Alkylpolyglycosides are used primarily in shampoos and skin cleansing preparations.

Generic alkylglucosides

$C_nH_{2n+1}O(C_6H_{10}O_5)_xH$

Alkylglucoside
(where x ranges from 1 to about 4)

Selected member

Lauryl glucose

Stability

Chemically, these molecules are acetals and may thus be subject to degradation at low pHs. The presence of glucose as an impurity may make these surfactants subject to the Maillard reaction.

Safety

The available data suggest that alkylpolyglycosides are mild and can lower the irritation potential of other surfactants.

Chapter 6

Silicone Surfactants

Silicone compounds have been known since 1860 but were of little commercial interest until the 1940s. Over the years, they have received growing acceptance in many personal care applications. In many ways, silicone is a unique hydrophobe. It not only is insoluble in water, but it also is insoluble in most fatty materials. This fact has limited the use of silicone in personal care products over the years. If early products contained silicone, it was in the form of emulsions. The white milky appearance of the emulsion was not desired by the consumer, and in some instances the resulting product would split over time.

Surfactant chemistry based on fatty hydrophobes has been well-understood for many years. It has been exploited to give formulators products tailored for specific applications. It is not surprising that silicone, an alternative hydrophobe, also would be exploited to make surfactants. There has been a recent explosion in the availability of chemically modified silicone compounds that provide conditioning, softening, irritation mitigation, barrier properties and emulsification. Many of these desirable effects are not achievable in all kinds of formulations using traditional surfactants or silicone fluids.

Before 1990, dimethicone copolyols were the principal silicone surfactants available to the formulating chemist. Dimethicone copolyols are nonionic compounds analogous to alcohol ethoxylates.

The following table shows the product classes available to formulators in silicone-based products and the more traditional hydrocarbon products. Introduction of functionalities onto the silicone backbone results in multi-functional products with a unique combination of properties.

Comparison of Hydrocarbon and Silicone Derivatives

Traditional Products	Silicone Products
Anionics	
Phosphate Esters	Silicone Phosphate Esters
Sulfates	Silicone Sulfates
Carboxylates	Silicone Carboxylates
Sulfosuccinates	Silicone Sulfosuccinates
Cationics	
Alkyl Quats	Silicone Alkyl Quats
Amido Quats	Silicone Amido Quats
Imidazoline Quats	Silicone Imidazoline Quats
Amphoterics	
Amino Propionates	Silicone Amphoterics
Betaines	Silicone Betaines
Nonionics	
Alcohol Alkoxylates	Dimethicone Copolyol
Alkanolamids	Silicone Alkanolamids
Esters	Silicone Esters
Taurine Derivatives	Silicone Taurine
Isethionates	Silicone Isethionates
Alkyl Glycosides	Silicone Glycosides

Dimethicone Copolyols

Dimethicone copolyols are silicone-based nonionic surfactants. They contain a water-insoluble silicone backbone and water-soluble polyoxyalkylene pendant group. The presence of these two groups makes the compound surface active. A key concept in dealing with silicone surfactants is an understanding that a polysiloxane backbone, while water-insoluble, also is insoluble in most hydrocarbon oils. When fatty-, silicone- and water-soluble groups all are present in the same molecule, unique surfactant properties result.

Dimethicone copolyol compounds are mild conditioners on hair. They, unlike silicone fluids, can be added to water-based formulations to provide conditioning without having a negative effect on foam. Dimethicone copolyol compounds also "de-tackify" many sticky formulations, most importantly polyacrylate-thickened systems. Dimethicone copolyol compounds also can be used to make emulsions of silicone in water and water in silicone. The ability to make the water in silicone emulsions is important in the making of antiperspirants. The dimethicone copolyol compounds used in this application are commonly referred to as *formulation aids*.

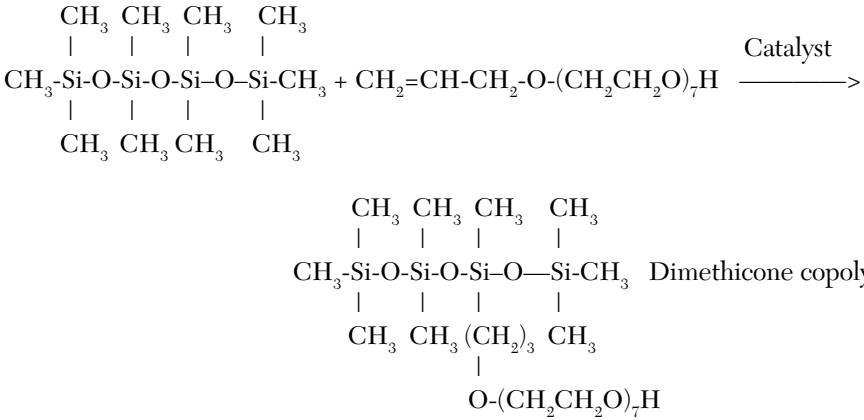
Many different compounds are classified as dimethicone copolyols. They differ in the number of polyoxyalkylene and polyoxypropylene groups present in the molecule, the molecular weight of the polymer and the amount of silicone contained in the polymer.

In addition to being a surfactant *per se*, dimethicone copolyol is a major raw material used to prepare silicone surfactants. Dimethicone copolyol compounds

have a carbanol hydroxyl group that can be substituted for the hydroxyl groups in alcohols to prepare surfactants. The processes are essentially identical to those using fatty alcohols or fatty alcohol ethoxylates. Molecules containing fatty-, silicone- and water-soluble groups have unique surfactant properties as emulsifiers.

Reaction

Dimethicone copolyol surfactants are made by the hydrosilylation of a polymer containing a silanic hydrogen moiety. The reaction is as follows:



The use of allyl alcohol ethoxylates to prepare dimethicone copolyols explains why they have three CH_2 groups between the silicon atom and the polyoxyalkylene group.

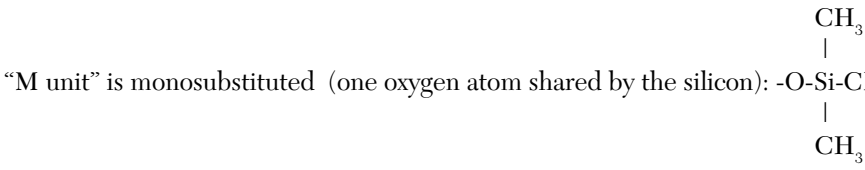
Properties

Dimethicone copolyols have been used per se in many formulations. Their conditioning effects on hair and skin are mild, and in many cases water-based formulations including these materials are clear.

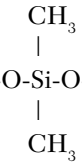
The structure of the dimethicone copolyol has a dramatic effect on the performance in many personal care products. To show the structure function relationship between molecular weight and properties, it is first necessary to review nomenclature for silicone compounds.

Silicone Nomenclature

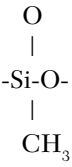
A shorthand based on the kind of groups present in the dimethicone copolyol molecule is used. That shorthand is:



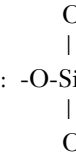
"D unit" is disubstituted (two oxygen atoms shared by the silicon):



"T unit" is trisubstituted (three oxygen atoms shared by the silicon):

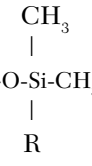


"Q unit" is tetrasubstituted (four oxygen atoms shared by the silicon):

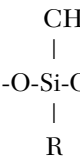


If organofunctional groups other than carbon are introduced, the group is given an asterisk "*", which is added to its designation.

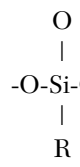
"M* unit" is monosubstituted (two oxygen atoms shared by the silicon):



"D* unit" is disubstituted (two oxygen atoms shared by the silicon) with organofunctionality:

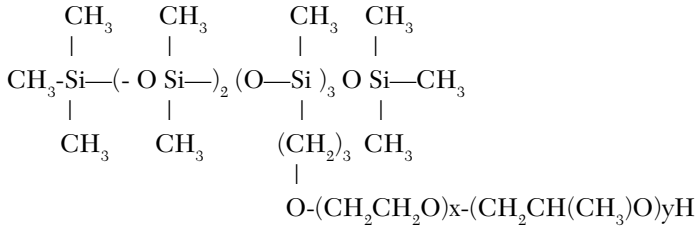


"T* unit" is trisubstituted (three oxygen atoms shared by the silicon) with organofunctionality:



There is no "Q* unit" because there is no possibility of functional groups.

Thus, for example, the structure for MD2D3*M is:



The formulation of products for the personal care industry require products that provide good wetting and spreading on hair and skin and likewise produce low irritation to eyes and skin. Dimethicone copolyol compounds were prepared and studied to understand the effect on molecular weight on wetting and eye irritation. The data used in the study and the results of the study appear in the table and graph below.

Designation	Molecular Weight	E.M.W.[a]
MD*M	607	607
MD*DM	808	612
MD_2*D_2M	1108	619
MD_3*D_5M	1610	630
MD_3*D_7M	2111	642
MD_4*D_8M	2412	648

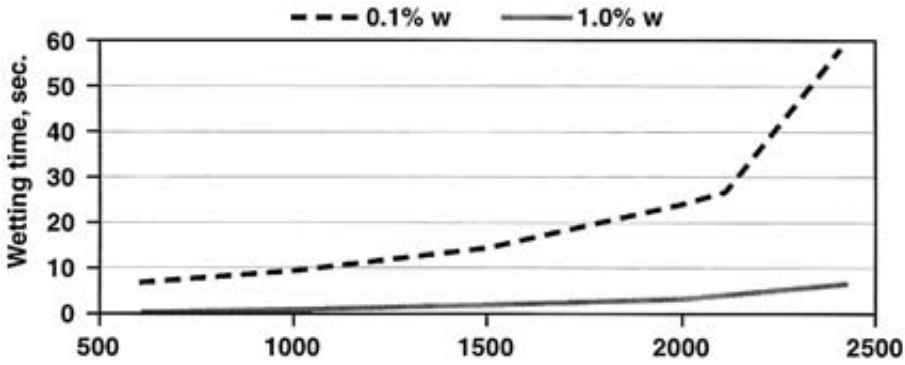
where D* is $(CH_2)_3$-O-$(CH_2CH_2O)_7$-H

a) EMW = Molecular weight divided by number of D* units

Wetting Properties

The study indicated that the molecular weight of the dimethicone copolyol is related to the wetting properties. As the molecular weight of the dimethicone copolyol increases, the wetting time increases, as seen in the graph below.

Draves Wetting of Dimethicone Copolyol as a Function of Molecular Weight

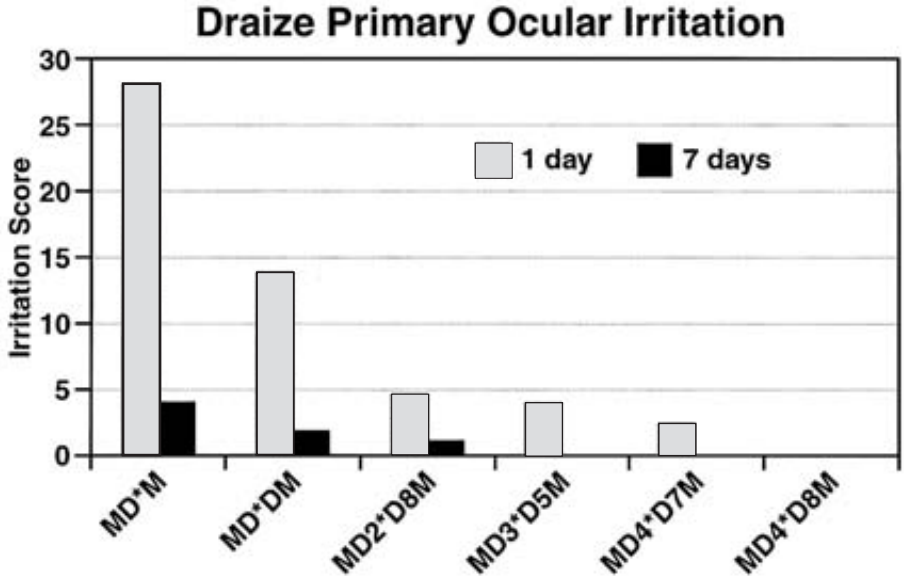


The data shows that there is a strong relationship between molecular weight (and structure) and wetting for dimethicone copolyol. The lower molecular weight materials have faster wetting times. This finding is a trend also observed for other surfactants where shorter or branched structures provide faster wetting. The smaller molecule allows for more efficient packing efficiency and dynamics. The materials with lower molecular weight were extremely effective at the higher concentration of 1.0 percent w. Their wetting speeds were almost instantaneous.

The shape of the curve is also very important. Specifically, the slope of the curve does not change much until the molecular weight of the dimethicone copolyol reaches just over 1,200. The nonlinearity of the graph of wetting time vs. molecular weight of the dimethicone copolyol predicts that molecules having a molecular weight between 600 and about 1,200 should be effective wetting agents.

Eye Irritation

Perhaps one of the mosts interesting properties evaluated in our studys is the effect of molecular weights on eye irritation. Many models have been proposed for the irritation properties of surfactants. We had thought that molecular weight might be one of the factors related to eye irritation because it would affect the diffusion of the material through the cell layers. As illustrated below, we found that the higher the molecular weight, the lower the ocular irritation.



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 results indicate that the irritation potential is related to molecular weight. The data also were quite surprising in that they showed a sharp drop in irritation as the molecular weight increased, specifically until the molecular weight of DMC exceeded 1,108.

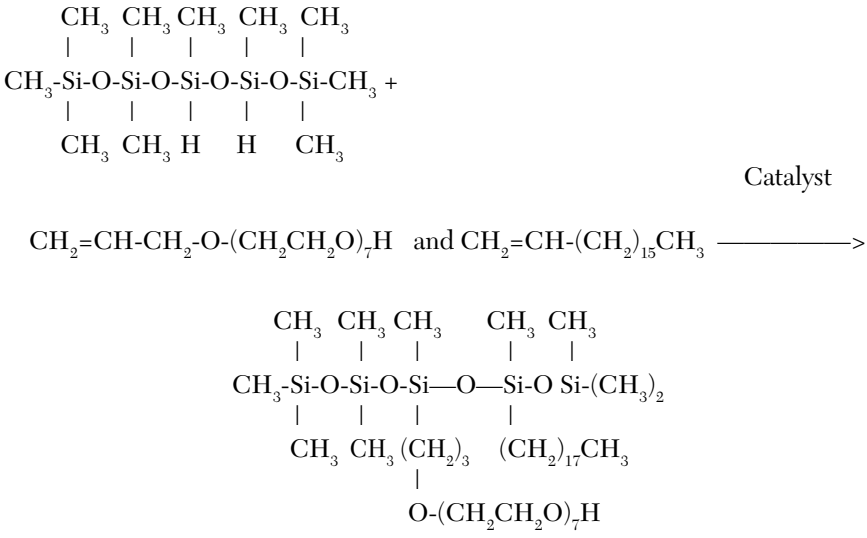
These findings indicate that formulators must select materials that give the optimum balance of wetting and conditioning effects while maintaining the low irritation values required by today's formulations.

Alkyl Dimethicone Copolyols

Alkyl dimethicone copolyols are a series of compounds that have alkyl groups and polyoxyalkylene groups. They have been widely promoted in the personal care market.

Reaction

Alkyl dimethicone copolyols have the following reaction sequence:



Alkyl dimethicone copolyol

Properties

Alkyl dimethicone copolyols contain water-soluble groups, fatty-soluble groups and silicone-soluble groups. These materials are used as emulsifiers in the preparation of water-in-silicone and silicone-in-water emulsions. These products provide advantages over traditional hydrocarbon chemistries because they can be used in the preparation of emulsions without heat. These silicone polymers can be used to prepare products that contain little wax, contain a large concentration of water and have a light spreadable feel on the skin.

Silicone Quaternium Compounds

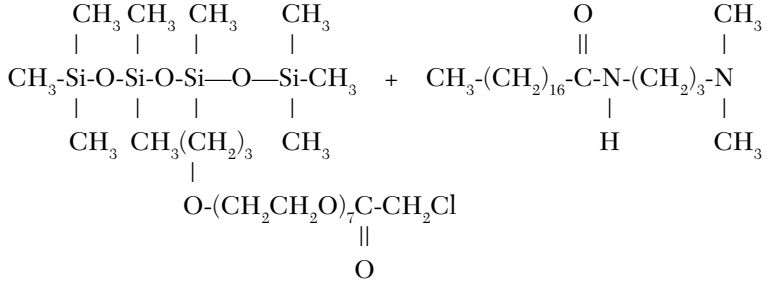
Fatty quaternary compounds, discussed in Chapter 4, are well-known conditioners. However, several undesirable attributes of fatty quats limit their usefulness in formulations. Cationics are considered somewhat toxic by ingestion and are eye irritants, but they tend not to be topical irritants. Fatty alkylamidopropyl dimethylammonium compounds commonly are found in conditioning treatments for hair, but they are difficult to formulate in clear shampoo systems.

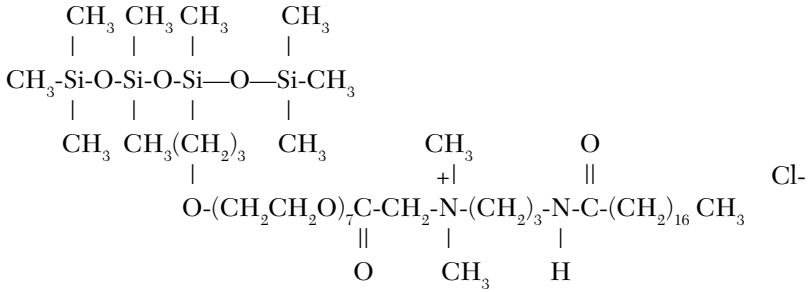
Alkylamido silicone quaternary compounds based on dimethicone copolyol chemistry have been developed. These materials are compatible with anionic systems over a limited range of concentrations, provide outstanding wet-comb properties, confer antistatic properties, provide nongreasy softening properties to hair, fiber and skin, and are not based on glycidyl epoxide or alkanolamine chemistries.

Alkylamido silicone quaternium compounds can be prepared having varying amounts of polyoxyalkylene oxide in the polymer. The ability to regulate the kind of alkylene oxide and the amount present in the silicone polymer results in a series of products varying in water/oil/silicone solubility. The Cosmetics, Toiletries and Fragrances Association (CTFA) has classified these materials as Silicone Quaternium 1-12.

Reaction

Silicone quaternary compounds can be made in accordance with the following reaction sequence:





Properties

Silicone quaternium compounds such as those illustrated in the previous reaction sequence have been designated by the CTFA as Silicone Quaternium 1-10. They can be easily formulated into a variety of personal care products without emulsification, the use of elaborate thickening systems or the need for homogenization.

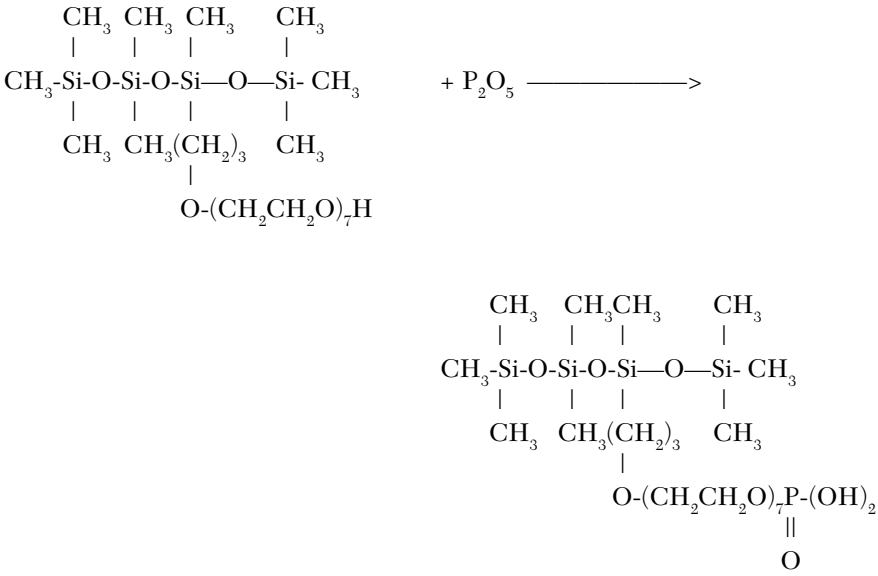
These compounds have outstanding compatibility with nonionic and other cationic materials and, more surprisingly, have significant compatibility with anionic surfactants. For example, 3 percent Silicone Quaternium 8 can be incorporated into 15 percent sodium lauryl sulfate with mild agitation and no heat. This results in a clear, simple base for the formulation of "two in-one" shampoos that are nongreasy and do not build up. Additionally, the silicone quaternium molecule gives antistatic properties, improved wet-comb properties and gloss. Any attempt to add silicone oil into this kind of formula results in a hazy, low-foaming product that separates quite rapidly into two phases.

Silicone Phosphate Esters

A series of silicone surface active agents containing an ionizable phosphate group has been developed. These silicone-based phosphate esters and their derivatives are the topic of numerous patents. Their properties have been compared and contrasted with those of traditional fatty phosphate esters.

Reaction

Silicone phosphate esters have the following reaction sequence:



Dimethicone Copolyol Phosphate

Properties

Silicone-based phosphate esters are substantive to hair, skin and fiber and provide antistatic properties. Because these compounds contain a pendant-ionizable phosphate group, they provide antistatic and lubrication properties to the hair or fiber.

Silicone phosphate esters are acidic and can be neutralized to any desired pH with alkaline materials. The pH of the final formulation affects the solubility of the phosphate ester and has a profound effect on other surfactant properties, such as wetting, foaming and emulsification. The partially neutralized phosphate ester has solubility characteristics intermediate between those of the free acid and the completely neutralized phosphate ester.

As emulsifiers, silicone-based phosphate esters are efficient, producing oil-in-water emulsions. They are useful as emulsifiers for personal care products, such as moisturizing creams and lotions. They are particularly effective in producing creams and lotions containing sunscreens (both organic and inorganic), pigments, skin protectants and medical ointments. Their emulsification properties allow for the use of these materials in "one-step" shampoos and other applications, including emulsion polymerization processes.

As water-soluble emollients, silicone phosphate esters can be used in aqueous systems. For example, they can be added to carbomer gels for emolliency without diminishing the clarity of the gel. Phosphating dimethicone copolyol renders the molecule more water-soluble, necessitating fewer moles of ethylene oxide for the same degree of water solubility. Increased levels of ethoxylation on dimethicone copolyol result in not only water solubility but also an undesirable sticky skin feel. Dimethicone copolyol with a lower level of ethoxylation can be subsequently phosphated to produce a water-soluble silicone phosphate with a greatly improved skin feel.

As foaming agents, silicone-based phosphate esters produce higher levels of copious foam than are produced by dimethicone copolyols. The sodium and potassium salts of the phosphate esters tend to be slightly better foaming agents than the phosphate esters in their free acid or amine salt forms. Salts formed by the neutralization of dimethicone copolyol phosphate and myristamidopropyldimethyl amine are excellent foam boosters and conditioners in shampoo systems. Salts formed by the neutralization of dimethicone copolyol phosphate and linoleylamidopropyldimethyl amine are excellent emulsifiers for dimethicone in shampoo systems.

Silicone-based phosphate esters show good detergency, surface tension reduction, wetting, emulsification, dispersing properties and solubilization. Their detergent properties are generally considered to be equal to those of nonionic surfactants. However, the presence of the silicone moiety in the molecule results in improved mildness, substantivity and conditioning properties over conventional fatty-based phosphate esters. These properties make the products excellent candidates for incorporation into shampoos and other detergent systems for personal care products.

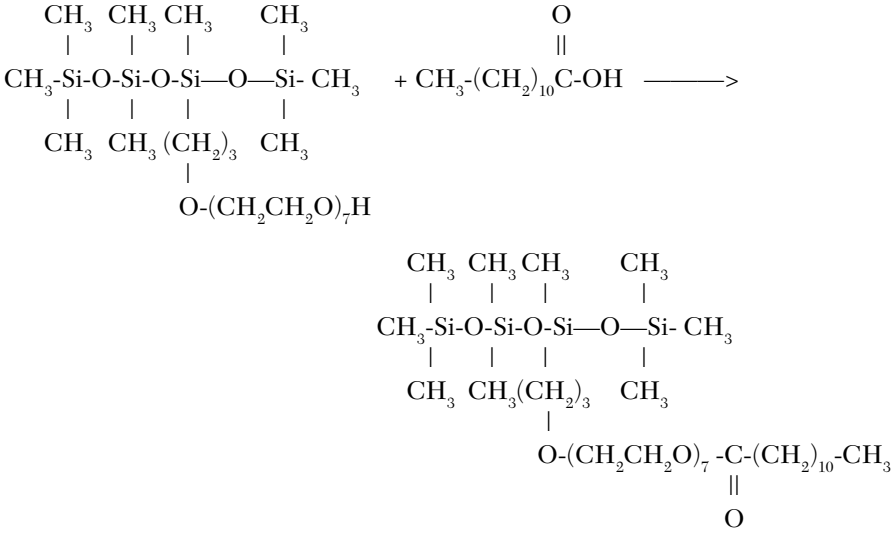
Silicone-based phosphate esters function as hair conditioners and have been found to have outstanding conditioning effects when applied to permanent-waved hair.

Silicone Esters

Silicone esters prepared by the esterification reaction of a dimethicone copolyol with a fatty acid have been introduced. The dimethicone copolyol group initially contains a silicone group and a polyoxyethylene group. Incorporation of the fatty group by the esterification reaction results in a product that has a water-soluble, silicone-soluble and fatty-soluble group present in the same molecule. The graphic on page 106 lists four typical products created with silicone esters.

Reaction

The reaction sequence for silicone esters is as follows:



Properties

Dimethicone copolyol esters have the following seven general properties:

1. Compounds that have fewer than 12 carbon atoms in the fatty group are liquids at room temperature.
2. Saturated linear compounds that have more than 14 carbon atoms in the fatty group are solids at room temperature.
3. Compounds in which the fatty group is unsaturated or branched are liquids at room temperature.
4. The most hydrophobic products have more than 16 carbon atoms in their fatty groups.
5. The greatest spreadability and lubrication is obtained from the liquid products where the fatty groups are isostearic.
6. The selection of the fatty group is extremely important in determining the solubility of the compound in many organic solvents.
7. All products are soluble in lower molecular weight alcohols such as isopropanol.

Typical Products

Product	Description
Silwax S (Stearic Acid)	A water-insoluble, highly lubricious silicone wax. The physical form is a white paste.
Silwax C (Hydroxy Stearic Acid)	A water-insoluble, highly lubricious silicone wax.
Silwax WD-IS (Isostearic Acid)	Forms a microemulsion in water. Conditions, softens and provides wet-comb properties in hair care products. Used as a fiber lubricant for microfibers.
Silwax WS-L (Lauric Acid)	A water-soluble product soluble in many polar solvents. It is soluble in water and propylene glycol and, consequently, is used in clear deodorant sticks.

Solubility Properties

The incorporation of silicone-, fatty- and water-soluble portions into a molecule results in unique solubilities and emulsification properties. To illustrate the range of solubilities achievable using this technology, products were tested at 5 percent solids in the solvents shown below.

	5% PRODUCT			
Solvent	**S**	**C**	**WD-IS**	**WS-L**
Water	Ins	Ins	Disp	Sol
Isopropanol	Sol	Sol	Sol	Sol
Mineral Spirits	Sol	Ins	Ins	Ins
Silicone Fluid (350 Visc.)	Disp	Disp	Ins	Ins
Polyethylene Glycol (PEG 400)	Ins	Ins	Disp	Disp
Glycerol Trioleate	Ins	Ins	Sol	Sol
Oleic Acid	Disp	Ins	Sol	Sol
Phoenix TGC Trioctyldodecyl Citrate	Disp	Ins	Sol	Sol
Mineral Oil	Disp	Ins	Ins	Ins

Ins = Insoluble Disp = Dispersible Sol = Soluble

Triglyceride-Derived Products

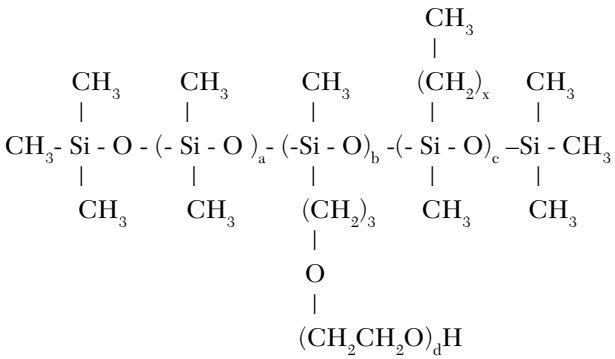
In addition to products that are prepared using fatty acids, distinct classes of products made from natural triglycerides also exist. These materials provide conditioning, gloss and softening properties when applied to hair or skin. Some representative products by CTFA designation are:

- Dimethicone copolyol avacodoate
- Dimethicone copolyol almondate
- Dimethicone copolyol olivate
- Dimethicone copolyol cocobutterate
- Dimethicone copolyol meadowfoamate
- Dimethicone copolyol cocoate

Products derived from many other triglycerides also are available. Silicone derivatives from these triglycerides function in formulations in the same manner as the silicone products made from the analogous fatty acids and are used predominantly for their name on the label. For example, dimethicone copolyol cocobutterate might be a good additive for after-sun products. Essentially any triglyceride can be used to prepare a dimethicone copolyol ester.

Silicone Compounds as Emulsifiers

Alkyl dimethicone copolyol compounds are a series of surface active materials that contain both alkyl and water soluble groups on the same polymer. These very versatile emulsifiers conforming to the following structure;



The series of products have been designed to have different solubility in a variety of solvents (see Table 1). The 3D HLB system developed by Siltech in 1996 describes these molecules, not only in terms of the % by weight of the water soluble groups present, but also by the percentage of hydrocarbon group present. This is because the introduction of three mutually insoluble groups into a molecule, results in the need for more descriptive information than is needed with standard surfactants that have only hydrocarbon soluble groups and oil soluble groups. This more descriptive information is provided in Table 6.

Unlike alkyl dimethicone copolyol polymers that have been offered before, these materials are available in a kit. This kit offers a series of related materials over a wide range of 3D HLB values. Not only does this allow the formulator an opportunity to select surfactants that can make a variety of emulsion types from a variety of oils, it offers the possibility of making emulsions using a silicone pair

of emulsifiers. This approach has long proven to be a very important step in the preparation of cosmetically acceptable emulsions. Silicone surfactants result in a less sticky, more cosmetically elegant emulsion than do the standard fatty surfactants; this is particularly in invert emulsions, the so called water in oil emulsions.

Table 1 Product Composition

%	3D HLB			
Product	**EO**	**Alkyl**	**x %EO/5**	**y %Alkyl/5**
Silsurf J208-212	48	6	9.6	1.2
Silsurf J208-412	39	13	7.8	2.6
Silsurf J208-612	28	22	5.6	4.4
Silsurf J208-812	16	32	3.2	6.4

Solubility

The polymers from this class of materials become more water soluble as the percentage of water soluble group increases. This is clearly seen in table below. As the % of water soluble group decreases the polymers go from water dispersible to water insoluble. The interesting fact is that all products are soluble in iso-propanol, regardless of their solubility in water.

Table 2

	Water		IPA		Mineral spirits		Mineral oil		Aromatic solvent		Cyclic silicone		Silicone Fluid	
Product	**1%**	**10%**	**1%**	**10%**	**1%**	**10%**	**1%**	**10%**	**1%**	**10%**	**1%**	**10%**	**1%**	**10%**
Silsurf J208-212	S	S	S	S	I	I	D	D	S	S	D	D	D	D
Silsurf J208-412	D	D	S	S	D	D	D	D	S	S	D	D	D	D
Silsurf J208-612	I	I	S	S	S	S	S	D	S	S	D	D	D	D
Silsurf J208-812	I	I	S	S	S	S	S	S	S	S	S	S	D	D

Legend: S is soluble; I is insoluble; D is dispersible

Typical Emulsion

The following example is offered showing the functionality of these emulsifiers. Typically we would recommend using a blend of two emulsifiers, the so called "emulsifier pair".

W/O Emulsion
SE 062504B

Material	Phase	%wt
Silsurf J-208-812	A	5.0
D-5 Cyclomethicone	A	35.0
Water	B	59.0
NaCl	B	1.0

Procedure

1. Mix Part A Ingredients
2. Mix Part B Ingredients
3. Add Phase B to Phase A
4. Mix Until Uniform

Remarks

W/O Emulsion, good stability and produces a waterproof film.

Sunscreen
SSS072604A

Part	Material	% Wt
A	Octyl Methoxycinnamate	7.50
A	Octyl Salicyate	5.00
A	Oxybenzone Benzophenone 3	5.00
A	Silsurf J-208-812	5.00
A	Octyldodecyl Neopentanoate	5.00
A	Beeswax	4.00
A	Propyparaben	0.2
A	Methylparaben	0.4
B	D-5 Cyclomethicone	15.0
C	Water	49.55
C	Propylene Glycol	2.00
C	Na_2 EDTA	0.10
C	NaCl	1.00
D	Grapefruit Fgragance	0.25

Procedure

1. Heat Part A to 70°C.
2. Mix until dissolved
3. Add Phase B to Phase A, keeping temperature at 65°C.
4. Heat part C to 60°C.
5. Add part C to part A and B with high sheer.
4. Cool to 30°C and add part D.

Recent Developments

Silicone compounds have experienced what can called an explosive growth in the personal care market. This explosive growth has resulted in the creation of a new book, available from Allured entitled *Silicones for Personal Care*, published in 2003 (ISBN: 0-931710-97-9). Visit www.allured.com for more information.

Chapter 7
Analytical Methods

This chapter on analysis is intended to give the chemist an overview of what the various analytical methods are and why they are of importance in establishing specifications and test methodologies for surfactants. It is intended to provide information on the theory of a particular test and why a particular test is chosen for a particular analysis. For full details on a specific analysis, refer to *Standard Analytical Methods,* published by the American Society of Testing Materials (ASTM).

Surfactants are not pure chemical species. As such, they are correctly described as compositions, not compounds. All surfactants contain traces of raw materials and some concentration of by-products of the reactions, such as inorganic salts. Many contain solvents, such as water. Still others contain additives that alter their performance. Finally, some contain preservatives. Therefore, determining how a chemist analyzes the surfactant that he or she purchases commercially is an important matter.

Before addressing this matter, one needs to understand the kind of analysis that may be employed for a specific surfactant and tailor an analytical regimen for the chemistry of the surfactant chosen.

There are two kinds of analyses: those that measure the concentration of specific compounds present in a surfactant and those that measure a colligative property — for example a particular functional group in a surfactant composition.

The tests in the specific analysis category include chromatographic methods like gel permeation chromatography. The result of such an analysis gives the percentage of each component in the mixture but does not give insight into the structural properties of the individual components.

Colligative analysis tests, on the other hand, measure the quantity of a specific functional group but give no insight into the distribution of species in the composition. Colligative analyses reveal the chemical functionalities present in the overall solution, but they do not provide insights into the concentrations of specific compounds that possess the properties.

It is very important for formulators to understand that both types of methods, properly used, give needed data.

Colligative Tests

The mg KOH/gm System

By far, the most commonly used system for the analysis of surfactants is the *mg KOH/gm system*. This system was originally developed for use by chemists in the

soap business. The concept behind the system is that all analyses that the system accommodates are expressed in units of milligrams of potassium hydroxide (KOH) per gram of sample tested. For surfactants, the analyses most commonly used in this system include alkali value, acid value, hydroxyl value and saponification value.

In the mg KOH/gm system, each compound evaluated is compared to KOH. KOH has a molecular weight of 56.11. By definition, 100 percent KOH has 1,000 mg of KOH per gram of KOH. Pure sodium hydroxide (NaOH), which has a molecular weight of 40, is equivalent to (56.11/40)(1,000 mg KOH/gm), or 1,402.7 mg KOH/gram.

The alkali value of one gram of 100 percent NaOH is 1,402.7 mg KOH/gm. The significance of this system is that the number relates to molar values, not weight values. Because all chemistry is done in molar quantities, this number is far more significant than the weight of compound added.

Looking at NaOH and KOH, one gram of NaOH provides 140 percent of the combining alkalinity as one gram of KOH. Therefore, if you were to neutralize one mg KOH/gm of acid determined by titration, you would need one gram of alkalinity to accomplish this. One gram of 100 percent KOH or 0.71 grams of 100 percent NaOH would accomplish this task.

The relationship between the mg KOH/gm value and molecular weight is an important formula. The apparent molecular weight (AMW) of any material can be determined by the formula:

$$AMW = 56{,}110/\text{mg KOH/gm}.$$

Because the number of mg KOH per gram can be determined by titration, this value is independent of the type or concentration of the pure compound. If one had two different concentrations of a fatty acid in isopropanol and water and wanted to make a salt, an acid value titration could be run on both samples. From the observed acid value, a required amount of base can be determined to exactly neutralize the acidity present. The alkali value of the base used could then be used to determine the exact quantity of each kind of base used. The values provided by this system are colligative, that is, not related to the specific species or combination of species that contribute the acidity.

This system does not give any information on the distribution of species in a given solution or on the diluents present, if any. Although the exact species that causes the value observed is not determined by the titration, important information is generated by this analysis.

The titration applies equally to products that have the particular functionality present in the molecule after the reaction and the monitoring of reaction progress for compounds that consume the functionality being titrated. Specifically, if an amphoteric is titrated for acid value, the observed value will be for the carboxyl group present. However, if the acid value is used to determine unreacted fatty acid in an ester, the value will be the result of unreacted acid raw material. Both analyses for the final product and the unreacted raw material are important to product quality.

Alkali Value

Alkali value (reference ASTM D 2074-66) is defined as the number of milligrams of alkalinity present in a sample that have the same alkalinity as one gram of KOH. The method requires a simple titration of the sample with a standardized acid to a pH of five. For water soluble surfactants, water is the solvent of choice, but if the material is not soluble a 50/50 blend of ethanol/water is used.

The following table lists the alkali value for commonly used bases:

Material	Molecular Weight	Alkali Value (mg KOH/gm*)
Diethanolamine	105.0	534.4
KOH	56.1	1,000.0
NaOH	40.0	1,402.8

**Calculated as:* (56,110/molecular weight) (number of equivalents/molecule)

Acid Value

Acid value (reference AOCS Te 1a-64 T) is defined as the number of milligrams of KOH equivalent to the acid content of one gram of sample. The method consists of a simple titration of the sample with a standardized base to a pink color using phenolphthalein solution. In most instances a 50/50 blend of ethanol/water is the solvent of choice.

The following table lists the acid value for commonly used acids:

Material	Molecular Weight	Alkali Value (mg KOH/gm*)
Acetic Acid	60	935.1
Lauric Acid	198	283.4

**Calculated as:* (56,110/molecular weight) (number of equivalents/molecule)

The preceding calculation shows that acetic acid (100 percent) has 3.3 times more acidity per gram than 100 percent lauric acid. The use of the mg KOH/gm system allows for the calculation of the corresponding amount of acid required to neutralize a titrated amount of alkali value. For example, consider that you have 500 grams of an aqueous solution with an alkali value of 50.2 mg KOH/gram. The amount of acetic acid needed to make the full salt is calculated below.

Acetic acid (100%) has an acid value of 935.1 mg KOH/gm.
(50.2 / 935.1) (500 grams) = 26.8 grams of acetic acid

Grams needed to neutralize =
(Alkali value/acid value of additive) (weight of sample)

If lauric acid were used, the calculation would be:
(50.2/283.4) (500 grams) = 88.6 grams of lauric acid

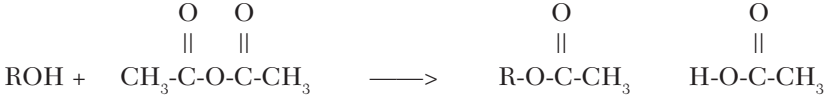
This concept can be extended to hydroxyl value and saponification value. Although you cannot titrate hydroxyl value with acid or base, the molar values for each can be determined and related to the amount of KOH in mg KOH/gm needed to react.

Hydroxyl Value

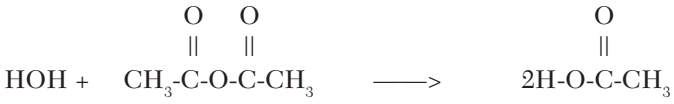
Hydroxyl value (reference AOCS Cd 13-60) is defined as the number of milligrams of KOH equivalent to the hydroxyl content of one gram of sample.

Several methods are used to determine hydroxyl value. The classical wet methods react the hydroxyl-containing materials with an anhydride, most commonly acetic or phthalic, to get the half ester. The reaction can be catalyzed to increase rate and sensitivity. The remaining anhydride is then hydrolyzed to give the diacid. The acid is then titrated, as shown in the following reaction sequences.

Reaction with alcohol



Reaction with water



The reaction of water with the anhydride gives two acetic acid molecules, and the reaction with an alcohol gives only one. This is the basis of the calculation.

Saponification Value

The saponification value (reference AOCS TI 1a-64 T) measures the alkali reactive groups present in a sample. This method, unlike acid value, which is a direct simple titration of acid with standardized base, uses a known amount of alcoholic KOH, which is reacted under heat for 60 minutes. This more aggressive procedure measures the consumption of KOH when titrated with standard acid. The method is useful for esters and also titrated acids. The table below shows the expected values for three types of surfactants.

Chemical Class	Acid Value	Saponification Value
Esters	Negative	Positive
Acids	Positive	Positive
Amids (Methyl Ester Derived)	Negative	Negative
Amids (Fatty Acid Derived)	Positive	Negative

Summary of mg KOH/gm System

The mg KOH/gm system can be a powerful tool for monitoring a given reaction, as illustrated below.

Reaction: Esterification
One mg KOH/gm of hydroxyl value (alcohol) reacts with one mg KOH/gm of acid value (acid) to give one mg KOH/gm of saponification value (ester).

Reaction: Neutralization
One mg KOH/gm of alkali value (amine) reacts with one mg KOH/gm of acid value (acid) to give a salt.

Reaction: Amidification
One mg KOH/gm of alkali value (amine) reacts with one mg KOH/gm of acid value (acid) to give an amid.

Other Wet Analysis Methods

Anionic Actives

The activity of anionic surfactants can be qualitatively determined by titration with a standardized cationic reagent. This relatively simple procedure involves the preparation of a standard solution of sodium lauryl sulfate and a mixed indicator solution, determination of sodium lauryl sulfate purity and standardization of Hyamine 1622. The titration end point is achieved by the transfer of a colored complex from an organic solvent phase to an aqueous phase. This method of activity determination is appropriate for alkylphenol ethoxy sulfates, fatty alcohol ethoxy sulfates, fatty alcohol sulfates and dialkyl sulfosuccinates.

The Epton and other titration methods make use of a molecular weight to allow one to calculate the percentage of actives from the calculated milliequivalents per liter. The molecular weight, therefore, is a major factor in the calculation. The specification for actives should be written in terms of milliequivalents per liter because this is what one actually measures and there is no question of the validity of the molecular weight used. The higher the molecular weight used in the calculation, the higher the apparent activity.

Cationic Actives

The method is essentially identical to the anionic actives method, but the cationic material is titrated with a standardized anionic surfactant.

Unsulfated Matter

The unsulfated matter portion of a sulfated surfactant has considerable importance to formulators. The by-products and water-insoluble additives are concentrated in this component. As one example, if the fatty alcohol feedstock is high in paraffin components, there will be a high concentration of paraffin in the unsulfated matter portion. The unsulfated matter analysis is run by extraction.

The method depends on the unsulfated matter present in the sulfate being more soluble in carbon tetrachloride than in water. A sample of the surfactant is dissolved in water and extracted several times with carbon tetrachloride. The organic phase is then filtered through anhydrous sodium sulfate, and, after evaporation of the solvent, it is weighed and expressed as a percentage of unsulfated matter.

After using extraction, the resulting oil should be subjected to infrared analysis to determine if any nonalcoholic components are present. Subsequently, a gas liquid chromatography (GLC) analysis should be run. (See the GLC Analysis section later in this chapter for more information on running a GLC analysis.) It is common for the unsulfated matter present to be different than the hydrophobe sulfated. If the alcohol added to increase unsulfated matter is different than the starting alcohol, it is generally a nonethoxylated alcohol of a higher molecular weight. This is done to improve viscosity performance.

Inorganic Salts

The total inorganic salt concentration and the kind of ion present in a sulfated product are important performance factors. Viscosity curves are very salt concentration-dependent. Products made with chlorosulfonic acid have the added problem of sodium chloride present as a by-product of sulfation. Specifications should be written to cover both chloride and sulfate ions and a total inorganic ion content.

The method used for analysis is titration with an ion-specific electrode.

Bleaching Agents

Several key additives can be added to sulfated products to improve color. All can have negative effects on fragrance, preservative, and other aldehydic and ketonic materials added by formulators.

Bleaching agents fall into two classes—oxidizing agents and reducing agents. Oxidizing agents include primarily hydrogen peroxide, and reducing agents include sodium borohydride and sodium sulfite. Simple screening tests will determine if oxidizing agents or reducing agents are present in a product.

The method recommended for screening is based on the fact that hydrogen iodide under acidic conditions will form iodine in the presence of peroxide or hypochlorite. The appearance of a yellow or brown color is a positive test for bleaching agents.

Instrumental Methods

Fourier transform infrared analysis

Fourier transform infrared analysis (FTIR) is one of the most valuable tools available to the chemist in working with surfactants.

FTIR is a computer-assisted spectroscopy that allows the operator to obtain quantitative information on a compound and compare that information to a spectrum in the computer's library for matching. The computer can match many of the spectral absorption intensities and give a correlation to the standard. This correlation tells the operator the degree of match to the standard.

Infrared spectroscopy has been available for many years. The basic concept with this form of analysis is that molecules, when excited by energy, have four different ways to dissipate the energy. These ways are translation, rotation, vibration and electronic changes. Various kinds of spectroscopy look at different aspects of these changes. Infrared spectroscopy affects the vibrational and rotational energy of the molecule.

When a given molecule is exposed to infrared radiation, it gives off a spectrum depending on the functional groups present in the molecule. The spectrum that is produced gives insight into the functional groups present in a molecule. Infrared spectroscopy has been used to identify compounds for many years.

Two recent developments have resulted in making this technique a tool for quantitative analysis. The first is the development of sample cells that can tolerate aqueous samples. Early infrared cells were made of sodium chloride. These cells were dissolved in water. Because many surfactants are aqueous products, this limited the use of infrared analysis. The only option of evaluating aqueous products was evaporating the water and making a dry-down. The problem here was that the dry-down process may have changed the spectrum.

Now, however, we have cells that are unaffected by water. Consequently, evaluation of aqueous products is now commonplace.

The second and more important advance in infrared spectroscopy is the development of computer technology that allows for many scans to be made and the average of these scans to be determined. This eliminates random noise, which is found in the infrared spectrum, during a single analysis. The original computer-assisted infrared was called CAT infrared. (CAT stands for "computer for analyzing transients.") If multiple scans were made and an average taken, the random noise in the spectrum would subtract out, and a clean spectrum would result.

As a quality control tool, FTIR is very powerful. It is not only quick and efficient, but the operator no longer needs to evaluate the scan to match salient absorption spectra. In fact, the operator doesn't even have to understand how to interpret the spectra.

In a research environment, FTIR can be used to analyze the kinetics of a reaction. Once the raw material and finished product spectra are placed into the computer, the ratios of each can be easily and efficiently calculated by spectral subtraction. Spectral subtraction is a computer technique that allows for a known component in a spectrum of a complex mixture to be calculated. If desired, the

contribution of that component can be subtracted from the original spectrum. This technique can be done several times until each component is calculated. The result is a percentage for each component.

It is recommended that FTIR analysis be run on all surfactants, but the operator must understand that this technique is colligative: The FTIR analysis shows all functional groups in the sample, but it does not guarantee that the functional groups in the spectrum are in the *same* molecule. For example, a blend of a methyl ester and a fatty alcohol is not distinguishable from a molecule having the same percentage of the components on the same molecule.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a powerful analytical technique for analyzing compounds. Certain nuclei have spin quantum numbers that make them act as tiny magnets when placed in magnetic fields. These nuclei have the ability to be analyzed by NMR.

The hydrogen, carbon, silicon and phosphorus nuclei are of particular interest to surfactant chemists. The test surfactant is placed in a strong magnetic field that affects the spin of the atomic nuclei of certain isotopes of common elements. A radio wave passes through the substance and then reorients these nuclei. When the wave is turned off, the nuclei release a pulse of energy that provides data on the molecular structure. Chemical shifts of the nuclei being tested are measured from the released pulse of energy and plotted on a spectrum. Because the chemical shifts are due to diamagnetic shielding effects produced by circulation of bonding and nonbonding electrons in the neighborhood of the nuclei, the spectrum gives both quantitative information on the number of nuclei of a given type and the chemical environment of the nuclei.

Carbon, phosphorus and silicon NMR are of the most interest because the spectra are simple and easily read. Such easily read spectra are referred to as *first order* by spectroscopists. Proton NMR is of interest, but, because of the complexity of the resulting NMR spectrum, it is of less interest than the other types of NMR described here.

The field of NMR has undergone a dramatic growth during the last decade, and the sophistication of the data generated by the technique has likewise grown. Part of the growth has been a direct result of improved computer technology. This has allowed for the implementation of pulsed Fourier transform NMR. This technique uses multiple analysis and reduces noise.

Proton NMR is the oldest kind of NMR. Although it provides some useful information, it provides very difficult spectra to read when used on surfactants. This occurs because many surfactants are complex mixtures. Other types of NMR that are more interesting to surfactant chemists include carbon, phosphorus and silicon NMR.

Carbon NMR

Carbon NMR provides valuable information on the structure of many surfactants. It can be used to determine and quantify the number of distinct types of carbon atoms in a sample. The distinctness depends on the electronic nature of groups close to the carbon atom. Historically, carbon NMR has been commonly used to determine the relative amounts of polyoxyalkylene groups to polyoxypropylene groups in block polymers. This depends on the fact that the propylene oxide portion of the block polymer has a distinctive methyl substitution pattern, as illustrated on the following page.

NMR Shift (ppm)	Description
0–30	Alkane carbon
110–150	Alkene carbon
50	Carbon bonded to an amine
60	Carbon bonded to an alcohol
70	Carbon bonded to a F
110–160	Aromatic carbon
200–220	Carbonyl carbon

The exact value can change slightly depending on other structural properties of the compound. Once the spectrum is saved, comparison of either new lots of materials or materials supplied by new suppliers to the standard spectra can easily be run.

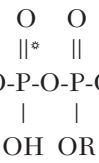
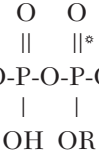
Phosphorus NMR

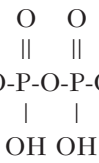
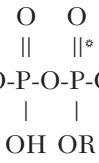
Recently, phosphorus NMR has been applied to phosphate esters. The data generated by this analytical tool have provided tremendous and heretofore unavailable information on the composition of phosphate esters. This has allowed for better structure elucidation and development of improved process control used to make phosphate esters.

Phosphorus NMR gives information on the amount of monoester diester and free phosphoric acid concentrations present in the product. It also gives insight into the polymeric products that are present in low concentrations that heretofore were difficult to analyze. Typical values for the NMR shift (in ppm) and the structures that cause the shifts are as follows. (The element with the * gives the shift shown.)

NMR Shift (ppm)	Structure	Description
+ 2.9	$O=P\text{-}(OH)_3$	Free Phosphoric
+ 1.8	$O=P\text{-}(OH)_2\ (OR)$	Monoester
+ 0.2	$O=P\text{-}(OH)\ (OR)_2$	Diester
- 1.1	$O=P\text{-}(OR)_3$	Triester

Polymaterials

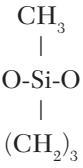
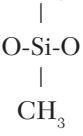
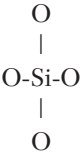
NMR Shift (ppm)	Structure	Description
-11.4		Polyphosphate – monoester
-12.2		Polyphosphate – monoester

NMR Shift (ppm)	Structure	Description
-12.8		Polyphosphate – diester
-13.5		Polyphosphate – Triester

This technique gives clean first-order spectra. Based on the information gleaned, it appears likely that this technique will become an important one in the future as access to the equipment and familiarity with the method become more commonplace.

Silicon NMR

Silicon NMR analysis is one of the more important new methods for the analysis of surfactants. It allows for much structural information to be generated for silicone surfactants. The technique measures the type and quantity of each kind of silicon nuclei present. Typical values for the NMR shift (in ppm) and the structures that cause the shifts are as follows. (The element with the * gives the shift shown.)

NMR Shift (ppm)	Structure	Description
+7.2	$(CH_3)_3$-Si-O	M unit
-11.4		D* Unit
-21.4		D Unit
-105.1		Q Unit

Specific Tests

Gas Liquid Chromatographic Analysis—Hydrophobe Preparation

To conduct a gas-liquid chromatographic (GLC) analysis, sulfated materials are hydrolyzed in acidic aqueous solution to give an oil phase and an aqueous phase. If no oil phase develops after the acidic hydrolysis procedure, the product is probably a sulfonate and not a sulfate.

To conduct the GLC analysis, 5 percent sulfuric acid is added to 20g of sulfated surfactant, and the resulting solution is refluxed for about four hours to hydrolyze the sulfate. The oil-soluble component is extracted with petroleum ether that is subsequently evaporated to give the oil-soluble component. Infrared and gas chromatographic analyses are then run on the residue. The presence of any nonalcoholic peaks in the GLC should be noted.

Gas Chromatographic Analysis Method

Successful GLC analysis systems have been developed for lower ethoxylates. These methods rely on the volatility of a sample, so highly ethoxylated species cannot be analyzed by this method. An analysis system by GLC is as follows:

Column: Sp 2100 on 100/120 Supelcoport
Temperature Profile: 90 degrees C initial
8 degrees/min
300 degrees C final

Retention Time (Min.)	Designation (Carbons in Hydrophobe–Moles Ethylene Oxide)
9.2	12 – 0
12.2	14 – 0
12.3	12 – 1
12.4	14 – 1
15.5	12 – 2
16.3	14 – 2
18.7	12 – 3
19.3	14 – 3
21.5	12 – 4
22.1	14 – 4
24.6	14 – 5

Chapter 8
Patent References

Patents are perhaps the single most important source of information on the basic synthetic processes and technology used in the preparation of surfactants. The patent system provides valuable property rights to the inventor and information to the public at large. Patents are the most important vehicles by which basic technology used in the synthesis of surfactants is made available to the interested public.

The word "patent" comes from the Latin *patere*, which means "to be open".[19] The U.S Constitution contains the legal root of the modern patent system. In Article I, Section 8, clause 8, it states, "The Congress shall have the power to promote the progress of science and useful arts by securing for limited times to authors and inventors the exclusive right to their respective writings and discoveries."

Patents are intensely real-life legal instruments. They have been afforded the attributes of property by law. One of the basic concepts of patent law is the right to exclude others from the enjoyment of the protected property. The basic concept in patent law is that the inventor be given rights for *limited times*, after which the invention is open to the public for use. The technology covered by the expired patent is then available to the public. Therefore, patents are very important teaching documents for the public.

In addition to technology available for public use in expired patents, a review of patent literature gives the chemist an understanding of how the creative process works. Each invention covered in a patent builds on another, called the prior art, and the technology as a whole advances. In addition, it is quite interesting to note just how long most of the basic technology of surfactants has existed and how much is now available to the public in the form of expired patents.

This chapter will review a few important patents covering surfactant technology. It is not meant to be extensive; such a treatment would fill many volumes. It is being presented to illustrate some examples of the valuable technical and historical information contained in patents.

Alkanolamids

Alkanolamids have been known since the 1930s. Kritchveski is perhaps the best-known and most important contributor to the science of alkanolamids. Here is a listing of important patents involving alkanolamids:

1. U.S. Patent 2,089,212, U.S. Patent 2,096,749 and U.S. Patent 2,173,058 issued in 1937 describe the pioneering work done by Kritchveski in developing the process for making 2:1 alkanolamids that bear his name.

2. U.S. Patent 2,404,297, issued in 1946 to Kroll, describes a process for making higher purity alkanolamids and the effects of age on product performance.
3. U.S. Patent 2,464,094, issued in 1949 to Meade, describes the process for making superamids.
4. U.S. Patent 2,546,521 and U.S. Patent 2,555,606, issued in 1951 to Potts, describe the synthesis of alkanolamids.
5. U.S. Patent 2,844,609 and U.S. Patent 2,863,888, both issued in 1958 to Tesoro, describe "an improved process" for making alkanolamids.
6. U.S. Patent 3,024,260, issued in 1962 to Ernst, describes the use of catalysts in making alkanolamids.
7. U.S. Patent 3,040,075, issued in 1962 to Lohr, describes a process for lowering amid ester content by regulating amine level and catalyst level.

The current problem with nitrosoamine compounds and the desire to eliminate the use of alkanolamines in personal care products will almost certainly result in new patented products in the alkanolamid field.

Alkoxylates

Most of the work done on alkoxylates is directed toward either alkoxylation of specific hydrophobes or to specific catalysts. Here is a listing of 10 important patents involving alkoxylates:

1. U.S. Patent 2,536,976, issued in 1951 to Chiddex, is an example of an early patent on catalysis of the alkoxylation process.
2. U.S. Patent 2,593,112, issued in 1952 to Cross *et al.*, is an example of an early patent covering a specific hydrophobe. In this case, the patent deals with alkoxylation of aryl ethers.
3. U.S. Patent 2,706,181, issued in 1954 to Pruitt, deals with preparation of high molecular weight alkoxylated block polymers.
4. U.S. Patent 3,127,358, issued in 1964 to Hill, deals with another aspect of the preparation of high molecular weight alkoxylated block polymers. High molecular weight block polymers, their properties and improved processes for their preparation remain topics of interest today.
5. U.S. Patent 2,913,416, issued in 1959 to Fineman *et al.*, deals with butylene oxide adducts. The use of butylene oxide and its effects on product properties remains a topic of interest today.
6. U.S. Patent 2,832,795, issued in 1958 to Hempel *et al*., describes the ethoxylation of alkylphenol. This class of compounds remains a commonly used material to this day.
7. U.S. Patent 3,141,854, issued in 1964 to Bailey, is an example of one of the first attempts to use catalysts to alter the properties of alkoxylates. Many additional patents in this field would later be issued.
8. A number of U.S. patents dealing with the use of specific catalysts to alter the distribution of oligomeric species in alkoxylated products have been issued. Among them are:
   - U.S. Patent 4,254,287, issued in 1981 to Ziengenhain.

- U.S. Patent 4,329,515, issued in 1982 to Yang.
- U.S. Patent 4,701,571, issued in 1987 to Soo.
- U.S. Patent 4,727,199, issued in 1988 to King.
- U.S. Patent 4,886,917, issued in 1989 to Knopf.

9. U.S. Patent 3,022,335, issued in 1962 to Lundsted, deals with a process of premixing propylene oxide and ethylene oxide and then using the mixture in a subsequent step to alkoxylate a hydroxy-containing compound.
10. U.S. Patent 5,525,702, issued in 1996 to Nace, is a recent patent dealing with polyoxyalkyeneglycol polymers having improved biodegradability. This property is achieved by incorporating butylene oxide groups into the polymer.

Alkylglucosides

This class of compounds is an example of a well-known chemistry. The process for the manufacture of alkylglucosides and applications for their use have been greatly expanded. Henkel Corporation scientists have developed new and improved processes for preparing light color, cosmetically acceptable products that make this older class of compounds commercially viable. Procter and Gamble has extensively patented the use of these materials in many formulations. Here is a listing of important patents involving alkylglucosides:

1. U.S. Patent 4,393,203, issued in 1983 to Mao, describes a process for the preparation of alkylglucosides.
2. U.S. Patent 4,939,245, issued in 1990 to Rasche, U.S. Patent 4,950,743, issued in 1990 to McCurry, U.S. Patent 4,959,468, issued in 1990 to Ravi, and U.S. Patent 5,003,057, issued in 1991 to McCurry, all deal with different aspects of a new and improved process for making alkylglucosides.
3. U.S. Patent 5,298,240, issued in 1994 to Schroder, describes the use of an alkylpolyglucoside in a hair-care emulsion.

Amphoterics

Amphoteric surfactants have been known since 1938. There have been numerous patents dealing with optimizing properties, differing ratios of components and applications. By far, the name most intimately associated with imidazoline-based amphoterics and related compounds is Mannheimer. The patents that bear his name are quite numerous, and they cover a great deal of technology. Although the structures professed to be present in the early patents are simply incorrect, the class of compounds based on the technology disclosed in these patents continues to be refined and developed to this day. Here is a listing of important patents involving amphoterics:

1. U.S. Patent 2,129,264, issued to Downing in 1938, appears to be the earliest reference to this class of compounds. The structures provided in the patent are incorrect, featuring a penta-valent nitrogen. However, this patent marks the start of what would become a very important class of surfactants.
2. U.S. Patent 2,195,974, issued in 1936 to the famous chemist Reppe, teaches that amphoteric surfactants can be made using amino compounds and acrylic acid.

3. The following patents, all issued to Mannheimer *et al*., are the pioneering patents in the field of amphoteric surfactants
   - U.S. Patent 2,528,378, issued in 1950.
   - U.S. Patent 2,528,379, issued in 1950.
   - U.S. Patent 2,528,380, issued in 1950.
   - U.S. Patent 2,773,068, issued in 1956.
   - U.S. Patent 2,781,349, issued in 1957.
   - U.S. Patent 2,781,350, issued in 1957.
   - U.S. Patent 2,781,351, issued in 1957.
   - U.S. Patent 2,781,353, issued in 1957.
   - U.S. Patent 2,781,354, issued in 1957.
   - U.S. Patent 2,781,355, issued in 1957.
   - U.S. Patent 2,781,356, issued in 1957.
   - U.S. Patent 2,781,357, issued in 1957.
   - U.S. Patent 2,781,358, issued in 1957.
   - U.S. Patent 2,781,375, issued in 1957.
   - U.S. Patent 3,231,580, issued in 1966.
   - U.S. Patent 3,231,581, issued in 1966.
   - U.S. Patent 3,231,582, issued in 1966.
   - U.S. Patent 3,359,275, issued in 1967.
   - U.S. Patent 3,408,361, issued in 1968.
   - U.S. Patent 3,452,042, issued in 1969.
   - U.S. Patent 3,452,065, issued in 1969.
   - U.S. Patent 3,452,066, issued in 1969.
   - U.S. Patent 3,661,945, issued in 1972.
   - U.S. Patent 3,703,535, issued in 1972.
4. U.S. Patent 2,961,451, issued in 1906 to Keough, is one of the first patents covering betaine compounds.
5. U.S. Patent 3,100,779, issued in 1963 to Mannheimer, describes the process for making sulfobetaines.
6. U.S. Patent 3,225,073, issued in 1963 to Gladrich, describes the process for making sulfatobetaines.
7. U.S. Patent 3,417,136, issued in 1968 to Hovden, teaches how to make ether amine-based amphoteric surfactants.
8. U.S. Patent 3,950,417, issued in 1976 to Verdicchio, a pioneer in the use of amphoteric surfactants in personal care applications, discloses the use of sulfobetaines in cosmetic formulations.
9. U.S. Patent 4,189,593, issued in 1980 to Wechsler, discloses an improved imidazoline amphoteric process.

Guerbet Alcohols

The development of Guerbet alcohols and their derivatives is an interesting study in perfecting the practice of chemistry known for a long time. Consequently, the patents deal with processes, catalysts and unusual derivatives. Here is a listing of important patents involving Guerbet alcohols:

1. U.S. Patent 2,862,013, issued in 1958 to Millers, is an example of early catalyst work done on a reaction that had been described in 1800s.
2. The following patents all deal with catalysts:
   - U.S. Patent 3,118,880, issued in 1964 to Kollar.
   - U.S. Patent 3,864,407, issued in 1975 to Yates.
   - U.S. Patent 3,916,015, issued in 1975 to Yates.
   - U.S. Patent 3,917,722, issued in 1975 to Yates.
   - U.S. Patent 4,011,273, issued in 1977 to Abend.
   - U.S. Patent 5,068,469, issued in 1991 to Young.
3. U.S. Patent 4,299,994, issued in 1981 to Sthel, discloses ethoxylated Guerbet alcohols.
4. U.S. Patent 4,731,190, issued in 1988 to O'Lenick, discloses Guerbet alkoxylates prepared by reacting both ethylene oxide and propylene oxide with the Guerbet alcohol.

Guerbet Compounds (Composition of Matter)

1. 6,093,856 Polyoxyalkylene surfactants, issued July, 2000 inventors: Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.
2. 6,060,443 Mid-chain branched alkyl sulfate surfactants, issued May, 2000 inventors; Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.
2. 6,013,813 Guerbet based sorbitan esters, issued Jan. 2000, inventor; O'Lenick, Jr. Anthony, assigned to Hansotech Inc.

Process

1. 5,808,158 Production of primary Guerbet amines, issued Sept1998, inventors; Conrads, Martin; Hermann, Albert; Scherf, Erich; Wagner, Arwed,, assigned to RWE-DEA.
2. 5,777,183 Process for the production of Guerbet alcohols, issued Jul 1997, inventors; Mueller, Gerhard; Gutsche, Bernhard; Schmid, Karl; Bougardt, Frank; Jeromin, Lutz; Peukert, Eberhard; Frankenbach, Herman, assigned to Henkel Kgaa.
3. 5,654,453 Process for the production of .alpha.-branched aliphatic monocarboxylic acids, issued Aug 1997, inventors;Mueller, Gerhard; Gutsche, Bernhard; Schmid, Karl; Bongardt, Frank; Jeromin, Lutz; Puert, Eberhard; Frankenbach, Herman, assigned to Henkel Kgaa.
4. 6,008,181 Mid-Chain branched Alkoxylated Sulfate Surfactants, issued Dec, 1999 inventors: Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.
5. 5,929,263 Guerbet branched quaternary compounds, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.
6. 5,919,959 Guerbet branched amine oxides, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.

7. 5,919,743 Guerbet branched quaternary compounds in personal care applications, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Petroferm Inc.
8. 5,786,389 Guerbet castor esters, issued Jul 1999, inventors; O'Lenick, Jr. Anthony; Parkinson, Jeff K. assigned to Lambent Technologies Inc.
9. 5,756,785 Guerbet betaines, issued May 1999, inventor; O'Lenick, Jr. Anthony assigned to Lambent Technologies Inc.
10. 5,744,626 Complex Guerbet acid esters, issued April 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.
11. 5,717,119 Polyoxyalkylene glycol Guerbet esters, issued February 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.
12. 5,646,321 Guerbet meadowfoam esters, issued Jul 1997, inventor; O'Lenick, Jr. Anthony, assigned to Siltech Inc.
13. 5,488,121 Di-Guerbet esters, issued Jan 1996, inventor; O'Lenick, Jr. Anthony, assigned to Siltech Inc.
14. 5,387,374 Guerbet carbonates, issued Feb 1995, inventors Westfechtel, Alfred; Bongardt, Frank; Ansmann, Achim, assigned to Henkel Kgaa.
15. 5,312,968 Fluorine containing Guerbet citrate esters, issued May 1994, inventors; O'Lenick, Jr. Anthony, and Buffa, Charles W., assigned to Siltech Inc. and Biosil Technologies Inc.
16. 5,264,006 Guerbet alkyl ether monoamines, issued Nov. 1993, inventors; Schilowitz, Alan; Krogh, James; Mokadam, Anita; Clumpner, Michael; and Berlowitz, Paul, assigned to Exxon Research.
17. 5,094,667 Guerbet alkyl ether mono amines, issued Mar. 1992, inventors; Schilowitz, Alan; Krogh, James; Mokadam, Anita; Clumpner, Michael; and Berlowitz, Paul, assigned to Exxon Research.
18. 4,830,769 Propoxylated Guerbet alcohols and esters thereof , issued May 1989, inventors; O'Lenick, Jr. Anthony, and Bilbo, Raymond Edward, assigned to GAF Corporation.
19. 4,800,077 Guerbet quaternary compounds, issued Jan1989, inventors; O'Lenick, Jr. Anthony, and Smith, Wayne C., assigned to GAF Corporation.

Applications (Formulations)

1. 6,087,309 Liquid cleaning compositions containing selected mid-chain branched surfactants- issued Jul 2000, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter and Gamble Co.
2. 6,046,152 Liquid cleaning compositions containing selected mid-chain branched surfactants, issued Apr 2000, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter and Gamble Co.
3. 6,036,947 Transfer resistant high lustre lipstick compositions, issued Mar 2000, inventors Barone, Salvatore; Krog, Ann; Jose, Natividad and Ordino, Renee, assigned to Revlon Consumer Products Co.
4. 6,015,781 Detergent compositions containing selected mid-chain branched surfactants , issued Jan 0, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas;

Connor, Daniel, assigned to Procter and Gamble Co.

5. 5,837,223 Transfer resistant high lustre cosmetic stick compositions, issued Nov 1998, inventors Barone, Salvatore; Krog, Ann; Jose, Natividad and Ordino, Renee, assigned to Revlon Consumer Products Co.
6. 5,736,571 Guerbet meadowfoam esters in personal care, issued Apr 1998, inventor O'Lenick, Jr. Anthony, assigned to ambent Technologies Inc and FanTech Ltd.
7. 5,709,739 Release agents for hydraulic binders, - issued Jan 1998, inventors Wittich, Leonhard; Heck, Stephan; Freichenhagen Lothar; Demmering, Guenther; Komp, Horst; Koehler, Michael; Wegener, Ingo and Sladek, Hans, assigned to Henkel Kgaa.
8. 5,686,087 Cosmetic and/or pharmaceutical formulations with an improved feeling on the skin based on mixed Guerbet alcohols, issued Nov 1997, inventors Ansmann, Achim; Kawa, Rolf; Mohr, Klaus and Koester Josef, not assigned.

Imidazolines

U.S. Patent 2,155,877, issued in 1939 to Waldmann, is an early example of the technology needed to make imidazolines. Imidazolines are the raw materials from which imidazoline-derived amphoterics are made.

Peaked Ethoxylates

Over the years, there has been a long-felt need to make ethoxylated and propoxylated materials that have a narrow distribution of oligomers in the alkoxylation process. This is easily seen in the number of patents and the number of years over which patents were issued in this area.

The graphic on page 126 lists 26 key catalyst patents associated with peaked ethoxylates.

Phosphate Esters

Phosphate esters are a class of surfactants that have been around for many years and have been the topic of numerous patents. Here are eight of the more important ones:

1. U.S. Patent 1,944,530, issued in 1934 to Schonburg, is one of the earliest patents covering phosphate esters. This early patent covers the synthesis of a triester.
2. U.S. Patent 2,005,619, issued in 1934 to DeWitt, uses phosphorous oxychloride and, like Schonburg's patent is directed to triesters.
3. U.S. Patent 2,656,372, issued in 1953 to Ernst, teaches the use of P_2O_5 and is similar to the technology widely used today.
4. U.S. Patent 3,004,056, issued in 1962 to Nunn *et al*., discloses a process improvement using P_2O_5.
5. U.S. Patent 3,033,889, issued in 1962 to Chiddix, discloses highly branched phosphate esters.

Key Patents Involving Peaked Ethoxylates

1. U.S. Patent 2,293,868, issued in 1942 to Toussaint (BF_3 catalyst).
2. U.S. Patent 2,623,875, issued in 1952 to Schlosser (caustic and metallic sodium).
3. U.S. Patent 2,782,240, issued in 1957 to Hefner (mono hydroxyalkylate).
4. U.S. Patent 2,807,651, issued in 1957 to Britton (sulfur dioxide).
5. U.S. Patent 2,870,099, issued in 1958 to Borrows (alkoxide).
6. U.S. Patent 2,870,100, issued in 1958 to Stewart (methyl alumnimum compounds).
7. U.S. Patent 2,870,220, issued in 1958 to Carter (Friedel-Crafts catalyst).
8. U.S. Patent 3,056,818, issued in 1962 to Werber (titanium and zirconium catalysts).
9. U.S. Patent 3,100,750, issued in 1963 to Bailey (metal alkoxylates and phenolates).
10. U.S. Patent 3,135,705, issued in 1964 to Vandenburg (organo-aluminum).
11 U.S. Patent 3,219,631, issued in 1965 to Kullman (cationic catalysts).
12. U.S. Patent 3,244,646, issued in 1966 to Naro (Group III metal alkoxylates).
13. U.S. Patent 3,275,598, issued in 1966 to Garty (dibutyl zinc).
14. U.S. Patent 3,969,417, issued in 1976 to Umbach (oxonium salts).
15. U.S. Patent 3,972,948, issued in 1976 to Laemmle (alkaline earth cations).
16. U.S. Patent 4,210,764, issued in 1980 to Yang (cresylic acid, cobalt catalyst and barium oxide).
17. U.S. Patent 4,223,164, issued in 1980 to Yang (strontium catalysts).
18. U.S. Patent 4,239,917, issued in 1981 to Yang (barium oxide and cobalt compounds).
19. U.S. Patent 4,278,820, issued in 1981 to Kametaka (ion exchange catalysts).
20. U.S. Patent 4,360,698, issued in 1982 to Yang (strontium catalysts).
21. U.S. Patent 4,375,564, issued in 1983 to Edwards (cobalt catalyst).
22. U.S. Patent 4,409,403, issued in 1983 to Sedon (insoluble heterogeneous catalyst).
23. U.S. Patent 4,453,023, issued in 1984 to McCain (barium catalysts).
24. U.S. Patent 4,456,697, issued in 1984 to Yang (hydrogen fluoride and metal alkoxylates).
25. U.S. Patent 4,540,828, issued in 1985 to Yang (dialkoxy metal fluorides).
26. U.S. Patent 4,593,142, issued in 1986 to Yang (hydrogen fluoride alkoxylates).

6. U.S. Patent 3,235,627, issued in 1966 to Mansfield, describes certain alkaline-stable phosphate esters.
7. U.S. Patent 3,770,855, issued in 1973 to Benson, discloses a process for breaking down polyphosphates using an aqueous digestion. This was a critical development in the commercialization of stable phosphate esters.

8. U.S. Patent 4,898,945, issued in 1989 to Weidemann, describes a Guerbet-based phosphate ester having both ethylene oxide and propylene oxide that is reported to be a good wetter.

Quaternaries

Quaternary ammonium compounds, or quats, have been known for quite some time. The following are some key patents involving quats:

1. U.S. Patent 2,127,476, issued in 1938 to Ulrich, discloses a process for making quats.
2. U.S. Patent 4,038,294, issued in 1977 to Conners, discloses amidopropyl quats.
3. U.S. Patent 4,450,174, issued in 1984 to Green, discloses germicidal quats based on a C_{10} hydrophobe.

Sorbitan Esters and Ethoxylates

Sorbitan esters are prepared in a multiple-step reaction sequence. Therefore, it is no surprise that many patents exist on processes for their preparation. Here are several important ones:

1. U.S. Patent 1,757,468, issued in 1930 to Mueller of I.G. Farben, discloses a process for making the cyclized sorbitol. This cyclic intermediate is a key step in making the final surfactant. The reaction of the intermediate with a fatty acid and ethylene oxide is not disclosed. Phosphoric acid, carbon, silica and various bases are disclosed as catalysts.
2. U.S. patents 2,322,820 and 2,322,821, issued in 1943 to Brown, disclose the monoesters of sorbitol.
3. U.S. Patent 2,374,931, issued in 1944 to Griffin (the Griffin who created the hydrophobe lipophile balance system in 1949), describes ethoxylated sorbitan esters.
4. U.S. Patent 2,387,842, issued in 1945 to Soltzberg, describes a process for the preparation of diesters of sorbitol.

Sulfates

U.S. Patent 1,932,180, issued to Gunther in 1929, is one of the first issued on this important class of surfactants. It was assigned to I.G. Farben. U.S. patents 4,476,045, 4,476,044, 4,476,043, 4,476,372, and 4,477,372, all issued to O'Lenick in 1984, disclose different aspects of a highly concentrated sulfated surfactant.

Sulfonates

U.S. Patent 2,205,950, issued in 1940 to Flett, discloses alkylphenol sulfonates as surfactants.

Sulfosuccinates

U.S. Patent 2,028,091, issued in 1936 to Jaeger, discloses the process for the

synthesis of sulfosuccinate diesters. U.S. Patent 2,879,214, issued in 1959 to Divine, discloses the use of ultraviolet light to catalyze the synthesis of sulfosuccinates.

Silicones

Silicone-derived surfactants have been a recent development. The following patents cover composition of matter on the classes of compounds described:

1. Silicone phosphate esters — U.S. Patent 5,149,765, issued in September 1992 to O'Lenick.
2. Silicone sulfates — U.S. Patent 4,960,845, issued in October 1990 to O'Lenick.
3. Silicone carboxylates — U.S. Patent 5,296,434, issued in March 1994 to O'Lenick.
4. Silicone sulfosuccinates — U.S. Patent 4,717,498, issued in January 1998 to Maxon.
5. Silicone alkyl quats — U.S. Patent 5,098,979, issued in March 1992 to O'Lenick.
6. Silicone amido quats — U.S. Patent 5,153,294, issued in October 1992 to O'Lenick.
7. Silicone imidazoline quats — U.S. Patent 5,196,499, issued in February 1993 to O'Lenick.
8. Silicone amphoterics — U.S. Patent 5,073,619, issued in December 1991 to O'Lenick.
9. Silicone betaines — U.S. Patent 4,654,161, issued in March 1987 to Kollmeier *et al*.
10. Silicone phosphobetaines — U.S. Patent 5,237,035, issued in August 1993 to O'Lenick.
11. Silicone alkanolamids — U.S. Patent 5,070,171, issued in December 1991 to O'Lenick.
12. Silicone esters — U.S. Patent 5,070,168, issued in December 1991 to O'Lenick.
13. Silicone taurines — U.S. Patent 5,280,099, issued in January 1994 to O'Lenick.
14. Silicone isethionates — U.S. Patent 5,300,666, issued in April 1994 to O'Lenick.
15. Silicone free radical polymers — U.S. Patent 5,120,812, issued in June 1992 to O'Lenick.

While many patents have been issued covering different aspects of surfactant production, many researchers are working in the area of product or process improvement. The creativity of these researchers will undoubtedly result in new and improved products and processes that result in better more reproducible products at lower costs.

Appendix I

"Three-Dimensional HLB"

This revolutionary development helps formulators choose surfactants for stable oil, water and silicone emulsions

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Today, silicone-soluble materials are an important aspect of emulsion technology. A growing number of silicone-based surfactants contain no hydrocarbon-based hydrophobes.[a] Other silicone-containing surfactants also contain hydrocarbon groups.

The development of the HLB — hydrophile/lipophile balance — system almost 50 years ago both simplified and systematized the selection of the optimal surface-active agent for a specific emulsification application. The system, proposed by Griffin[1] and widely promoted by ICI,[2] has provided formulators very valuable assistance over the years. Despite that, our ability to predict the performance of specific emulsifiers in the preparation of stable emulsions remains a formulating challenge.

Formulators truly need an expansion of the traditional HLB concept that will work with these new surfactants and anhydrous systems. We have developed a system that gives formulators a powerful tool to help them make stable emulsions using combinations of water-, silicone- and/or hydrocarbon-soluble ingredients.

Adding Dimension to HLB

The current HLB system has helped predict the emulsifiers needed for water-in-oil (w/o) and oil-in-water (o/w) emulsions. However, it has predicted the performance of silicone-based molecules less well and fails completely for those surfactants having silicone, hydrocarbon and polyoxyalkylene portions. Any attempt to expand the current HLB system must be able to assign meaningful values to the surfactants that contain all three of these chemical entities because each is insoluble in the others.

This mutual insolubility led us to design an HLB system that would consider oil, water and silicone solubilities to determine the emulsion properties of surfactants. Because of the three solubility parameters we consider, we call our system "3D-HLB."

[a]We will use the generic term "hydrocarbon" to designate the oil-soluble portion of the molecule. This generic term encompasses the more specific terms "fatty," "lipid" and "alkyl."

The Original HLB System

The HLB system was originally developed for ethoxylated products and, in fact, predicts emulsification properties best for alcohol ethoxylates — surfactants based on fatty alcohols modified by reaction with ethylene oxide (Figure 2-1). The system is also designed for emulsions containing water.

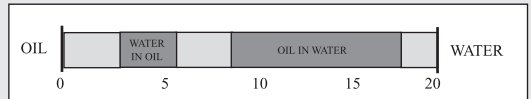

Figure 2-1. Traditional HLB scale

The current HLB system envisions two basic types of emulsions: oil-in-water (o/w) and water-in-oil (w/o). The phase listed first is the discontinuous phase, the phase that is emulsified into the other, continuous phase.

Bancroft postulated that the emulsifier forms a third phase, a film at the interface between the two phases being mixed together.[3] He also predicted that the phase in which the emulsifier is most soluble will become the continuous phase. The continuous phase must be the larger one; emulsions exist in which the discontinuous phase makes up a greater weight percent. A simple test: If the emulsion is readily diluted with water, water forms the continuous phase.

Calculation of HLB

The original system compares the ratio of the oil- to the water-soluble portions of a surfactant molecule. Table 2-1 lists some approximate HLB values for surfactants as a function of their solubility in water. Values assigned based on that table form a one-dimensional scale, ranging from 0 to 20.

Table 2-1. Some approximations for the HLB value for surfactants as a function of their solubility in water

Solubility in water	*HLB*	*Description*
Insoluble	4 - 6	water in oil emulsifiers
Poorly dispersible (milky appearance)	7 - 9	wetting agents
Translucent to clear	13 - 15	detergents
Very soluble	8 - 18	oil in water emulsifiers

In Adamson's *Physical Chemistry of Surfaces*, this statement appears: "The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far, however, the system tends to lose itself to complexities."[4] We agree with this and believe that a system that helps formulators select an emulsifier is of primary importance. A mathematical model that has been developed allows calculated approximations of HLB.

The HLB system, in its most basic form, calculates HLB using the following formulation:

$$\text{HLB} = \frac{\%\ \text{Hydrophile by weight of molecule}}{5}$$

For instance, oleyl alcohol (5 EO), with a total MW of 489 and a hydrophile MW of (5)(44) = 220, is 45.0 percent hydrophile. Dividing that by five, we get 9.0 for the HLB of oleyl alcohol.

Using such calculations, formulators can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates of which surfactant or combination of surfactants are appropriate to a given application (Table 2-2). When blends are used, the HLB can be estimated by using a weighted average of the HLBs of surfactants used in the blend. For materials not listed on Table 2-2, formulators should test the oil using specific blends of known emulsifiers to calculate the HLB needed to emulsify it.

The appearance of the resultant emulsion depends on the particle size of the discontinuous phase (Table 2-3).

Table 2-2. HLBs needed to emulsify some common cosmetic materials[2]

Acetophenone	14	Lanolin	12
Beeswax	9	Lauric acid	16
Benzene	15	Lauryl amine	12
Butyl Stearate	11	Mineral spirits	10
Carbon Tetrachloride	16	Nonylphenol	14
Castor oil	14	Oleic acid	17
Chlorobenzene	13	Orthodichlorobenzene	13
Chloronated paraffin	8	Petrolatum	7
Cottonseed oil	6	Pine oil	16
Cyclohexane	15	Toluene	15
Kerosene	14	Xylene	14

Table 2-3. Emulsion appearance related to particle size

Particle size (nm)	*Appearance*
> 1	White
0.1 -1.0	Blue-white
0.05 - 0.1	Translucent
< 0.05	Transparent

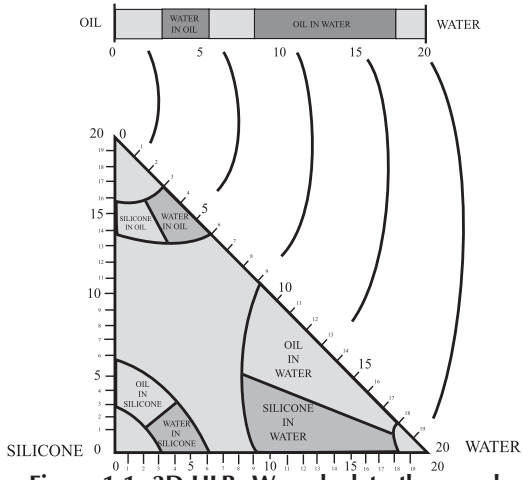

Figure 1-1. 3D-HLB: We calculate the x and y coordinates within our system (Table 1-1). Essentially, the silicone HLB becomes the difference between the x and y values. The corners of the graph are defined by the reference materials shown in Table 1-2.

Table 1-1. Calculation of coordinates for 3D-HLB

	% Water sol./5 (x coordinate)	*% Oil sol./5 (y coordinate)*
Standard hydrocarbon surfactant (standard HLB, on oil/water line)	50%/5 = 10.0	50%/5 = 10.0
Standard silicone surfactant (on silicone/water line)	50%/5 = 10.0	0%/5 = 0.0
Combination surfactant (three-dimensional)	30%/5 = 6.0	20%/5 = 4.0

Table 1-2. Materials defining the 100% soluble states for water, hydrocarbons and silicones.

Material	*x*	*y*	*x,y*
Mineral oil	0/5	100/5	0,20
Silicone oil	0/5	0/5	0,0
PEG 600	100/5	0/5	20,0

Our first efforts to build a new HLB model attempted to use a cube with x, y and z coordinates. However, such a system is conceptually difficult, and the mathematics are not easy to handle. Fortunately, experimental data solved our problem. As we worked with selected compounds, some of which appear in Table 1-4, we found that a much less complex system would work.

Because the standard HLB system has proven helpful and is widely recognized, we wanted our new system to expand on the existing one. We kept the 0-20 scale used by the standard HLB.

We discovered that we actually needed to calculate only two values, the weight-percentages of the water- and oil-soluble segments for the surfactant in question. Subtracting the sum of those from 100 percent, we obtained the percentage of silicone soluble. The standard HLB uses the calculation of % hydrophile/5; in fact, the standard HLB is the hypotenuse of our new system (Figure 1-1). Molecules with no silicone component will fall on that line.

The three sides making up our 3D-HLB triangle represent the three pos-

sible pairs of component types: oil/water, silicone/water and oil/silicone. We originally thought that the triangle would be equilateral. However, experimental data generated values best accommodated by the right triangle that we propose. You can clearly see that the hypotenuse, representing the standard HLB and connecting the 100 percent oil -and water-soluble loci, is longer than the other two sides. This difference in length seemed unsettling at first. However, silicone and hydrocarbon compounds are not equally hydrophobic at equal weight-percents. As we worked with the new system, we realized that this inequity explains why the standard HLB does not give useful values for silicone surfactants.

As we said before, the standard, water/hydrocarbon HLB line forms the hypotenuse. It connects the points for 100 percent oil-soluble (20,0) and 100 percent water-soluble (0,20) substances. All points on this line represent materials with no silicone portion; traditional surfactants fall on this line.

The silicone HLB line on the bottom of the triangle connects points for 100 percent

Formulas A–F Test Emulsions

	A *s/w*[a]	*B* *o/w*[b]	*C* *w/s*[c]	*D* *w/o*[d]	*E* *o/s*[e]	*F* *s/o*[f]
Silicone oil (350 visc)	15.0%	-	80.0%	-	80.0%	15.0%
Mineral oil	-	15.0%	-	80.0	15.0	80.0
Test surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water	80.0	80.0	15.0	15.0	-	-

Procedure: We added the test surfactant to the internal (discontinuous) phase under good agitation for 5 minutes. We then slowly added the continuous phase.

[a]Silicone-in-water
[b]Oil-in-water
[c]Water-in-silicone
[d]Water-in-oil
[e]Oil-in-silicone
[f]Silicone-in-oil

Table 1-3. Predicted values for test compounds

Compound Tested	*% Water sol.*	*% Oil sol.*	*x,y*
1. Dimethicone copolyol isostearate "A"	47.5/5	24/5	9.5,4.8
2. Dimethiconol stearate	0/5	15/5	0.0,3.0
3. Dimethicone copolyol isostearate "B"	32/5	20/5	8.0,4.0
4. Cetyl dimethicone	0/5	20/5	0.0,4.0
5. Dimethicone copolyol amine	19/5	0/5	3.8,0.0
6. Dimethicone copolyol isostearate "C"	55/5	10/5	11.0,2.0
7. Dimethicone copolyol isostearate "D"	48/5	16/5	9.6,3.2
8. Dimethicone copolyol amine "B"	27.5/5	5/5	5.5,1.0
9. Dimethicone copolyol amine "C"	20/5	75/5	4.0, 15.0
10. Dimethicone copolyol amine "D"	19/5	30/5	3.8, 6.0
Blends			
11. Dimethiconol stearate (and) steareth (2) alcohol	21.5/5	70/5	4.3,14.0
12. Dimethiconol stearate (and) steareth (2) alcohol	6/5	55/5	1.2,11.0
13. Dimethiconol stearate (and) steareth (2) alcohol	0/5	79/5	0.0,15.8

Silicone Surfactants

Ethoxylated silicone surfactants: In recent years, ethoxylated silicone surfactants have found a greater acceptance in emulsion preparation. Direct application of the HLB concept to these materials generates only an approximate value. Many manufacturers of silicone surfactants, rather than dealing with the differences between calculated and observed silicone HLBs, have stopped providing specific values and adopted the use of such nebulous terms as "high," "middle" or "low" to classify silicone HLB values. This approach simply begs the issue.

Blends: Most formulations that use silicone-based surfactants also have traditional hydrocarbon surfactants present. These blended systems present a challenge for formulators trying to predict emulsification properties. A recent paper dealing with the difficulties in predicting the behavior of silicone-based surfactants used with hydrocarbon surfactants concluded that, even when using silicone compounds of low molecular weight, there is "varying non-ideal behavior" depending on the type and concentration of the surfactants used.[5] This conclusion, while supported by the data, does not help the formulator.

Table 3-1. Comparison of fatty and silicone derivatives

Hydrocarbon-Based	*Silicone-Based*
Anionics	
Phosphate esters	Silicone phosphate esters
Sulfates	Silicone sulfates
Carboxylates	Silicone carboxylates
Sulfosuccinates	Silicone sulfosuccinates
Cationics	
Alkyl quats	Silicone alkyl quats
Amido quats	Silicone amido quats
Imidazoline quats	Silicone imidazoline quats
Amphoterics	
Amino proprionates	Silicone amphoterics
Betaines	Silicone betaines
Phosphobetaines	Silicone phosphobetaines
Nonionics	
Alcohol alkoxylates	Dimethicone copolyol
Alkanolamides	Silicone alkanolamides
Esters	Silicone esters
Taurine derivatives	Silicone taurine
Isethionates	Silicone isethionate
Free-Radical Polymers	
PVPquats	Silicone free-radical quats
Polyacrylates	Silicone/polyacrylate copolymers
Polyacrylamides	Silicone/polyacrylamide copolymers
Polysulfonic acids	Silicone/polysulfonic acid copolymers

Mixed silicone/hydrocarbon surfactants: To further complicate the situation, the market has experienced a virtual explosion of new silicone compounds (Table 3-1). These combine water-soluble polyoxyethylene, silicone and oil-soluble hydrocarbon components into one molecule. The introduction of these molecules and our inability to fit them into the classical HLB concept has resulted in confusion on how to use the new compounds.

silicone-soluble (0,0) and 100 percent water-soluble (0,20) substances. All points on this line represent molecules or mixtures with no hydrocarbon portion. Traditional dimethicone copolyol compounds fall on this line.

The vertical, oil HLB line connects points for 100 percent silicone-soluble (0,0) and 100 percent oil-soluble (20,0) substances. This last line predicts an interesting possibility not previously considered, emulsifying silicone and hydrocarbon oils as anhydrous products. While this clearly makes sense now, we had not originally contemplated such an emulsion definition.

With a triangular system, if one of the three groups is missing from the surfactant molecule or mixture, the calculation produces a point on one of the exterior lines. And, because no system can have less than 0 percent of an element or more than 100 percent of the other two, no points will fall outside the triangle.

Because one of the three paired component scales represents the standard HLB line, we adopted its 0-to-20 scale for all three sides. As we worked with the system, we clearly saw that predictions of the system qualitatively matched the compounds available. In addition, the system suggests new compounds to synthesize.

Table 1-4. Silicone surfactant performance in test emulsions

	Emulsion Formula					
Compound Tested	***A*** ***s/w***[a]	***B*** ***o/w***[b]	***C*** ***w/s***[c]	***D*** ***w/o***[d]	***E*** ***o/s***[e]	***F*** ***s/o***[f]
1. Dimethicone copolyol isostearate "A"	4	5	0	0	0	0
2. Dimethiconol stearate	0	0	0	3	5	0
3. Dimethicone copolyol isostearate "B"	5	2	0	0	0	0
4. Cetyl dimethicone	0	0	0	0	5	2
5. Dimethicone copolyol amine	0	0	5	0	0	0
6. Dimethicone copolyol isostearate "C"	4	2	0	0	0	0
7. Dimethicone copolyol isostearate "D"	5	3	0	0	0	0
8. Dimethicone copolyol amine "B"	0	0	5	0	3	0
9. Dimethicone copolyol amine "C"	0	0	3	4	0	0
10. Dimethicone copolyol amine "D"	0	0	0	0	0	0
Blends						
11. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	4	5
12. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	0	0
13. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	3	5

[a]Silicone-in-water
[b]Oil-in-water
[c]Water-in-silicone
[d]Water-in-oil
[e]Oil-in-silicone
[f]Silicone-in-oil

Experimental Confirmation

The 3D-HLB system predicts six types of emulsions, so we set up test formulas for each type (Formulas A-F). We evaluated emulsion stability on a scale with 5 representing a stable emulsion and 0, completely unstable.

We then tested the predictive value of the 3D-HLB graph by using a variety of surfactants we synthesized to cover a broad range of the possible silicone/water/hydrocarbon solubilities. We compared our predictions (Table 1-3) with the actual data (Table 1-4). The performance of the surfactants studied helped define the system boundaries.

Conclusions

The evaluation of silicone and mixed surfactant systems has led us to a practical modification of the standard HLB system. This modified 3D-HLB system apparently works for a broad range of emulsifiers and emulsion types.

Before devloping this system, we had not thought of making anhydrous emulsions with mineral and silicone oils forming the continuous phase. The 3D-HLB system not only predicts the existence of such emulsions (Formulas E and F), but identifies the surfactant molecules that will work in them.

The 3-D HLB system predicts an overlap in those materials that can make two closely related emulsions. For example, surfactants on the cusp between o/w and silicone-in-water (s/w) emulsions will have properties typical of each. This implies that these materials will be good emulsifiers for systems co-emulsifying both oil and silicone in water.

Using the 3D-HLB system will allow formulators to select the most suitable emulsifiers for w/o, o/w, s/w, water-in-silicone, oil-in-silicone and silicone-in-oil emulsions. By eliminating much trial and error and thus saving laboratory time, the system will be a valuable tool for the formulating chemist.

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"Applying the Three-Dimensional HLB System"

Tests varying the structure of a dimethicone copolyol surfactant molecule demonstrating the 3D-HLB system's predictive power

Anthony J. O'Lenick, Jr., and Jeffrey K. Parkinson

Formulators in the personal-care field have a vast number of traditional surfactants from which to choose in the preparation of new products. There are non-ionic, cationic, amphoteric and anionic products available. Each product class is composed of products with different functional properties. Within each class there are numerous products with specific formulation nuances. A novice formulator might ask, "Why are there so many types of surfactants?" The answer is clear. The structure of the surfactant determines the functionality. It is, therefore, not surprising that when scientists developed a series of surfactants containing silicone they found that the structure determined the properties of these new materials, just as it did with the traditional surfactants.

Silicone is unique when placed into molecules. It confers substantivity, lowers irritation and alters feel on skin and hair. When silicone is incorporated into a surface-active agent, with polyoxyalkylene and hydrocarbon portions of the molecule, unique emulsifiers result.

Recently, as an expansion to the 50-year-old hydrophile/lipophile balance (HLB) system, we proposed incorporating silicone as one of the components to make up what we call the three-dimensional HLB system, or 3D-HLB system.[1,3,4] To investigate the system further, we looked at the effect of introducing a fatty ester group onto specific dimethicone copolyols. Specifically, we were interested in the changes in solubility and emulsification properties that result as a consequence of the introduction of the fatty group into the molecule. We studied the following types of emulsions:

- Silicone in water (s/w)
- Oil in water (o/w)
- Water in silicone (w/s)
- Water in oil (w/o)
- Oil in silicone (o/s)
- Silicone in oil (s/o)

In this article, we compare the results of our evaluation with the predictions of the 3D-HLB system. The study tested molecules with no fatty group as well as molecules with a fatty ester group. The standard HLB system has been found to work least well with these types of molecules.[2]

The 3D-HLB System

The 3D-HLB system uses a right triangle to predict the effectiveness of various compounds in making emulsions. The 3D-HLB system assigns an x and y value to a compound. The x coordinate is the old HLB value. The new y coordinate is calculated using the percentage of oil soluble in the molecule. By definition, the calculations are as follows:

x coordinate = (% water soluble)/5 y coordinate = (% oil soluble)/5

This calculation gives the two values that define a point on the three-dimensional graph. The point will fall into a region that specifies a type of emulsion for which the molecule is predicted to be applicable.

Compounds

Dimethicone copolyol compounds: Compounds evaluated are branched dimethicone copolyols and isostearic esters thereof. The former conform to the structure in Figure 1-1. We varied the "n" value in that structure to get dimethicone copolyols with a variety of molecular weights.

Dimethicone copolyol esters: To obtain the best comparisons, we used esters that were based on the same polymer backbone as the dimethicone copolyols and also conformed to the structure shown in Figure 1-2, where R is isostearic.[a]

The use of a common silicone backbone for both the dimethicone copolyol and the ester results in molecules that vary only with the presence or absence of the isostearic portion. We will refer to the dimethicone copolyol compounds as DMC A through DMC E and the ester compounds as Ester A through Ester E. The nomenclature allows for a direct comparison. The compounds with the same letter designation are prepared from the same silicone backbone. Therefore, DMC A has the same silicone backbone as Ester A; the only difference is that the ester has the added isostearic portion of the molecule.

We calculated the percentage of water soluble, oil soluble and silicone soluble to ascertain the 3D-HLB value for each molecule. Then we compared the observed solubility properties of the resulting molecules, and their emulsification properties. Finally, we compared the emulsification properties with the predictions made by the 3D-HLB system.

We studied the compounds shown in Table 1-1. The compounds were all clear yellow liquids as prepared.

Testing

Solubility testing: We tested the 10 compounds in the following solvents for solubility at 5 percent by weight:

- Water
- Mineral oil
- Cyclomethicone
- Dimethicone

Emulsion testing: The 3D-HLB system predicts the following emulsion types:

[a]Lambent Tehnologies markets compounds of this type under the Silwax® trade name.

- Silicone in water (s/w)
- Oil in water (o/w)
- Water in silicone (w/s)
- Water in oil (w/o)
- Oil in silicone (o/s)
- Silicone in oil (s/o)

We prepared an emulsion system for each of the emulsion types (Table 1-2). In each case, we prepared the formulation by adding the test surfactant to the discontinuous (internal) phase under good agitation for five min. Then we slowly added the continuous phase.

We evaluated the emulsions on a 0-5 scale with five being a stable emulsion and 0 being completely unstable.

Results: Table 1-3 summarizes the results for solubilities in various solvents at 5 percent weight compound in solvent. Table 1-4 summarizes the results of the experimentation on emulsification properties.

Table 1-1. The test compounds

Compound	% Silicone soluble	% Fatty soluble	% Water soluble	3D-HLB x, y
DMC A	40.0	0.0	60.0	12, 0
DMC B	60.0	0.0	40.0	8, 0
DMC C	70.0	0.0	30.0	6, 0
DMC D	75.0	0.0	25.0	5, 0
DMC E	80.0	0.0	20.0	4, 0
Ester A	30.0	25.0	35.0	7.5, 5.0
Ester B	48.8	19.2	32.0	6.5, 4.8
Ester C	58.5	16.5	25.0	5.0, 3.3
Ester D	65.2	13.0	21.8	4.4, 3.2
Ester E	72.0	10.0	18.0	3.6, 2.0

Table 1-2. Formulations of the test emulsion systems

Material	S/W	O/W	W/S	W/O	O/S	S/O
Silicone oil (350 visc)	15.0		80.0		80.0	15.0
Test surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water	80.0	80.0	15.0	15.0		
Mineral oil		15.0		80.0	15.0	80.0
	100.0	100.0	100.0	100.0	100.0	100.0

Table 1-3. Solubility properties of test compounds

Compound	*Water*	*Mineral oil*	*Cyclo-methicone*	*Dimethicone (visc 350)*
DMC A	sol	disp	disp	ins
DMC B	micro	disp	disp	ins
DMC C	disp	disp	sol	disp
DMC D	ins	disp	sol	disp
DMC E	ins	disp	sol	disp
Ester A	micro	disp	disp	ins
Ester B	disp	trans	disp	disp
Ester C	disp	trans	sol	disp
Ester D	ins	trans	sol	disp
Ester E	ins	disp	sol	disp

Legend: micro = microemulsion; ins = insoluble; disp = dispersible; sol = soluble; trans = translucent

Table 1-4. Stability range of the test compounds

	Emulsion formulation (from Table 1-2)					
Compound	*S/W*	*O/W*	*W/S*	*W/O*	*O/S*	*S/O*
DMC A	3	1	0	0	0	0
DMC B	0	0	0	0	0	0
DMC C	0	0	4	0	0	0
DMC D	0	0	5	0	0	0
DMC E	0	0	4	0	0	0
Ester A	4	3	0	0	0	0
Ester B	0	0	0	0	0	0
Ester C	0	0	4	0	3	0
Ester D	0	0	5	0	4	0
Ester E	0	0	5	0	2	0

Legend: 0 = unstable (split in two layers); 5 = stable emulsion

Discussion

Solubilities: The tested compounds reveal several interesting trends:

- As the percentage of silicone in the molecule increases, the water solubility decreases. Molecules go from soluble, to micro emulsions, to dispersible and, finally, to insoluble. This trend occurs both in the dimethicone copolyol compounds and in the ester compounds. However, the presence of the fatty group in the ester further lowers water solubility of the molecule.
- As the percentage of silicone in either set of compounds increases, there is no effect on solubility in mineral oil. Incorporation of the fatty group into the molecule changes the mineral oil surfactant blend from milky white to translucent stable emulsions. Incorporation of fatty groups into the molecule improves oil compatibility.

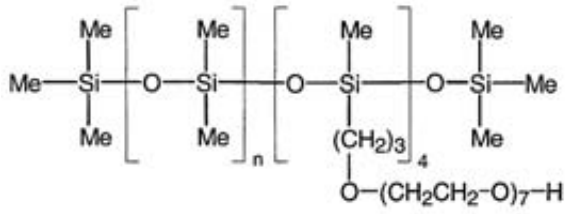

Figure 1-1. Dimethicone copolyol

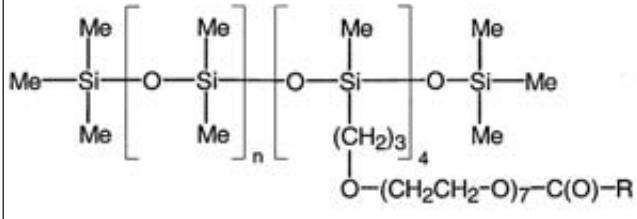

Figure 1-2. Dimethicone copolyol ester

- As the percentage of silicone in the molecule increases, the solubility in cyclomethicone increases. Molecules go from dispersible to soluble. This is true in esters and dimethicone copolyols. One compound (DMC C) is dispersible in water and soluble in cyclomethicone, and another (Ester B) is dispersible in both.
- As the percentage of silicone in the molecule increases, the dispersibility in 350 visc dimethicone increases. Molecules go from dispersible to insoluble. This trend occurs in the dimethicone copolyol compounds and in the ester compounds. However, the presence of the fatty group in the ester compounds improves dimethicone compatibility.
- The ratio of (a) silicone, (b) fatty and (c) water-soluble portion of the molecule alters solubility of compounds in various solvents. The trends are predictable. Consequently, it is possible to choose molecules for specific applications.

Emulsification properties: Figure 1-3 presents a graph based on the 3D-HLB theory. The figure shows the lines that are generated by connecting the 3D-HLB values of the dimethicone copolyol and the ester made from the same silicone backbone; that is, we join the 3D-HLB value for a lettered dimethicone copolyol with the 3D-HLB value for a similarly lettered ester.

Figure 1-3 shows that the inclusion of the fatty group not only increases the amount of fatty from zero, but also dilutes the other percentages. This is why the lines slope upward to the left. The slope of the lines decreases as one looks at lines A through E. The reason for this is that as you go from A to E the polymers have an

Table 1-5. Effect of esterification on the stability of dimethicone copolyols shown in Figure 1-1

Line	*Connects*	*Predicted*	*Observed*	
A	DMC A to Ester A	Improved S/W Improved O/W	S/W O/W	3 to 4 1 to 3
B	DMC B to Ester B	No change	No change	
C	DMC C to Ester C	Improved O/S	O/S	0 to 3
D	DMC D to Ester D	Improved O/S	O/S	0 to 3
E	DMC E to Ester E	Improved W/S Improved O/S	W/S O/S	4 to 5 0 to 2

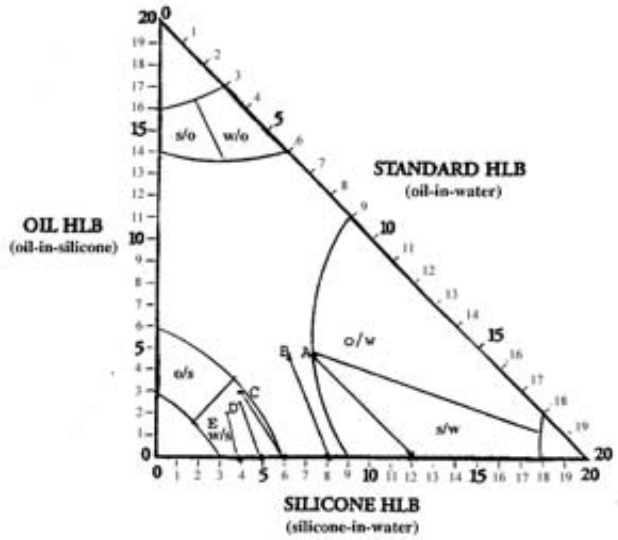

Figure 1-3. 3D-HLB plot of five pairs of a dimethicone copolyol and an isostearic ester with the same polymer backbone

Line A joins DMC A and Ester A
Line B joins DMC B and Ester B
Line C joins DMC C and Ester C
Line D joins DMC D and Ester D
Line E joins DMC E and Ester E

increasing amount of silicone in the molecule. Consequently, there is less isostearic needed to react on a mole-to-mole basis. This is also why the percentage of fatty continues to be lower as one progresses from A to E.

Figure 1-3 also predicts the effects of the alteration of structure on the emulsification properties. It is significant to look at what we call the "cusp surfactants." In each corner of the triangle are two regions that have a common line between them. These three pairs share a common border. They are (o/w : s/w), (o/s : w/s) and (s/o : w/o). A surfactant whose 3D-HLB value falls on these border lines is called a cusp surfactant. Cusp surfactants are predicted to be good as emulsifiers in both types of emulsions that share the common border.

The inclusion of the fatty groups into the molecules and the shifts that occur in the emulsification properties result in some near cusp surfactants. In Figure 1-3, the closest to the border line is Ester A. This material as predicted is good for making both s/w and o/w emulsions, unlike the dimethicone copolyol based on the same silicone backbone (DMC A). Esters C, D, and E are all closer to the cusp than the dimethicone copolyol sharing the common backbone. Consequently, they are predicted to be better emulsifiers for o/s than the dimethicone copolyol based on the same backbone. The way one would make Esters C, D and E true cusp surfactants would be to increase the amount of fatty in the molecule to fall on the border line between the o/s and the w/s regions.

Conclusion

We continue to believe that the predictions made by using the 3D-HLB system will be helpful in engineering emulsifiers that will allow for the formulation of complex emulsions. We have learned that if one makes an emulsion using the three-dimensional surfactants the emulsion can be emulsified into mixed emulsions using our system in two easy steps. This simplified process makes multiple-phase emulsions by making two simple emulsions one after another. We expect to address the multiple emulsion aspect of the 3D-HLB system in a subsequent work.

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Appendix II

Surfactant Interactions with Skin

A critical review of the adverse reactions of surfactants once applied to human skin and the mechanisms driving these reactions

Martin M. Rieger

A critical review of the adverse reactions of surfactants once applied to human skin and the mechanisms driving these reactions. The cosmetic industry's use of surface-active agents ("surfactants") is well-established. There is no need to enumerate the many beneficial cosmetic applications of surfactants, ranging from cleansing to emulsification. However, cosmetic scientists also know that surfactants can, at times, produce adverse reactions upon contact with skin.

There is general agreement among experts in the field that monomeric surfactants can penetrate the skin. (See "Surfactant Characteristics,"page 39, for discussion of micellar and monomeric concentrations.) Monomeric molecules are also the species that are initially adsorbed to the various surfaces within the skin, and we cannot ignore the secondary bonding by hydrophobic effects. Thus, the concentration of monomeric species probably plays a principal role in surfactant/skin interactions. However, in most testing, skin responds in a dose-dependent fashion to surfactant concentrations above the CMC. So far, investigators have not developed a plausible theory explaining this fact.

Skin

Human skin is designed to resist permeation by foreign materials. It has been described as a trilaminate structure. The principal barrier is the outer, hydrophobic stratum corneum (SC), a 20 m-thick layer; the other layers are the viable, hydrophilic epidermis and the dermis.1 This simple model may be adequte for some work,

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but it ignores variations within the SC and the keratinocyte (KC) epidermal layers, the source of SC cells. Molecules traveling through the skin encounter continuously changing layers within the SC and the epidermis.

Stratum corneum

The SC consists of interdigitated dead cells surrounded by a specialized epidermal lipid synthesized by KCs. The cellular material is routinely identified as "keratin," although it is an assembly of diverse filaments that includes a large number of nonkeratinous cross-linked proteins.

The surface of the skin is covered with the residues of sweat, sebum and metabolites created during SC formations. Depending on the proliferative cycles and the amounts of noncellular substances present, the surface may appear rough or scaly. Shedding of these topmost cells is biologically programmed and has not been thoroughly explained. The general assumption is that cosmetic products should encourage the removal of dead SC cells ("cell renewal") and minimize the precursor to this shedding ("scaliness").

Penetration of Surfactants

The currently accepted model of skin permeation restricts penetration to relatively small particles. Intact SC is, indeed, a barrier to microbial species, and the literature has not documented the penetration of substances with a molecular weight more than 3,000 D. Thus, micellar aggregates containing more than about 10 surfactant molecules should not be able to permeate the SC barrier.

Much has been said about the ability of liposomes and similar vesicles to penetrate the SC. Evidence is now accumulating that liposomes can reach KCs; the route of passage (at least in mice) is predominantly transfollicular.85

Drug Studies

Most current knowledge of skin permeation is based on information obtained during studies of drug penetration. Researchers believe that surfactant-induced irritation enhances a topical drug's ability to penetrate skin.9,10 They point out that SLS irritation does not impact the flux the same way at all concentrations or over time.

The penetration enhancement or interference by nonionic surfactants is reasonably well-documented but has not been rigorously explained.11 One explanation may be that the surfactant improves the wetting of hydrophobic SC, which may facilitate the transfer of the drug. Another explanation may relate to the surfactant's ability to wet various appendageal ducts within the skin. Solubilization of the drug is often cited, but a vesicular or solubilized drug system may be too large to penetrate the skin and may, in fact, interfere with penetration.12,13 Finally, the sorption of a surfactant on skin proteins may alter the skin's polarity and thereby reduce drug sorption or enhance permeation. The phenomenon is complex, and we lack a valid mechanism to explain penetration enhancement.

Sorption

During a compound's passage through the SC, some sorptive processes may occur. In addition, the molecules may undergo hydrolytic attack from enzymes in the skin.6 For example, the appearance of a surfactant fragment, SO4=, in a diffusion experiment does not prove that an intact alkyl sulfate molecule has permeated. It only indicates the ability of metabolic by-products to reach that location.

During passage of a surfactant through the epidermis, the monomolecular surfactant (or a premicellar aggregate) permeates first. Any binding or other attachment of surfactant molecules to skin shifts the monomer:micelle equilibrium in the bulk solution, reducing the percentage of the micellar species.

The specific nature of the epidermal sorptive processes is obscure. They may include various types of binding as well as multilayer phenomena. Only the surfactant molecules still unbound after all the epidermal (protein or lipid) sorption has been completed continue moving into the epidermis.

Overt toxic responses (erythema, allergic symptoms or corrosive effects) must involve the vascular dermis. These may result from the presence of surfactant molecules in the dermis or from messengers (cytokines) liberated by KCs.8 Once a substance reaches the KC layer, it may provoke adverse or beneficial biochemical events. Regardless of the pathway, lipid or hydrophilic pore, permeating molecules obey Fick's postulates (discussed in References 2 and 7). Unfortunately, we do not know much about the lipidic or polar characteristics of a surfactant molecule placed on the skin surface nor about the changing environment as the molecule passes through the SC. As a result, we can only speculate on why micellization does not limit concentration-dependent toxicity.

Concentration dependence

Adverse responses to surfactants are concentration-dependent. We have known for many years that the uptake (binding) of SLS to neonatal rat SC is concentration-dependent.3 This has recently been confirmed via more sophisticated techniques.4

Fullerton's human skin data regarding concentration effects on in vitro surfactant permeation exhibit much variability and require careful interpretation. All available data suggest that penetration into the dermis is low with aqueous solutions of 0.5% and 1.0% SLS (concentrations above the CMC). Only about 15% of the amount of SLS applied to full-thickness human skin in vitro reaches the KC layer after 24 hours. The amount of SLS found in the dermis in this type of experimentation is dose-dependent, although most of the surfactant remains on the skin's surface and in the upper layers of the SC.

Similar observations have been reported for other surfactants. Earlier in vivo data by Van Neste clearly demonstrate the dependence on SLS concentration of irritation, transepidermal water loss (TEWL) and skin capacitance.5

We still face the difficult task of explaining why a 0.5% solution of SLS is less irritating than a 5% solution, knowing they contain identical amounts of the presumptive irritating penetrant, the monomeric SLS molecule. Before we try to explain this conundrum, however, we need to examine some of the basic phenomena of skin permeation.

Impact on cosmetics

What is important to cosmetic formulators is the fact that the presence of a surfactant can alter skin permeation.14 While a cosmetic ingredient might be systemically absorbed if administered in combination with a surfactant, this is usually of secondary concern to cosmetic compounders. Cosmetic ingredients, as a rule, have little or no systemic toxicity. A few ingredients, such as some fragrance components or sunscreens, may be exceptions to this rule, particularly regarding potential allergic sensitization. However, the permeation of surfactants themselves clearly plays an important role in safety assessment.15,16,17

Formulators must remember that a surfactant's ability to enhance a drug's permeation is quite specific. For example, SLS does not enhance the permeation of methyl nicotinate, but about 0.5% to 1.2% SLS does enhance the permeation of hexyl nicotinate. Laureth-10 increases the permeation of methyl nicotinate in a concentration-dependent fashion; however, laureth-10 *reduces* hexyl nicotinate activity due to micellization of the drug.13

Surfactant-Initiated Swelling

Aqueous surfactant permeation of skin is not a simple static process. It probably is accompanied by extensive swelling of the SC.18 This water imbibition not only contributes to surfactant permeation but may even open sites big enough to allow micellar aggregates to penetrate.

Entry of foreign substances is generally described as either intercellular or transcellular. The diffusion of a substance through the SC, described as "passive," is controlled by Fick's laws of diffusion. This is, again, a simplistic picture. The exact mechanism or pathway by which a surfactant moves through the skin is obscure; it may simply follow a follicular duct. Skin may also possess hydrophilic or water "channels" that facilitate passage of hydrophilic substances (see, for example Ref. 2).

Some investigators have recently pointed out that holes (glandular ducts and hair follicles) in the SC play a significant role in transdermal penetration. As a rule, however, investigators have ignored the potential contribution of holes — the glandular and follicular ducts — and of lateral diffusion — diffusion parallel to the skin's surface. By following continuing studies in this area, we may ultimately learn how a basketball (the micellar aggregate) finds its way through several layers of chicken wire (the epidermis).a

Micelles or similar aggregates may form within the skin if concentration/solubility requirements are met. Ultimately, however, the surfactant may either be internalized by KCs or elicit responses from these cells without being internalized.

aThis analogy was first used by Dr. D. Lasic

Surfactant Characteristics

As a group, surfactants have two defining characteristics: the abilities to concentrate at interfaces and to form micelles.

Interface behavior

The accumulation of a surfactant at an interface is real. The concentration of a water-soluble nonionic surfactant at an interface (such as with air) is higher than its concentration in the bulk (aqueous) solution. Gibbs developed the thermodynamic argument for this phenomenon more than 100 years ago.

This accumulation is responsible for a variety of surface phenomena, such as wetting characteristics, lowered interfacial tension and, sometimes, a change in surface charge. By acknowledging a surfactant's attraction to different surfaces (lipid or proteinaceous) within the skin, we can better understand surfactant/skin interactions.

Micelle formation

The second characteristic of surfactants is their tendency to aggregate and form micelles. Micelles are not the beautiful, geometrically perfect structures often depicted in textbooks. They form and reform readily and have short half-lives. In aqueous systems, the size of the surfactant aggregates increases as concentration increases. Thus the often-quoted aggregation numbers must be viewed with caution.

There is general consensus that micelles — and this applies to the swollen micelles commonly associated with solubilization — are too large to penetrate the stratum corneum (SC). However, micellar instability constantly provides a source of individual surfactant molecules, which are small enough to pass through the network of skin cells. In addition, micellization (at least in cosmetic use) requires the presence of water. The loss of water after rubbing a micellar system into the skin is likely to modify any micellar system in the product, leaving behind a "dry" blend of surfactant molecules. An important consequence of this phenomenon can be the occasional failure of a closed-patch test to elicit the same dermatitic response as in-use testing.

The CMC

A surfactant forms micelles once its bulk concentration exceeds the critical micelle concentration (CMC). When two or more surfactants are present in a product, a phenomenon known as "mixed micelle formation" occurs. The CMC of the blend is different from that of each individual surfactant.

The CMC plays a key role in skin interactions. Its value drops with increasing hydrophobicity and controls the concentration of monomeric surfactants in aqueous systems. The CMC of sodium lauryl sulfate (SLS) is about 0.23%; in other words, an aqueous solution of SLS — regardless of concentration—— can contain no more than 0.23% monomeric SLS molecules. Quaternaries, such as cetyl ammonium bromide, have lower CMCs, about—0.1%. Ceteth-20 reportedly has a CMC of only 0.007%.

We know that water-induced SC swelling occurs in vitro. Swelling also results from closed-patch testing of aqueous products. However, we have no hard data on SC swelling during short-term (in-use) exposure to surfactant solutions, such as occurs during washing.

The in vitro swelling response to aqueous surfactants reportedly correlates with the propensity of surfactants to elicit skin tightness.19 Although researchers have made much progress in the past 10 years toward understanding the binding of surfactants to skin,18,20,21 we still cannot provide a scientific rationale for these correlations.

Attempting to demonstrate a correlation between SC swelling and irritancy, Rhein et al20 noted that the "extent of swelling does not correctly predict the irritation potential of all surfactants." Corneal swelling and the resulting morphological distortion do seem to parallel skin irritation.22 Nevertheless, we cannot conclude that corneal swelling is responsible for the observed irritational response to surfactant exposure.

Surfactant-Initiated Binding

Recently, Robbins et al proposed that both ionic and hydrophobic sorption processes affect the behavior of hair.25 This suggestion, based on hair-surface changes with surfactant treatment, probably applies to skin sorption as well. The theory is not well enough established to allow a good description of surfactant behavior based on pH or surfactant structure, but further work in this area should prove most useful for explaining sensory effects as well as the enigma of skin penetration.

Nonionic binding

There is general belief that nonionic surfactants, as a group, aid drug permeation through skin.11 Based on their hydrophobicity and their ability to form micelles or bilayers, however, this may be wrong. Current evidence suggests that oleth-10 and steareth-3 have limited effects on skin; only laureth-3 induced structural changes.24

Based on our general knowledge of substantivity, we could expect minimal binding of nonionic surfactants. Because they carry no charges, they should not interact with polar protein molecules. However, they are capable of forming all types of hydrogen and hydrophobic bonds with skin components, especially lipids. They are probably soluble in epidermal lipids and may modify the skin's physical properties as well as alter penetration.23

Penetration changes depend on several factors: the nature of the system (solution, emulsion or vesicle), the physical nature of the preparation (gel or liquid), and the nature of the film left on the skin after inunction. Thus, investigators should avoid generalizations about the impact of nonionics on skin because of the wide variation of nonionics, as evidenced by their HLBs.

Anionics

The penetration of anionic surfactants has been extensively studied. Within the SC, anionics can react with postively charged sites. It is more likely that bonding

occurs via hydrophobic binding.20 Because hydrophobic binding of anionics should produce new polar sites in the SC, this mechanism may play an important role in SC swelling.

Other surfactants

Cationics probably react with anionic sites in the SC, creating a more-hydrophobic membrane accompanied by less-extensive swelling.20 Transdermal permeation of quaternaries is slower and lower (based on mole surfactant/g of skin) than that of anionics.

Amphoterics must be examined individually and at specific pHs. In the cosmetic and dermatological literature, certain quaternaries are commonly misidentified as amphoterics. It is hazardous, therefore, to base information concerning substantivity on these doubtful chemical characterizations.

In summary, permeation of surfactant molecules is dependent on concentration and is compound-specific. The first step is adsorption of the surfactant to active sites within the SC. Once this "substantivity" has been satisfied, any additional permeating surfactant molecules can be expected to find their way into deeper skin strata. The supply of surfactant required for deep permeation can theoretically originate from single or multiple dosing but probably requires the presence of monomolecular surfactants or those with low aggregation numbers.21

Skin-Testing Surfactants

Almost two decades ago, Frosch and Kligman noted the many benefits accruing to humans from the regular use of surfactant-based cleansing products.26 Nevertheless, as a group, surfactants are identified as bad for the skin.

Following World War II, extensive studies of the transdermal penetration of surfactants documented the widely held belief that these materials can damage skin. Skin responds to surfactant exposure in many ways. Scaling, roughness, dryness, itching, redness and tightness are symptoms of surfactant usage readily identified by clinicians or commonly reported by consumers.

The intensity of the observed response depends on the type of exposure. The most severe responses occur after repeated closed-patch testing; casual use followed by rinsing may be totally asymptomatic.

Thus, investigators have devised testing protocols to differentiate the ability of surfactants or mixtures of surfactants to elicit adverse reaction on normal or compromised skin. Batteries of tests, such as patch tests, washing and scrubbing tests, and extensive use tests, are employed to provide a broad experimental basis for the conclusion that some surfactants, including soaps, can damage the skin.

Test Protocols

Test protocols for examining the innocuousness of surfactants, surfactant blends or finished products are important tools for all distributors of products containing surfactants. Test protocols deal not only with the details of the product's application to the skin but commonly specify one or more of the parameters used to assess the results.

Many reasons have been advanced to explain the adverse effects of surfactants. Soap has been implicated in disruption of the protective lipids on the skin surface. The results of exhaustive testing have been interpreted on the basis of pH or fatty acid composition. Recently, though, the impact of pH has been questioned.27 Soap chamber tests have shown that certain adverse responses (scaling and erythema) to normal use are predictable and that some soap formulations are less damaging tham others.26

The technical literature fails, however, to explain why the normal use of soap during warm weather is less likely to produce adverse effects (itching and scaling) than similar use when it is cold and dry. We might almost conclude that routine soap usage is "safer" in Florida than in northern Minnesota. Evidently, the adverse effects from surfactant use are — in part — dependent on the skin's condition before exposure.

There is no one test universally accepted to examine a surfactant's potential for irritancy or damage. Rather there are invasive, in vitro, acute and subacute tests. Selection is commonly dictated by cost or marketing considerations. As a result, cosmetic scientists and evaluating clinicians trying to select the most meaningful and cost-effective protocol face a complicated task.

Table 1. Testing parameters

To predict and assess effects of surfactants on skin (in vitro or in vivo)
Transepidermal water loss (barrier integrity)
Cutaneous blood flow volume (Laser-Doppler)
Dielectric constant (capacitance/impedance)
Patch/Soap chamber (quantitative)
Cytotoxicity (vital staining)
To quantify surfactant-induced skin damage
Skin lipid loss (sebaceous and intercellular)
Amino acid loss
Acid phosphatase loss
Skin thickness (hyperplasia)
Visual scoring (color, roughness)
Surfactant sorption
Skin pH
Eicosanoid formation
Langerhans formation
ICAM-1 increase
Tightness

The criteria for assessment can range from erythema to roughness and may include attempts to assess TEWL, scaling or even water content after exposure. The rules of the game are variable and subjective. For example, in a protocol requiring dilution of the product with water, is it justifiable to compare shampoos differing only in fragrance or preservative using a 24-hour closed-patch test? The hapless formulator is frequently forced to modify compositions on the basis of data obtained during overly stressful protocols.

Despite such uncertainties, predictive safety testing of surfactants and surfactant-containing products is widely practiced. The results guide product development and are used in promotional efforts. However, test protocols are highly variable:

- Subjects may be exposed to a surfactant in any one of many different ways.
- Tests may use different body sites or scrubbing procedures.
- Skin may have been previously manipulated through repeat usage, patch-testing or other procedure.

Prior or repeated exposure of a skin site to slight damage had been associated with less exuberant irritation responses due to

"hardening." Recent studies by Patil et al suggest, however, that, in the case of SLS, repeat patch-testing on the same site can enhance irritation.28

Assessing test results

Some of the more popular measurable parameters for assessing irritation or damage appear in Table 1. Irritative symptoms resulting from surfactant exposure are relatively easily identified without recourse to instrumental procedures.29 However, examiners generally support their observations of skin irritation through a series of noninvasive tests. One monumental review of these procedures (with 124 references) describes the techniques used to support a diagnosis of contact dermatitis.29

As with most toxicological testing, tests for surfactant irritation are designed to elicit responses on or in the skin. Investigators then attempt to find an explanation for a given response and to quantitatively rank irritancy. Unfortunately, relatively few surfactants have received such scrutiny. Even soaps have received only a fraction of the attention given alkyl sulfates. Today, research-oriented investigators expend more effort on understanding the mechanisms of contact dermatitis induced by SLS than all other surfactants combined. Yet, despite all the work, our current understanding of how even SLS damages skin remains woefully inadequate.

Some useful protocols

TEWL, cutaneous blood flow volume (CBFV), and arm immersion tests (with or without scrubbing) have yielded pertinent conclusions.30-37, 42 As a rule, investigators combine instrumental methods with visual or morphological observations. On this basis, Van der Volk et al.31 ranked the irritancy of several surfactants:

SLS>cocobetaine>sodium laurate>polysorbate 40

Like other investigators, the authors meticulously detailed the patching procedure but failed to provide a precise chemical description of the test substances.

Numerous other investigators found use of multiple parameters in an assess-

ment helpful.37,39-41 Kawasaki et al emphasize the value of visual scoring after exposure.38

Assessing surfactant irritancy using in vitro cell-culture techniques is complicated by questions concerning exposure and cell response.43,44 The viability of cells in a dilute surfactant solution may not reflect a surfactant's impact on cells in vivo since the skin's response may not be to the surfactant but to some unknown cytokine. These tests deliberately overcome the concentration gradients that exist in vivo, and our current knowledge is insufficient to base a surfactant's in vivo irritancy exclusively on in vitro data.

Choosing Surfactants

Test chemical purity

An important and widely ignored variable in determining irritancy is the quality of the test chemical. About 5 years ago, Agner et al. reported that some grades of SLS were more irritating than others on the basis of TEWL and CBFV results after patch testing (24 hours, 2.5% active).52 High-pressure liquid chromatography data disclosed that the grade with the highest level of non-C12 alkyl sulfates was less irritating than a grade with essentially only C12 alkyl sulfates. The authors concluded that researchers should identify the purity of test materials because substances of high purity are required to obtain comparable test results.

This reasonable proposition has been ignored in dozens of subsequent publications dealing with skin alterations induced by alkyl sulfates. The cause of the variability remains obscure, but investigators persist in conducting ever-more-sophisticated tests with commercially procured surfactants of unchecked purity.

The critical role of a test substance's purity was established during the in vitro testing of the swelling of human SC.20 Although there is no cause-and-effect evidence linking irritancy and swelling, swelling is a measurable parameter for documenting interactions between SC and a surfactant solution.

This study showed that the swelling response of SC to 1% solutions of alkylbenzene sulfonates, olefin sulfonates and alkyl sulfonates peaked for C12 or C14 alkyl chains. The swelling of human SC by alkyl sulfates also peaks at C12.18,53 Swelling due to alkyl trimethyl ammonium bromide exposure was not dependent upon chain length and was unexpectedly low.

Less troubling is a report examining cocamidopropyl betaine.54 This surfactant can be expected to contain impurities that may contribute to irritation. The authors report that irritation responses, possibly related to the presence of amidoamine, varied from lot to lot. In addition, they found no dose-dependency as measured visually by TEWL or by CBFV. These are important findings, especially since betaines, as a group, reportedly lower alkyl sulfate irritancy.

Mixtures

Safety testing requires identifiable and essentially chemically pure surfactants. Mixtures are, however, routinely studied whenever investigators attempt to modify the irritative qualities of a surfactant by mixing it with a second surfactant.39 This

is a particularly interesting approach when it comes to alkyl sulfates. For example, the industry has known for some time that the irritative qualities of SLS can be reduced when mixed with a nonionic (ethoxylated) surfactant.

Goldemberg described the use of anti-irritants about 30 years ago.45 He cited the patented use of lauroyl sarcosinates, potassium cocoyl hydrolyzed collagen, sodium cocoa-mphoacetate and lauryl dimethyl amine oxide to reduce skin/eye irritation from typical anionic detergents. But, although formulators knew of this phenomenon for many years, they could not offer any rational explanation.46

Today, after extensive studies of SC swelling and of protein denaturation by surfactants,47 there is general agreement that Faucher and Goddard's early interpretation of this phenomenon is correct.3,38,39,48 Briefly, the mixed micelles of blended mixtures reduce the concentration of the irritating, monomeric surfactant species. There is a general pattern suggesting that the anti-irritant effect increases with increasing degree of ethoxylation. However, the "detoxifying" surfactant need not be nonionic; substances such as sodium lauroyl glutamate, alkyl ether sulfates or alkyl ether carboxylates also work.

A recent example of the successful application of this principle was provided by Lee et al.49 Patch tests using blends of SLS and sodium lauroyl glutamate (SLG) revealed (via visual scores and TEWL measurements) that SLG reduced the irritancy of SLS in a dose-dependent fashion. Other studies have provided similar data on the reduction of SLS-induced irritation with the addition of other surfactants.20,39,47,50,51

Site Selection

Site of testing and the subject's age are additional variables investigators must control. Again, published studies are limited to SLS. Some of the more recent studies are those by Elsner et al55 and by Cua et al.56 The test parameters included visual scoring, TEWL and capacitance after closed-patch testing.

Although they found vulvar skin to be more responsive than forearm skin, the differences in regional responses were unexpectedly erratic. TEWL data did not correlate well with clinical grading. The TEWL of ankle and palm skin was less affected (as a percentage) than that of the upper arm, thigh, back and abdomen.

Damage assessed by TEWL appears to be a function of the site's lipid content. Interestingly, SLS damaged the skin of the aged (74.6 ± 1.9 years) less than that of the young (25.9 ±1.4 years).

Within the skin

While the literature on site variations of irritation is quite comprehensive, it is less certain about what portion of the skin is responding to the insult. However, this information is critical for assessing the value of various techniques for measuring surfactant-caused skin damage.

Table 2. Surfactant ranking on the basis of tightness (maximum to minimum)

SLS
Sodium dodeceth-2 sulfate
TEA cocoyl glutamate
Potassium myristate
TEA lauryl phosphate

This problem was addressed by a study of facial cleansing products and one soap.57 Simion et al used TEWL and photographic erythema measurements after soap-chamber testing for one or two days. Their results were not startling, but their interpretation is noteworthy. TEWL increased within the first day of testing, while erythema (with the exception of soap) did not reach significant levels until the second day. The investigators concluded that TEWL, as a response to barrier damage, is a more sensitive and earlier predictor of irritation than erythema, a sign of increased blood flow in the dermis. They also consider TEWL the most sensitive tool for differentiating among mild (non-irritating) cleansing products.

Test procedures (and user responses) can frequently, as in the previous example, identify the level in the skin at which damage has occurred. The most important point is the sequence of irritation responses. This, in turn, depends on the depth of surfactant penetration. A similar conclusion was reached a few years earlier by Patrick et al,58 who studied a number of irritants, including benzalkonium chloride, in mice.

The SC's hydration level, as assessed by TEWL, also shows some time-dependence related to the presence of surfactant.42,59,60 After occlusive patch testing, TEWL is elevated for some time before the skin equilibrates with the ambient humidity.60 After a dry patch (patching with no test material), the increased TEWL persists only about 30 minutes. After patching with water, the TEWL decreased significantly between 60 and 180 minutes. TEWL after 24-hour patch-testing with 0.5% SLS solution remained elevated for at least 3 hours, suggesting more permanent barrier disruption.

In-Use Observations

Users experience and clinicians readily observe phenomena resulting from the irritative impact of surfactants on skin. The technical descriptors used can be misleading. "Rough skin" is a well-defined syndrome. The symptoms may include scaling and even cracking.

Tightness

Another common report is of taut and stiff skin, possibly related to some poorly defined rheological characteristic of skin. Soap-treated skin is reported to be stiffer and less resilient than skin treated with a mild detergent bar.61 The physical nature of this phenomenon has received insufficient attention.

Presumably, the reported stiffness reflects the need to exert greater-than-normal force to effect a given facial movement. We know nothing about the skin layer that plays a role in this tautness. Swelling (by the imbibition of water) should make SC more compliant. A more likely — but totally speculative — cause might be some unknown change in the SC resulting from drying out after surfactant-induced swelling.62

About 10 years ago, researchers made a serious effort to understand the tightness subjects reported after brief exposure to 5% solutions of SLS, sodium laureth-2 sulfate, TEA cocoyl glutamate, potassium myristate and TEA lauryl phosphate.19 The results are surprising since the testers ranked tightness in an

unexpected order (Table 2).

The soap had a pH of about 10.8, while the other surfactants exhibited pHs near neutrality. The authors attempted to explain these observations based on the elution of amino acids, the solubilization of skin lipids and surfactant sorption. They found some correlations between these parameters and tightness but could not establish a cause-and-effect relationship. It is interesting that TEA cocoyl glutamate caused little or no sensation of tightness compared with SLS, especially since it has also been found to be less irritating than SLS.49

At about the same time, Prottey and colleagues reported that the reduction of acid phosphatase during hand-dipping experiments with 0.1% solutions of four surfactants correlated with skin dryness.63 Some of their data are shown in Table 3. While we cannot refute the documented correlation, we must also reject the notion that the acid phosphatase assay is a means for assessing or predicting surfactant irritancy.

Erythema

Erythema (redness) is clearly evident to all observers and has been measured by all types of techniques. Erythema is evidence of inflammation due to an increased blood flow in the dermis. Research has not yet identified the trigger for this response. At the moment, investigators believe that this reaction is due to cytokines and similar substances elaborated by KCs in response to surfactant exposure.8

Dryness

The least understood and frequently misidentified skin response is dryness. Reports suggest that dryness and tightness are early responses, occuring long (hours) before erythema or even in the absence of any inflammatory response.21

Ironically, most investigators of surfactant/skin interactions report excessive hydration of the skin. TEWL remains elevated for some time after the surfactant is "removed" from the skin, yet the phenomenon of dryness reportedly persists. Dryness is at times equated with tightness; at other times, with scaling. Cause and effect remain confused, and dryness is sometimes related to the absence (or reduction) of skin lipids. Only a few voices cry in the wilderness, suggesting that the word "dryness" always refers to a lack of water. Scientifically, dryness should never be postulated without an accompanying water assay.

Table 3. Relationship of acid phosphatase to skin dryness

Solution	Acid phosphatase remaining	Hand drying score (units)
Water 94.9	11.8	
Sodium laurate	74.8	13.2
Sodium lauroyl isethionate	63.6	15.8
Sulphated alkylate	3.8	23.8
ABS	9.5	20.5

The Search for a Mechanism

Our ability to eliminate or at least reduce the adverse effects of surfactant treatment on skin depends to a large extent on our understanding of the mechanism. At this time, there is no compelling evidence that any of the symptoms elicited or studied in testing programs are directly responsible for the skin stigmata of surfactant exposure.

Surfactant sorption

Sorption to sites in the epidermis has already been described in some detail. The sorption-dependent changes in SC or viable epidermis properties may play a role in eliciting symptoms. Imokawa and his collaborators consider keratin's sorption of surfactants a primary cause for skin tightness and related phenomena.64,65 This postulate is in accord with the speed with which adverse phenomena occur and remains a viable option, although no mechanism for tightness is currently available.21

The tendency for surfactants — at least SLS — to be sorbed appears to be a function of the solvent. Almost 20 years, ago, Gracia-Dominguez et al reported that, with wool, SLS sorption was markedly reduced when they used a solution of 50:50 ethanol:water instead of pure water.53 Because blends of water and hydrophilic solvents reduce keratin swelling, the degree of surfactant sorption may be tied to the extent of skin swelling.

Swelling and superhydration

These phenomena may play a critical role in surfactant/skin interactions. They are likely to cause profound changes in the skin's structural integrity and thus could be responsible for incipient skin damage.

Some of the testing protocols to study swelling in vivo are rather complex. Short-term open-patch testing for several days may be followed by occlusion.66,67 After occlusion for 24 hours, the evaluation of relative surfactant irritancy is then based on visual scoring and TEWL or skin-surface water loss (SSWL — the sum of TEWL and the post-occlusion drying-out process). Of the surfactants tested in this program, SLS had the highest SSWL, implying maximum irritancy. A commercial blend (cocamidopropyl betaine 23%, an unidentified alkylaminoethylglycine 2%, an alkylamidomethyl monooxide 0.7% and lactic acid to pH 5) had a lower SSWL. Less damage resulted from exposure to cocamidopropyl betaine, followed by benzalkonium chloride. Sorbitan monolaurate produced no SSWL elevation.67

The SC hydrates rapidly, within minutes of an application of alkylsulfate under occlusive patching, with SSWL and corneometer readings sharply elevated. The change toward normal SSWL can be followed readily and is a measure of skin barrier damage.68 Sodium octylsulfate causes only a slight increase in SSWL. The decyl and tetradecyl homologues cause much more dramatic changes in SSWL; the dodecyl homologue is the most aggressive. Numerous studies have provided a rank order of these materials over the years. Even so, it is comforting to learn that reliable parametric procedures confirm this irritancy rating.

In summary, there is no reason why surfactant-induced swelling could not account for the phenomena of skin damage. The process is relatively rapid, and the

return to normal TEWL values is delayed by the presence of SLS.

Lipid removal

Removal of lipids due to solubilization or detergency is, intuitively, a most attractive mechanism behind skin damage. It is also in accord with all reports of surfactants damaging the skin's barrier. The early history of this concept and its possible links to skin damage and irritation was reviewed by Froebe et al.69 Imokawa and associates19 have consistently viewed lipid removal as a major contributor to surfactant-induced skin damage.

In recent years, however, many prominent investigators have rejected lipid removal as a possible mechanism. Fulmer and Kramer70 were among the first who failed to find evidence that surfactants degreased the skin. Similar results were reported by Lévêque et al32 and Fartasch et al.71

On the other hand, SLS and LAS, which are relatively poor solubilizers even above their CMCs, were the surfactants of choice in studies of lipid removal.

Particularly disturbing is the neglect of a report by Dykes and associates,72 who studied the effects of octoxynol-9. The authors reported isolating a nonionic, detergent-soluble lipid from human SC. The extraction conditions are evidently critical; in this study, collecting the lipid involved scrubbing the skin with a dilute, nonionic surfactant, a procedure that can be faulted.

A recent study by Rawlings et al85 supports the hypothesis that lipid removal may contribute to skin damage. The authors reported lipid removal from the SC's topmost layer during soap-induced winter xerosis. The reported loss of ceramides was associated with some increase in fatty acid levels and was accompanied by defects in desquamation, disorganization of lipids in this SC layer, and reduced desmosomal degradation.

This study was limited to the skin on the backs of women's hands. The authors did not identify the composition of the soap tested nor the climatic conditions during the study's 1-week period.

At this time, it seems necessary to re-examine lipid extraction as a possible contributor to skin damage. It is likely that conditions may exist under which a suitable solubilizing surfactant might elute some lipids from the skin. We know that lipid removal by organic solvents results in skin damage. There is, however, scant evidence that skin-lipid loss — if any — during in-use surfactant exposure is responsible for skin damage.

Lipid synthesis changes

SLS modifies lipid synthesis and composition within human skin.70 Repeated exposure of human skin to SLS does not alter the total amount of SC lipid but causes the symptoms of rough, scaly skin. However, the distribution among the skin's ceramide species was altered. This change in the ceramide profile is probably the result of an SLS-induced alteration in keratinization. Although the total cholesterol content is not modified, the ratio of free:esterified cholestrol is changed from 2.3:1 to 3.4:1. In addition, SLS exposure significantly reduces the amount of long-chain (C22-C28) fatty acids. The data clearly suggest that SLS exposure has an effect on skin lipids and that this is reflected in barrier integrity.73

A different skin lipid modification — an increase of phospholipids in human skin when treated with polysorbate 85 — was reported earlier by Mezei.74 The location of this (about 3%) higher phospholipid content was not identified but appears to be primarily in the upper portion of the epidermis. The data suggest that a nonionic surfactant may interfere with phospholipid hydrolysis during terminal differentiation.75,76

Lipid disorganization

The idea that surfactants can disturb the SC's lipid structure is relatively new. Ribaud et al examined the effect of heat denaturation and of surfactant (SLS) exposure on the structural organization of ceramides in skin.77 The resulting disturbance of barrier function is in accord with the results of TEWL measurements and related observations.32

Protein denaturation

Black reviewed denaturation.17 By assessing changes in the specific rotation of a soluble protein (bovine serum albumen) in the presence of various surfactants, denaturation can be correlated with some of the skin-roughness and protein denaturation phenomena caused by surfactants:65

SLS > linear alkylbenzene > a-olefin
sulfonate > laureth-7 sulfonate

Harrold used an entirely different approach about 40 years ago. He examined the release of SH groups in keratin under the influence of surfactants.78 He ranked them:

SLS > linear alkylbenzene sulfonate > soap > talloweth-10

Surfactants are known to denature enzymes (such as acid phosphatase), but no data are available suggesting that this inactivation plays a role in skin damage.63 Proteins in the SC are presumably insoluble and unrelated to the bovine serum albumen tested by Imokawa.64 However, Harrold's finding is more suggestive of actual use conditions and could relate to skin damage and irritation.78

Cytokine formation

Cytokine production is probably is the only mechanism that can directly account for inflammatory responses. Whenever the skin's barrier function is perturbed, KCs respond by generating a cascading series of cytokines.8 These substances are primarily responsible for inflammatory responses and erythema.

Cultured human epidermal KCs generate proinflamma-tory cytokines (such as IL-8) in the presence of 5 mg/ml of SLS. The activity of this (and related) inflammogens was monitored during a mouse ear swelling test using SLS and benzalkonium chloride.79 The response of the KCs is not unexpected and is similar to the reported histamine release from rat peritoneal cells under the influence of various nonionic surfactants.58,80 Guenicne and Ponec report human cell cultures readily liberate interleukin-6 in the presence of surfactants.81 The basis for this phenomenon is fully supported by in vitro studies.82

Imokawa has observed a dose-dependent increase in the expression of ICAM-1 when human KCs are grown in the presence of surfactants.83 The differing

response to different surfactants is unexpected since cells appear to be more reactive to the presence of an isethionate than of SDS or soap.

Despite the excellent data on cytokine elaboration by KCs, the resulting inflammatory response develops relatively slowly and probably cannot account for the sensation of tightness or the increased TEWL observed shortly after contact with surfactants.

There is ample evidence that skin damage from normal surfactant use is accompanied by biochemical changes within the skin. These changes may precede, occur simultaneously with or follow the observable symptoms of skin damage. So far, no direct cause-and-effect relationships have been established. For example, SLS exposure is known to induce p53 protein expression, but no one has suggested that this tumor suppressor is related to skin damage.

Relative Irritancy of Surfactants

It is next-to-impossible to rank various surfactants on the basis of their irritancy. Unreliable rankings are the rule and result from:

- Different test protocols (site, concentrations)
- Different end points (roughness, scaling, erythema, tightness)
- Different grades of the same chemical compound

Even under the best circumstances, relative rankings are hazardous. As an example, you might conclude from the published data that surfactants should be a cause of concern. If soap were a modern invention, I venture to guess that it would be introduced to the public only under some sort of control. However, despite all adverse publicity and continuous brainwashing, the use of soap — the earliest surfactant developed — has persisted.

In fact, under normal-use conditions (short exposure, low concentration, casual use and water rinsing), it is difficult to obtain overt clinical symptoms on the skin of healthy subjects. Daily shampooing does not appear to be associated with obvious skin damage. Hundreds of millions of shavers expose their facial skin to a variety of soaps daily. Despite somewhat scary results of shampoo or soap patch-testing, these products seem well-tolerated.

The holy grail for cosmetic chemists would be a simple means for overcoming all types of skin reactions to surfactants. Some progress has been made by blending surfactants. Use of some monoglycerides and a (human) skin extract of mixed ceramides has also been suggested to modify irritant reactions to surfactants. Much has been written on the ability of protein fractions to reduce skin damage. These benefits are the result of purely empirical experimentation based on the investigator's intuition.

The most practical and simplest approach to avoiding surfactant irritation might be avoiding unnecessary surfactant use. For many years, our industry and companies engaged in the sale of household cleansers have tried to convince consumers that foam quantity and quality affect the quality of cleansing. This is an invalid assertion; foaming is not a prerequisite for cleansing. Deliberate avoidance of

foaming in topical cleansing products would go a long way toward the creation of kinder-to-skin products.

Conclusions

Investigators have studied the adverse effects of surfactant exposure on skin for many years. Severe adverse symptoms occur after prolonged or repeated patch testing, especially with the research emphasis on the effects of anionic surfactants, particularly SLS. Short-term exposure (with rinsing) results in much less severe reactions and is of greater importance to cosmetic practitioners. Damage ranges from mild scaling to noticeable erythema, reflecting the sites within the the skin that respond to the insult.

There is no evidence to suggest that all surfactants have the same adverse effects or elicit identical responses. The responses of different anionics can range from no effect to severe damage; irritation (as opposed to overt toxicity) from cationics seems less common than from anionics. The diversity of nonionics (as evidenced by their HLBs) precludes any type of generalization. Few nonionics have been carefully studied, and reactions to ethoxylated ethers may be different from those to ethoxylated esters.

No mechanistic interpretation of responses to surfactant exposure exists, although some correlations between measurable parameters and irritation responses have been reported.

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Appendix III
Analytical Methods

Table of Contents

Methods M–001 through M–020 provided with permission from Lambent Technologies Corp., Skokie, Ill.

ANALYTICAL METHOD

M–001—Appearance

Scope: This method applies to all products.

Summary: The sample is heated to the desired temperature. Once the temperature is reached, the sample is removed from the heat source and observed. A description similar to those illustrated in Table I below should be reported.

Apparatus: 1. Programmable oven.
2. Steam bath.
3. Thermometer capable of reading °C and °F.

Reagents: None required.

Procedure: Loosen the cap on the sample and place the sample on a steam bath or in an oven set for the desired temperature. Remove the sample occasionally and mix well. Check the temperature of the sample using a thermometer. Once the desired temperature is reached, remove the sample from the steam bath and observe for appearance. Use Table I to assign an appearance.

Calculations: None required.

Safety: The heated samples may cause burns. Use caution when handling.

Table I—Appearance Classifications

Classification	Description
Sparkling Clear	No visible haze or Tyndall effect in the black box.
Clear	No visible haze in ordinary lighting, but may exhibit a Tyndall effect in the black box
Slightly Hazy	No visible haze in ordinary lighting but visible in fluorescent lighting.
Hazy	Visible haze in ordinary lighting.
Opaque	Liquid or solid through which one cannot see.

ANALYTICAL METHOD

M–002—Acid Value

Scope: This method applies to animal and vegetable fats and oils and various products derived from them.

Summary The acid value is the number of milligrams of potassium hydroxide necessary to neutralize fatty or rosin acids in one gram of sample. The sample is weighed into an Erlenmeyer flask, diluted with neutral alcohol and titrated with 0.1N methanolic potassium hydroxide (KOH) or 0.5N aqueous sodium hydroxide (NaOH), depending on the expected acid value.

If the molecular weight of the fatty acid is known, the free fatty acid content can be calculated using the titration results.

Apparatus:
1. Erlenmeyer flasks, 250 mL.
2. Burette, 10 mL class A.
3. Burette, 50 mL class A.
4. Analytical balance, capable of determining weights to three-decimal-place accuracy.
5. Stir plate.
6. Stir bars.
7. Steam bath or hot plate.

Reagents:
1. Potassium hydroxide (KOH), 0.1N in methanol (standardized using LTC-0010).
2. Sodium hydroxide (NaOH), 0.5N in water (standardized using LTC-0020).
3. Isopropyl alcohol (IPA), reagent grade.
4. Toluene, reagent grade.
5. Chloroform, reagent grade.
6. Phenolphthalein indicator solution, 1.0 percent in ethanol.

Procedure:
1. Using Table I on the following page as a guide, weigh an appropriate amount of sample into a tared Erlenmeyer flask. Record the weight.
2. Add 100 mL of an appropriate neutral alcohol and a few drops of the phenolphthalein indicator solution (**Remark 1**). Place a stir bar in the flask and mix thoroughly to dissolve sample, using heat if necessary.
3. Using Table I on the following page as a guide, titrate with the appropriate solution until a faint, pink endpoint appears and persists for 30 seconds. Record the volume of titrant used to reach this endpoint and use Equation 1 in the Calculations section of this method to calculate the acid value.
4. The free fatty acid content can be calculated using Equation 2 in the Calculations section of this method.
5. The acidity (meq/gram) can be calculated using Equation 3 in the Calculations section of this method.

Calculations:

Equation 1

$$\text{Acid Value, mg KOH/gram} = \frac{(\text{mL of titrant})(\text{N of titrant})(56.1)}{(\text{sample wt.})}$$

Equation 2

$$\text{\% Free Fatty Acid} = \frac{(\text{mL of titrant})(\text{N of titrant})(\text{Mwt. of fatty acid})}{(\text{sample wt.})(10)}$$

Where Mwt. lauric acid = 200 Mwt. palmitic acid = 256
Mwt. oleic acid = 282 Mwt. acetic acid = 60
Mwt. formic acid = 46

Equation 3

$$\text{Acidity, meq/gram} = \frac{(\text{mL of titrant})(\text{N})}{(\text{sample wt.})}$$

Precision: The relative standard deviation for acid value determinations has been determined to be ±0.5 percent when one sample was analyzed 36 times by different chemists on different days within the same laboratory. This relative standard deviation was determined on a sample with an average acid value of 199.8.

Based on the free fatty acid carbon chain distribution, the theoretical acid value of the sample analyzed was 199.7. Thus, this method reports 100 percent of the fatty acid present in the sample.

Safety: Isopropyl alcohol is flammable and a dangerous fire risk. Only handle in well-ventilated areas.

Chloroform is a known carcinogen. Use in a well ventilated area. Do not get in eyes, on skin or on clothing.

Toluene is flammable and a dangerous fire risk. Only handle in well-ventilated areas.

Potassium hydroxide is corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Sodium hydroxide is corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Remarks:

1. A solvent system should be chosen that completely dissolves the sample and gives a sharp phenolphthalein endpoint. The three types of solvent systems which can be used are neutralized IPA, chloroform and neutralized 50:50 IPA/toluene.

References:

1. A.O.C.S. Official Method Cd 3a-63.
2. Calgene Chemical Laboratory Notebook #501, page 71.

Table I—Sample Weight Needed to Obtain a Titration Volume Under 7 mL

Expected Acid Value	Wt. of Sample (±10%), g	Weighing Accuracy, (± grams)	Titrating Solution
0 to 1	20	0.05	0.1N KOH
1 to 4	10	0.02	0.1N KOH
4 to 15	2.5	0.01	0.1N KOH
15 to 75	0.5	0.001	0.1N KOH
75 to 375	0.5	0.001	0.5N NaOH
375 to 1875	0.1	0.0002	0.5N NaOH

ANALYTICAL METHOD

M–003—Base Value

Scope: This method applies to all products that require a phenolphthalein endpoint, such as hydroxyl value correction and assaying KOH and NaOH.

Summary: The sample is dissolved in neutralized 3A alcohol and titrated to a phenolphthalein endpoint using a dilute solution of hydrochloric acid. The results are reported internally as "strong" base value.

Apparatus:
1. Erlenmeyer flasks, 250 mL.
2. Burette, 10 mL class A.
3. Analytical balance, capable of determining weights to three-decimal-place accuracy.
4. Steam bath or hot plate.
5. Stir plate.
6. Stir bars.

Reagents:
1. Hydrochloric acid (HCl), 0.1N in 3A (standardized using LTC-0030).
2. Hydrochloric acid (HCl), 0.5N in 3A (standardized using LTC-0030).
3. 3A alcohol absolute, 95:5:5 ethanol/methanol/IPA, reagent grade (neutralized to first phenolphthalein endpoint).
4. Phenolphthalein indicator solution, 1.0 percent in ethanol.

Procedure:
1. Using Table I on the following page as a guide, weigh an appropriate amount of sample into a tared Erlenmeyer flask. Record the weight.
2. Add about 75 mL of neutralized 3A alcohol and a few drops of phenolphthalein indicator solution. Place a stir bar in the flask and mix thoroughly to dissolve sample, using heat if necessary. Allow the sample solution to cool to room temperature before titrating.
3. Titrate with the appropriate HCl solution (See Table I) until the pink color disappears from the sample solution. Record the volume of titrant used to reach this endpoint. Using Equation 1 in the Calculations section of this method, determine the amine value. Report this value to one decimal place.

Calculations:

Equation 1

$$\text{Base Value} = \frac{(\text{mL of titrant})(\text{N of titrant})(56.1)}{(\text{sample wt.})}$$

Safety: The samples are basic in nature and therefore corrosive. Caution should be used when handling. Do not get in eyes, on skin or on clothing.

Hydrochloric acid can burn skin. Do not get in eyes, on skin or on clothing.

3A alcohol is flammable and a dangerous fire risk. Only handle in well-ventilated areas.

References: 1. Hodag Method B-4.

Table I—Sample Weight Needed to Obtain a Titration Volume Under 7 mL

Expected Base Value	Wt. of Sample (+10%), g	Titrating Solution
0 to 1	20	0.1 N HCl
1 to 4	10	0.1 N HCl
4 to 15	2.5	0.1 N HCl
15 to 75	0.5	0.1 N HCl
75 to 375	0.5	0.5 N HCl
375 to 1875	0.1	0.5 N HCl

ANALYTICAL METHOD

M–004—Color, Gardner

Scope: This method applies to products in the liquid or solid state that do not differ in hue appreciably from the standards.

Summary: This method will assign a number between 1- and 18+ that corresponds to the color of the sample as compared with a set of 18 standards. A Gardner Color may be reported on a product that differs in hue from the standards. This color will be reported as the resulting color plus the designation "Off Hue."

Apparatus:
1. 18 glass standards, 1963 series.
2. Gardner-Delta Color Comparator.
3. Comparison tubes.
4. Funnel.
5. Filter paper, Ahlstrom #505.
6. Ring stand.

Reagents: None required.

Procedure:
1. Melt the sample if it is not in a liquid state. Inspect the sample for any foreign matter and filter the sample if any is present.
2. Mix the sample thoroughly and pour into a comparison tube. Place the comparison tube in the comparator and compare with the standards to determine which standard is nearest in color to the sample.
3. Report the color of the sample as the number of the standard most closely matching the sample. If the sample falls between two standards, it will be reported as "+" or "-" (depending on whether it is darker or lighter than the standard it most closely

resembles). Thus, between colors 5 and 6, the steps will be 5, 5+, 6-, and 6. If the color is lighter than 1, it will be reported as 1-. If the color is darker than 18, it will be reported as 18+.

Calculations: None required.

Precision: The color should not vary more than 1/3 unit from chemist to chemist. Off-hue products may vary up to three units.

Safety: The molten product is hot and may cause thermal burns. Use caution when handling.

References: A.O.C.S. Official Method Td 1a-64.

ANALYTICAL METHOD

M–005—Hydroxyl Value by Acetylation

Scope: This method applies to any nonionic product that has primary hydroxyl values.

Summary: The hydroxyl value is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of sample. The sample is weighed into an Erlenmeyer flask and diluted with 20 mL of acetylating reagent. This mixture is refluxed for 30 minutes and titrated to a phenolphthalein endpoint with 2.0N sodium hydroxide.

Apparatus:
1. Erlenmeyer flasks, 250 mL with ground glass joints.
2. Burette, 100 mL class A with 0.1 mL divisions.
3. Analytical balance, capable of determining weights to three decimal places.
4. Stir plate.
5. Stir bars.
6. Reflux condensers with ground glass joints.
7. Pipette, 20 mL class A volumetric.
8. Graduated cylinder, 25 mL.
9. Glass bottle, >500 mL.

Reagents:
1. Sodium hydroxide (NaOH), 2.0N (Standardized using LTC-0010).
2. Pyridine, reagent grade.
3. Acetic anhydride, reagent grade.
4. Phenolphthalein indicator solution, 1.0% in ethanol.

Procedure: Preparation of Acetylating Reagent:
1. In a glass bottle, add 1.4 mL deionized water and 400 mL pyridine. Mix thoroughly.
2. Add 50 mL acetic anhydride to the solution and mix thoroughly again.

Hydroxyl Value Analysis:
1. Every sample should be analyzed in duplicate. Use Equation 1 in

the Calculations section of this method to determine the appropriate sample size (**Remark 1**). Weigh this calculated amount into a tared Erlenmeyer flask. Record the weight.

2. Pipette 20 mL of the acetylating reagent into each of the flasks containing sample and two Erlenmeyer flasks, which will act as blanks. Add boiling stones to the samples and blanks.
3. Place all of the flasks on hot plates and connect to reflux condensers (**Remark 2**). Reflux for 30 minutes.
4. After refluxing is complete, wash down each condenser with about 10 mL of deionized water and catch the rinsing in the respective Erlenmeyer flasks.
5. Remove the flasks from the condensers and allow them to cool.
6. Add a few drops of phenolphthalein indicator solution and a stir bar to each flask. Titrate each blank and sample with 2.0 N NaOH to a faint, pink endpoint. Record the respective titration volumes and use Equation 2 in the Calculations section of this method to determine the uncorrected hydroxyl value of each sample. The corrected hydroxyl value can be determined using equations 3 or 4, whichever is appropriate.
7. Equations 5, 6 and 7 can be used for determining the calculated hydroxyl value, average molecular weight and percentage of residual alcohol.

Calculations:

Equation 1

$$\text{Appropriate Sample Size} = \frac{(2.5)(2.0)(56.1)}{(\text{expected OHV})}$$

Equation 2

$$\text{Uncorrected OHV} = \frac{(\text{mL Blank} - \text{mL Sample})(N)(56.1)}{\text{sample wt.}}$$

Where Blank = average of two blank runs

Equation 3

Corrected OHV = Uncorrected OHV + Acid Value (from LTC-1010)

Equation 4

Corrected OHV = Uncorrected OHV - Base Value (from LTC-1020)

Equation 5

$$\text{Calculated OHV} = \frac{56100}{\text{Mwt of product}} \times \#\text{ of OH groups}$$

Equation 6

$$\text{Average Mwt} = \frac{56100}{\text{OHV}} \times \#\text{ of OH groups}$$

Equation 7

$$\text{Residual Alcohol, \%} = \frac{\text{OHV}}{\text{Mwt of product}} \times 100$$

Precision: The relative standard deviation for hydroxyl value determinations has been determined to be ±1.1 percent when one sample was analyzed 36 times by different chemists on different days within the same laboratory. This relative standard deviation was determined on a sample with an average (uncorrected) hydroxyl value of 278.6.

The corrected hydroxyl value of this sample was 278.7, and the theoretical hydroxyl value of 100 percent pure tridecyl alcohol is 280.5. Therefore, this method reports at least 99.3 percent of the hydroxyl-bearing molecules present in a sample.

Safety: Pyridine is flammable and toxic. Avoid breathing in fumes. Handle in well-ventilated areas at all times. Do not get in eyes, on skin or on clothing.

Acetic anhydride can cause burns and irritate eyes. Avoid breathing in fumes. Handle in well-ventilated areas at all times. Do not get in eyes, on skin or on clothing.

Sodium hydroxide is corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Remarks:
1. The ideal titration volume of the sample is about 3/4 the titration volume of the blank. This calculation will give these titration volumes.
2. Before condensing begins, verify that cold water is passing through the condensers. This will aid in the condensing of the samples.

References:
1. A.O.C.S. Official Method Cd 13-60.
2. Calgene Chemical Laboratory Notebook #501, page 73.

ANALYTICAL METHOD

M–006—Saponification Value

Scope: This method applies to all fats and oils and products derived from them, such as esters and fatty acids.

Summary: The saponification (SAP) value is the amount of alkali necessary to saponify a definite quantity of the sample. It is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of the sample.

A sample is refluxed in 0.5N methanolic KOH for 1.5 hours and titrated using 0.5N HCl.

Apparatus:
1. Erlenmeyer flasks, 250 or 300 mL with ground glass joints.
2. Liebig condensers, with ground glass joints.
3. Pipettes, 20 mL class A volumetric.

4. Burette, 50 mL class A with 0.2 mL divisions.
5. Stir bars.
6. Stir plate.
7. Hot plate.
8. Analytical balance, capable of determining weights to three-decimal-place accuracy.
9. Syringes, 3 and 5 mL.
10. Graduated cylinder, 25 mL.
11. Boiling stones.

Reagents:

1. Potassium hydroxide (KOH), ethanolic 0.5N (prepared using LTC-0010) (**Remark 1)**.
2. Hydrochloric acid (HCl), 0.5N (standardized using LTC-0030).
3. Phenolphthalein indicator solution, 0.1 percent in ethanol.

Procedure:

1. Melt the sample, if not a liquid, and mix thoroughly to ensure homogeneity. Using Table 1 on the following page as a guide, weigh the appropriate amount of sample into an Erlenmeyer flask (**Remark 2**). Record the weight.
2. Pipette 50 mL of 0.5N KOH into the flask, add some boiling stones and reflux for 1.5 hours. Make sure that cold water is going through the condensers to aid in the condensing of the sample back into the Erlenmeyer flasks.
3. Prepare and run a blank simultaneously with the samples by pipetting 50 mL of 0.5N KOH into an empty flask, adding some boiling stones, and refluxing along side the samples (**Remark 1**).
4. After 1.5 hours of refluxing, rinse the inside of the condensers with about 25 mL of deionized water and catch the rinsings in the Erlenmeyer flasks. Remove the flasks from the condensers and allow the sample solutions to cool to room temperature.
5. To each flask, add three to five drops of phenolphthalein indicator and a stir bar. Titrate, while mixing, with 0.5N HCl until the pink color just disappears. Record the respective titration volumes used to reach each endpoint.
6. Using Equation 1 in the Calculations section of this method, calculate the SAP value of the samples analyzed. Report the results to one decimal place.
7. The ester value of a product can be determined using Equation 2 if the acid value is also known.

Calculations:

Equation 1

$$\text{SAP value} = \frac{(\text{mL Blank} - \text{mL Sample})(\text{N of HCl})(56.1)}{(\text{wt. of sample})}$$

Equation 2

Ester value = SAP value – Acid value

Precision: The relative standard deviation for SAP value determinations has been determined to be ±0.5 percent when one sample was analyzed 36 times by different chemists on different days within the same laboratory. This relative standard deviation was determined on a sample with an average saponification value of 336.0.

Using the free fatty acid carbon chain distribution of this sample, the theoretical saponification value was determined to be 336.7. Therefore, this method reports approximately 99.8 percent of the theoretical SAP value.

Safety: Potassium hydroxide is corrosive and can burn skin. Do not get in eyes, on skin or on clothes.

Hydrochloric acid can burn skin. Do not get in eyes, on skin or on clothes.

Remarks:
1. The 1.0N KOH solution is usable for at least three months provided the solution is protected from carbon dioxide and blanks are determined with each analysis.
2. The flask must be completely clean and dry before using.

References:
1. A.O.C.S. Official Method Cd 3c-91.
2. Calgene Chemical Laboratory Notebook #501, page 77.

SAP Value Expected	Sample Wt. (grams)	SAP Value Expected	Sample Wt. (grams)
0 to 59	10.0 to 12.0	180 to 199	3.3 to 4.1
60 to 79	9.0 to 11.0	200 to 219	3.0 to 3.7
80 to 99	7.0 to 8.6	220 to 239	2.7 to 3.4
100 to 119	5.7 to 7.0	240 to 259	2.5 to 3.1
120 to 139	4.9 to 5.9	260 to 279	2.2 to 2.7
140 to 159	4.2 to 5.1	280 to 300	2.2 to 2.7
160 to 179	3.9 to 4.8		

ANALYTICAL METHOD

M–007—Iodine Value (Wijs Method)

Scope: This method applies to all normal fatty acids, oils and fatty amines that do not contain conjugated double-bonds. It cannot be used for quaternary ammonium compounds.

When iodine value is determined on fatty acids containing conjugated double-bonds, the result is not to be used as a value of total unsaturation, but rather as a value to compare with similar systems' degree of unsaturation (**Remark 1**).

Summary: The iodine value is a measure of the unsaturation of fatty acids and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (percent iodine absorbed).

A sample is dissolved in chloroform and then reacted, in the dark, with Wijs solution for a set amount of time. KI and deionized water are added to the flask, and the solution is titrated with 0.1N sodium thiosulfate.

Apparatus:

1. Erlenmeyer flasks, 250 mL iodine determination with ground glass stoppers.
2. Analytical balance, capable of determining weights to four decimal places.
3. Pipette, 10 and 25 mL class A volumetric.
4. Burette, 50 mL class A with 0.2 mL divisions.
5. Graduated cylinders, 50 mL.
6. Stir bars.
7. Stir plate.
8. Steam bath.

Reagents:

1. Chloroform, reagent grade.
2. Wijs solution, reagent grade (**Remark 2**).
3. Potassium iodide (KI) solution, 15 percent in deionized water.
4. Mercuric acetate solution, 2.5 percent in acetic acid.
5. Sodium thiosulfate, 0.1N (standardized using LTC-0050).
6. Starch indicator solution, 1 percent in deionized water (**Remark 3**).

Procedure:

1. Weigh an appropriate amount of sample into a tared Erlenmeyer flask (**Remarks 4 and 5**). Record the weight. Label the flask accordingly.
2. Dissolve the sample by adding 25 mL of chloroform to the flask and swirling the flask. If needed, heat the flask on a steam bath to completely dissolve the sample.
3. After the sample solution has cooled to room temperature, pipette 25 mL of Wijs solution into the flask and swirl the contents till thoroughly mixed (**Remarks 2 and 6**).
4. Prepare a blank sample by pipetting 25 mL of chloroform and 25 mL of Wijs solution into an empty Erlenmeyer flask (**Remark 4**). Label the flask accordingly.
5. Stopper the flasks with a ground glass stopper. Pipette about 5 mL of the 15 percent KI solution into the stopper well.
6. Using a timer, store the flasks in a dark place for 30 minutes (60 minutes for expected iodine values greater than 150) to allow the reaction to take place completely (**Remark 7**).
7. After the reaction is complete, remove all of the flasks from the dark at the same time. Add about 20 mL of the 15 percent KI solution and 75 mL of deionized water to each of the flasks. Add a stir bar to each flask and mix well.
8. Using 0.1N sodium thiosulfate, titrate the blank sample to a pale yellow endpoint (**Remark 8**). Add about 2 mL of the starch

indicator solution to the flask and continue titrating until the blue color just disappears (usually a white endpoint). Repeat this titration for each of the samples.

9. Using Equation 1 in the Calculations section of this method, calculate the iodine value. Report this value to one decimal place.

Calculations:

Equation 1

$$\text{Iodine Value (IV)} = \frac{(\text{mL Blank - mL Sample})(\text{N})(12.69)}{\text{sample wt.}}$$

Precision: The relative standard deviation for iodine value determinations has been determined to be ±1.3 percent when one sample was analyzed 36 times by different chemists on different days within the same laboratory. This relative standard deviation was determined on a sample with an average iodine value of 134.7.

Safety: Chloroform is a known carcinogen. Do not breathe in vapors. Use in a well-ventilated area at all times. Do not get in eyes, on skin or on clothing.

Wijs solution causes severe burns, and the vapors can cause lung and eye damage. Use in a well-ventilated area at all times. Do not get in eyes, on skin or on clothing.

Acetic acid is corrosive and toxic. Use caution when handling. Do not get in eyes, on skin or on clothing.

Mercuric acetate is corrosive and highly toxic. Use caution when handling. Do not get in eyes, on skin or on clothing.

Remarks:

1. This is due to the fact that addition to one double-bond of a conjugated diene and two double-bonds of a conjugated triene goes rapidly, but saturation of the remaining double-bond is extremely slow.
2. Because the preparation of the Wijs solution is time-consuming and involves the use of hazardous and toxic chemicals, this solution may be purchased from a chemical supplier. Only use solutions that contain no carbon tetrachloride. Store in an explosion-proof refrigerator to keep the solution cool and out of the light. Never allow the temperature of the solution to rise above 25-30°C. All Wijs solutions are sensitive to temperature, moisture and light.
3. The 1 percent starch solution can be purchased from a chemical supplier. However, if it is to be made in the lab, Potato Starch for Iodometry is recommended because it produces a deep blue color in the presence of the iodonium ion. Soluble Starch is not recommended because a consistent deep blue color may not be developed when some soluble starches interact with the iodonium ion. The following are suitable starches: Soluble Starch for

Iodometry, Fisher S516-100; Soluble Potato Starch, Sigma S-2630; Soluble Potato Starch for Iodometry, J.T. Baker 4006-04.
4. All glassware must be completely clean and completely dry.
5. When analyzing dehydrated castor oil fatty acids or its derivatives, weigh 0.11–0.13 grams of sample. Due to the amount of free hydroxyl groups in castor oil, it yields high iodine values.
6. When analyzing fatty amines, add 10 mL of 2.5 percent mercuric acetate solution along with the Wijs solution. Add 10 mL of this solution to the blank as well. The reaction time is only three minutes for fatty amines.
7. If the reaction is not terminated within three minutes of the designated reaction time (30 or 60 minutes), the sample must be discarded and reanalyzed.
8. The samples must be titrated within 30 minutes of the reaction completion (when they were removed from the dark). Otherwise, the samples must be discarded and reanalyzed.

References:
1. A.O.C.S. Official Method Cd 1-25.
2. A.O.C.S. Official Method Tg 1a-64.
3. A.O.C.S. Official Method Tg 2a-64.
4. Iodine Value Wijs Method, Hodag Co., Semega, Jayne L., 1978.
5. Calgene Chemical Laboratory Notebook #501, page 86.

ANALYTICAL METHOD

M–008—Cloud Point of Nonionic Surfactants

Scope: This method applies to all nonionic surfactants.

Summary: The cloud point is the temperature at which, under the conditions of this test, the sample loses solubility and an emulsion appears.

A sample solution is cooled to below the cloud point (if necessary) and then heated at a rate of 1-2°C per minute. The cloud point is reached when the thermometer can no longer be seen through the side of the bottle. The cloud point is reported to the nearest 0.1°C.

Apparatus:
1. Thermometer capable of measuring between 0°C and 100°C, with 0.1°C divisions.
2. Beaker, 150 mL.
3. Stir bars.
4. Stir/hot plate.

Reagents:
1. Sodium chloride solution, 10 percent in deionized water.

Procedure:
1. Prepare 100 mL of the appropriate sample solution in a 150 mL beaker. Add a stir bar and mix well.
2. Cool the sample solution in an ice water bath until it is clear (**Remark 1**). Stir the cooling sample with a thermometer at a rate sufficient to keep the temperature throughout the sample uniform.

3. Suspend the thermometer in the solution with the bulb 1/2 inch from the bottom of the beaker (**Remark 2**).
4. With mild stirring, heat the beaker at a rate of 1-2°C per minute. The cloud point is the temperature at which the immersed portion of the thermometer is no longer visible when viewed horizontally through the bottle and sample. Report the cloud point to the nearest 0.1°C.

Calculations: None required.

Safety: The hot plate and sample may be hot and can cause thermal burns. Use caution when handling.

Remarks:
1. It is important to cool the sample solution until it is clear (or completely solublized). If the sample solution is not clear, inaccurate cloud point values will be obtained.
2. Do not remove the thermometer from the sample. Doing so may introduce air bubbles, which will interfere with the test.

References:
1. A.O.C.S. Official Method Cc 6-25, Reapproved 1989.

ANALYTICAL METHOD

M–009—Cloud Point, °C

Scope: This method applies to all normal animal and vegetable fats and oils.

Summary: The cloud point is the temperature at which, under the conditions of this test, a cloud is induced in the sample caused by the first stage of crystallization.

A liquid sample is cooled in an ice water bath while constantly being stirred with a thermometer. The cloud point is reached when the thermometer can no longer be seen through the side of the bottle. The cloud point is reported to the nearest 0.1°C.

Apparatus:
1. Water bath prepared with water, ice and salt (temperature >2°C).
2. Bottle, 4 ounce.
3. Thermometer capable of measuring between -2°C and 68°C, with 0.1°C divisions.

Reagents:
1. None required.

Procedure:
1. This test is performed on samples that are in a liquid form. If the sample is not a liquid, heat about 75 grams of sample to 130°C.
2. Pour about 45 grams of the sample into a four-ounce bottle and begin cooling in an ice water bath (**Remark 1**). Stir the cooling sample with a thermometer at a rate sufficient to keep the temperature throughout the sample uniform.
3. When the sample has reached a temperature of about 10°C above the expected cloud point, begin stirring steadily and rapidly in a circular motion to prevent super cooling and solidi-

fication of fat crystals on the sides or bottom of the bottle (**Remark 2**).

4. Remove the bottle from the bath and inspect regularly. The cloud point is that temperature at which the immersed portion of the thermometer is no longer visible when viewed horizontally through the bottle and sample. Report the cloud point to the nearest 1.0°C.

Calculations: None required.

Safety: The thermometers contain mercury. Mercury is a poisonous and highly toxic material. Use caution when using thermometers. If a thermometer should break, use a mercury spill clean-up kit to properly clean up the mercury.

Remarks:
1. The bottle should be submerged in the ice water bath so that the sample level in the bottle is even with the water level of the bath.
2. Do not remove the thermometer from the sample. Doing so may introduce air bubbles, which will interfere with the test.

References:
1. A.O.C.S. Official Method Cc 6-25, Reapproved 1989.

ANALYTICAL METHOD

M–010—% Solids

Scope: This method is applicable to all products.

Summary: A sample is weighed into two separate aluminum dishes and exposed to 105°C temperatures for two hours. The percentage of solids or percentage of volatiles is then determined based on the residue in the aluminum dishes.

Apparatus:
1. Analytical balance, capable of determining weights to three decimal places.
2. Oven, capable of maintaining a temperature of 105°C.
3. Thermometer, capable of measuring 105°C.
4. Aluminum weighing dishes.
5. Dessicator capable of maintaining a moisture-free environment.

Reagents: None required.

Procedure:
1. Weigh two aluminum dishes. Record the weights respectively as TARE.
2. Weigh about two grams of sample into each aluminum dish. Record the sample weights respectively as INITIAL.
3. Spread the sample evenly across the entire surface of each aluminum dish.
4. Place the aluminum dishes in a 105°C oven for two hours.
5. After two hours, remove the aluminum dishes from the oven and cool to room temperature in a dessicator.
6. Weigh the aluminum dishes. Record the weights respectively as FINAL.

7. Using Equation 1 in the Calculations section of this method, determine the percentage of solids for each aluminum dish. (Equation 2 can be used to determine percentage of volatiles.)
8. Repeat steps 4 through 7, heating for 30 minutes rather than two hours, until the percentage of solids for each aluminum dish does not change by more than 0.1 percent.

Calculations:

Equation 1

$$\% \text{ Solids} = \frac{\text{FINAL - TARE}}{\text{INITIAL - TARE}} \times 100$$

Where: FINAL = Final wt. of the residue and aluminum dish
TARE = Tare wt. of the aluminum dish
INITIAL = Initial wt. of the sample and aluminum dish

Equation 2 % Volatiles= 100 - % Solids

Safety: The oven and sample may be hot and cause thermal burns. Use caution when handling.

ANALYTICAL METHOD

M–011—Viscosity by Brookfield Viscometer

Scope: This method applies to nonthixotropic liquid samples.

Summary: The sample is heated to the desired temperature and analyzed for viscosity using a Brookfield viscometer. The sample must be relatively free of entrained air bubbles for the instrument to function properly.

Apparatus:
1. Brookfield viscometer, Model RVF (or equivalent).
2. Steam bath.
3. Programmable oven.
4. Thermometer capable of °C and °F.
5. Beakers, varying sizes.

Reagents: None required.

Procedure: The attached diagram can be used to aid in understanding how the instrument is operated.

1. Select the proper spindle (A). Transfer the sample to a beaker large enough to hold the viscometer spindle. Place the beaker on a steam bath or in an oven set for the desired temperature. Remove the sample occasionally and mix well. Check the temperature of the sample using a thermometer. Once the desired temperature is reached, remove the sample from the heat source and check viscosity.
2. Attach the spindle (A) to the upper coupling (B) by holding the coupling between the thumb and forefinger while cautiously rotating the spindle counterclockwise. Avoid undue side pressure.

3. Set the knob (H) to the minimum speed that includes the centipoise range on the material to be tested. The uppermost number on the knob indicates the revolutions per minute (rpm).
4. Immerse the spindle into the sample up to the middle of the indentation in the shaft (E).
5. Turn the viscometer on and allow it to run until a constant reading appears (usually five to 10 revolutions). Using Equation 1 in the Calculations section of this method, determine the viscosity of the sample. Report the viscosity to one decimal place accuracy for viscosities of less than 100. For viscosities of more than 100, report the viscosity to the nearest whole number.

Calculations:

Equation 1

Viscosity = (Reading obtained) x (Factor for the spindle/speed comb.)

Safety: The heated samples may cause burns. Use caution when handling.

Use caution when operating the Brookfield viscometer. Dangling objects may get caught in the spindle and cause injury.

References: 1. "More Solutions to Sticky Problems", Brookfield Engineering Laboratories, Inc., 1992.

ANALYTICAL METHOD

M–012—Titer, °C

Scope: This method applies to fatty acids.

Summary: This method determines the solidification point, or "titer," of fatty acids.

Apparatus:
1. Titer stirring assembly consisting of:
   a. Water bath (2,000 mL beaker).
   b. Wide mouth bottle.
   c. Test tube, 25x100 mm.
   d. Thermometer.
   e. Wire stirrer with one end bent into a loop.
   f. Corks, six.

Reagents: None required.

Procedure:
1. Add water to the designated level of the bath.
2. Adjust water bath temperature to 15-20°C below the expected titer point.
3. Melt sample (if solid) not greater than ~15°C above expected titer.
4. Pour the sample into the test tube to the immersion mark of the thermometer.
5. Place the thermometer and wire stirrer into the test tube, keeping them equidistant from the sides.
6. Place test tube assembly into wide-mouth bottle.

7. The agitation with the wire stirrer is started while the temperature of sample is 10°C above the titer point.
8. Stir sample at a rate of 20 strokes per minute.
9. Record temperature of sample every minute.
10. Stir until the temperature remains constant for 30 seconds or it begins to rise.
11. Discontinue stirring immediately. Observe and record the increase in temperature.
12. The titer point is the highest temp reached by the thermometer during this rise.

Calculations: None required.

Precision: Not determined.

References: 1. A.O.C.S. Official Method Da 13-48.

ANALYTICAL METHOD

M–013—Unsaponifiable Matter

Scope: This method alpplies to products containing mineral oil, wax or fatty alcohol.

Summary: This method determines the amount of matter soluble in fats and oils that cannot be saponified by caustic alkali.

Apparatus:
1. Erlenmeyer flask w/ ground glass joint, 250 mL.
2. Hot plate.
3. Condenser with cold water running through.
4. Separatory funnel, 250 mL.
5. Stokes flask w/ stopper and tubing, 250 mL.
6. Analytical balance, capable of measuring to three-decimal-place accuracy.
7. Dessicator capable of maintaining moisture-free environment.
8. Forced-air oven capable of maintaining 105°C temperature.
9. Thermometer capable of measuring 105°C temperature.
10. Pipette bulb.
11. Pipette, 50 mL class A.

Reagents:
1. Reagent alcohol, ACS reagent grade diluted to 10 percent with deionized water.
2. Saponification reagent, prepared using LTC-1150.
3. Petroleum ether, ACS reagent grade.

Procedure:
1. Weigh five grams of sample into a 250 mL Erlenmeyer flask with ground glass joint. Record the weight to three decimal places.
2. Pipette 50 mL of saponification reagent into the flask.
3. Place the flask on a hot plate and connect a condenser to it with cold water running through it. Allow the solution to reflux for one hour.

4. After one hour, quantitatively rinse the inside of the condenser with about 20 mL of deionized water.
5. Remove the flask from the hot plate and quantitatively transfer the solution to a Stokes flask using deionized water.
6. Add enough water to the Stokes flask to bring the fluid level to the neck of the flask (just below the bulb of the flask).
7. Add about 50 mL of petroleum ether to the Stokes flask. Stopper the flask and shake gently for one minute.
8. Using the stopper and glass tubing assembly, transfer the petroleum ether layer to a 500 mL separatory funnel.
9. Repeat steps 7 and 8 until a total of five extractions are performed. Keep adding the petroleum ether layer to the same separatory funnel.
10. Add about 25 mL of the 10 percent reagent alcohol solution to the separatory funnel. Stopper the separatory funnel and shake gently for one minute.
11. Dispose of the 10 percent reagent alcohol layer.
12. Repeat steps 10 and 11 until three washes of the petroleum ether layer are performed.
13. Transfer the washed petroleum ether layer to a tared 250 mL beaker. Place the beaker on a steam bath and evaporate the petroleum ether to dryness.
14. Place the beaker in a 105°C oven for approximately 10 minutes (or until a constant weight is achieved).
15. Weigh the beaker and determine the weight of the residue to three-decimal-place accuracy.
16. Using Equation 1 in the Calculations section of this method, calculate the percentage of unsaponifiable matter in the sample. Report the results to two decimal places.

Calculations:

Equation 1

$$\% \text{ Unsaponifiable Matter} = \frac{\text{Wt. of residue}}{\text{Sample wt.}} \times 100$$

Safety: Petroleum ether is extremely flammable. Use in a well-ventilated area and keep ignition sources away.

Reagent alcohol is flammable and a dangerous fire risk. Handle only in well-ventilated areas.

Saponification reagent is corrosive. Do not get in eyes, on skin or on clothing.

Methanol is flammable and toxic. Use in well ventilated areas and avoid getting in eyes, on skin or on clothing.

References: 1. A.O.C.S. Official Method Tk 1a-64, Reapproved 1989.

ANALYTICAL METHOD

M–014—Monoester, Diester and Free Phosphoric Acid Determination

Scope: This method applies to all phosphate esters.

Summary: This method can be used to determine the three acid values for phosphate esters and the amount of monoester, diester and free phosphoric acid in the sample.

A phosphate ester sample is titrated with 0.1N methanolic KOH to three endpoints. The first endpoint represents the amount of KOH needed to neutralize one H+ of the phosphoric acid, one H+ of the monoester and the H+ of the diester. The second endpoint represents the amount of KOH needed to neutralize a second H+ of the phosphoric acid and the second H+ of the the monoester. The third endpoint represents the amount of KOH needed to neutralize the third H+ of the phosphoric acid.

Apparatus:

1. Analytical balance, capable of determining weights to three decimal places.
2. Brinkmann 716 Titrino (or equivalent) with a glass combination electrode.
3. Beakers, 250 mL.
4. Stir bars.
5. Stir plate.
6. Hot plate.
7. Syringe, 5cc.
8. Kimwipes.

Reagents:

1. Potassium hydroxide (KOH), 0.1N in methanol (standardized using LTC-0010).
2. Isopropyl alcohol (IPA), reagent grade, neutralized to phenolphthalein endpoint.
3. Saturated calcium chloride solution, prepared using neutralized deionized water.
4. Deionized water, neutralized to pH 7.
5. Phenolphthalein indicator solution, 1.0 percent in ethanol.
6. Bromocresol green indicator solution, 1.0 percent in ethanol.

Procedure:

Instrument Set-up:

1. Program the autotitrator to contain the two sets of parameters outlined in figures II and III of this method. Modify common variable C31, in the configuration, to reflect the normality of the KOH solution.
2. Verify that the electrode contains 3N KCl in the inner-cell. Fill if necessary.
3. Uncap the electrode and clean with IPA. Dry with a Kimwipe.
4. Remove any air bubbles from the dispenser tip of the exchange unit.

Potentiometric Titration to Inflection Endpoints (**Remark 1**):

1. Using Equation 1 in the Calculations section of this method, determine the appropriate sample size. Weigh this calculated amount into a 250 mL beaker. Record the weight and label the beaker as Sample #1.
2. Weigh the calculated amount into a second 250 mL beaker. Record the weight and label the beaker as Sample #2.
3. Add about 100 mL of the appropriate solvent and a stir bar to each beaker. Stir each sample solution at medium speed until the sample is completely dissolved, using heat if necessary.
4. Titrate Sample #1 with 0.1N methanolic KOH using the parameters outlined in Figure II. Continue titrating until two titration endpoints are observed and the pH is greater than 12 (**Remark 2**). Record the pH of EP2.
5. Modify the titration parameters to stop at the pH of the second endpoint (EP2). The parameter to be changed is specified in Figure II of this method.
6. Titrate Sample #2 with 0.1N methanolic KOH, using the modified parameters of Figure II until the specified pH is reached. (The instrument will automatically stop at the specified pH.) Record AV-1.
7. Add two drops of saturated calcium chloride to the sample solution (**Remark 3**).
8. Titrate with 0.1N methanolic KOH, using the parameters outlined in Figure III until an endpoint (the third endpoint) is observed and the pH is greater than 12 (**Remark 2**). Record AV-2 and AV-3.
9. Using equations 2, 3 and 4 in the Calculations section of this method, determine AV-1, AV-2 and AV-3 (if necessary). Using equations 5, 6 and 7 in the Calculations section of this method, determine the monoester, diester and free phosphoric acid content.

Manual Titration to Colorimetric Endpoints (**Remark 1**):

1. Using Equation 1 in the Calculations section of this method, determine the appropriate sample size. Weigh two times this calculated amount into two 250 mL beakers and label as Sample #1 and Sample #2. Record the respective weights.
2. Add about 100 mL of the appropriate solvent (See Table I) and a stir bar to each beaker. Stir each sample solution at medium speed until the sample is completely dissolved, using heat if necessary.
3. Add a few drops of bromocresol green indicator solution to the Sample #1 solution.
4. Titrate with 0.1N methanolic KOH until a blue endpoint appears and persists for 30 seconds. Record the volume of titrant used to reach this endpoint as EP1.

5. Add a few drops of phenolphthalein indicator solution to the Sample #2 solution.
6. Titrate with 0.1N methanolic KOH until a faint, pink endpoint appears and persists for 30 seconds. Record the volume of titrant used to reach this endpoint as EP2.
7. Add two drops of saturated calcium chloride to the sample solution (**Remark 3**).
8. Titrate with 0.1N methanolic KOH until a faint, pink endpoint appears and persists for 30 seconds. Record the volume of titrant used to reach this endpoint as EP3.
9. Using equations 2, 3 and 4 in the Calculations section of this method, determine AV-1, AV-2 and AV-3. Using equations 5, 6 and 7 in the Calculations section of this method, determine the monoester, diester and free phosphoric acid content.

Calculations:

Equation 1

$$\text{Sample wt.} = \frac{56.1}{(\text{Acid Value})}$$

Equation 2

$$\text{Acid Value \#1} = \frac{(EP1)(N)(56.1)}{\text{Sample wt.}}$$

Equation 3

$$\text{Acid Value \#2} = \frac{(EP2)(N)(56.1)}{\text{Sample wt.}}$$

Equation 4

$$\text{Acid Value \#3} = \frac{(EP3)(N)(56.1)}{\text{Sample wt.}}$$

Equation 5

$$\%\ \text{Monoester} = \frac{[(2)(AV2) - AV1 - AV3]\ (\text{Monoester Mwt.})}{(56.1)(10)}$$

Equation 6

$$\%\ \text{Diester} = \frac{[(2)(AV1) - AV2)]\ (\text{Diester Mwt.})}{(56.1)(10)}$$

Equation 7

$$\% \text{ Free } H_3PO_4 = \frac{(AV3 - AV2)\,(97.97)}{(56.1)(10)}$$

Safety: Isopropyl alcohol is flammable and a dangerous fire risk. Handle only in well-ventilated areas. Potassium hydroxide is corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Remarks:
1. The inflection points are the "true" endpoints. Therefore, the potentiometric procedure should be used whenever possible. The colorimetric endpoints do not exactly agree with the inflec tion endpoints. Therefore, the colorimetric procedure should be used only as a back-up procedure in case the autotitrator is malfunctioning.
2. The first endpoint typically occurs at a pH of 5.0-6.5. The second and third endpoints typically occurs at a pH of 9.5-11.0. These pHs can vary and should be used only as a guide.
3. Unless the free phosphoric acid level is very high, two drops of saturated calcium chloride should be sufficient. However, in samples where higher free phosphoric acid levels are expected, larger quantities of saturated calcium chloride should be used. Solubility problems may arise when adding greater amounts of calcium chloride.

References:
1. Calgene Laboratory Notebook #483, pages 139-141.

ANALYTICAL METHOD

M–015—Glycerine Determination (USP)

Scope: This method applies to the assaying of USP grade glycerine.

Summary: The sodium metaperiodate oxidizes all glycerine present in the sample to form two moles of formaldehyde and one mole of formic acid per mole of glycerine. The formic acid is neutralized to a pH of 8.13±30.1 using 2.0N sodium hydroxide. The glycerine content is calculated after determining the volume of titrant needed to react with all formic acid present.

Apparatus:
1. Analytical balance, capable of determining weights to four decimal places.
2. pH meter capable of ±0.05 pH unit readings.
3. Electrode, combination (**Remark 1**).
4. Burette, 50 mL class A with 0.2 mL divisions.
5. Beakers, 600 mL.
6. Volumetric flasks, 100 and 1,000 mL.
7. Pipettes, 1, 10, and 50 mL, class A volumetric.
8. Reagent bottle with ground glass stopper, 1 liter amber.
9. Syringes, disposable 3cc plastic.

10. Watch glasses.
11. Timer.
12. Stir plate.
13. Stir bars.

Reagents:

1. Sodium metaperiodate, reagent grade.
2. Sulfuric acid (0.1N), concentrated (80 percent).
3. Sodium hydroxide (0.05N), prepared and standardized using LTC-0010.
4. Ethylene glycol, reagent grade.
5. Glycerine, 99.5 percent+ purity.

Procedure:

Preparation of Reagent Solutions:

Sodium Periodate Solution

Dissolve 60 grams of sodium metaperiodate in sufficient water containing 120 mL of 0.1 N sulfuric acid to make 1,000 mL of solution.

0.1N Sulfuric Acid Solution

Weigh about 5.15 grams of 80 percent sulfuric acid into a 1,000 mL volumetric flask. Dilute to volume with deionized water and mix well. Label accordingly.

Ethylene Glycol Solution

Pipet 50 mL of ethylene glycol into a 100 mL volumetric flask. Dilute to volume with deionized water.

Bromothymol Blue Indicator Solution

Weigh 0.1 grams of bromothymol blue into a 100 mL volumetric flask. Pipet 1 mL of ethanol into the flask and dilute to volume with deionized water. Mix well and label accordingly.

Sample Preparation and Analysis:

1. Weigh about 0.4 grams of sample into a 600 mL beaker. Record the weight and label accordingly.
2. Add 50 mL of deionized water and 1 mL bromothymol blue indicator solution to the beaker. Add a stir bar to the beaker and mix well.
3. Acidify with 0.1N H_2SO_4 to a green or greenish yellow color.
4. Neutralize with 0.1N NaOH to a definite blue endpoint (no green).
5. Prepare a blank by adding 50 mL deionized water and 1 mL of bromothymol blue to a 600 mL beaker. After adding a stir bar and mixing well, acidify and neutralize (steps 3 and 4) the blank solution. Label the flask as "Blank."
6. Pipet 50 mL of the sodium periodate solution into each of the beakers. Swirl gently. Cover each beaker with a watch glass and allow to stand in the dark for 30 minutes.
7. Pipet 10 mL of the ethylene glycol solution to each of the beakers. Swirl gently. Allow to stand for 20 minutes.

8. Add 150 mL of deionized water to each beaker and mix well. Titrate each blank and sample solution with 2.0N sodium hydroxide. The "Blank" endpoint is reached when the pH reaches 6.5 3± 30.1. The "Sample" endpoint is reached when the pH reaches 8.1 3±30.1.
9. Using Equation 1 in the Calculations section of this method, determine the percentage of glycerine content to one decimal place.

Calculations:

Equation 1

$$\% \text{ Glycerine} = \frac{(\text{mL Sample - mL Blank})(N)(92.10)(100)}{(\text{Sample wt.})(1{,}000)}$$

Precision: Initial studies indicate that the relative standard deviation of the glycerine determination is 3±30.6 percent.

Safety: Sodium metaperiodate is an oxidizer. Use caution when handling and storing. Do not get in eyes, on skin or on clothing.

Ethylene glycol is an eye irritant. Do not get in eyes, on skin or on clothing. Use in well-ventilated area.

Sodium hydroxide is corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Sulfuric acid is extremely corrosive. Do not get dilute solutions in eyes, on skin or on clothing.

Remarks:
1. Follow the care and maintenance procedures outlined by the manufacturer of the electrode.

References:
1. U.S. Pharmacopeia and National Formulary, 1995, USP 23 & NF 18, Glycerin Official Monograph, pages 713-714, 2056, and 2057.
2. Calgene Chemical Laboratory Notebook #494, pages 85-91.

ANALYTICAL METHOD

M–016—Anionic Actives, %

Scope: This method determines the anionic active content (of known molecular weight) of synthetic detergents (i.e., DOSS-70, DTSS, and DHSS).

Summary: A hyamine titration is performed in a stoppered graduated cylinder, to a methylene blue endpoint. The endpoint is reached when the two layers in the graduated cylinder have the same intensity of blue. If the molecular weight of the anionic active is known, the percentage of anionic active can be calculated.

Apparatus:
1. Graduated cylinder, 100 mL with stopper.
2. Analytical balance, capable of determining weights to four decimal place accuracy.

3. Pipette, 10 mL class A volumetric.
4. Volumetric flask, 100 mL.

Reagents:

1. Chloroform, reagent grade.
2. Methylene blue indicator solution (**Remark 1**).
3. ~0.0033N hyamine solution (**Remark 2**).
4. ~0.007N sodium lauryl sulfate solution (**Remark 3**).
5. Concentrated sulfuric acid, reagent grade.
6. Isopropyl alcohol (IPA), reagent grade.

Procedure:

1. Using Table I as a guide, weigh an appropriate amount of sample into a 100 mL volumetric flask (**Remark 4**).
2. Add some deionized water to the flask and dissolve the sample. If the sample does not fully dissolve in deionized water alone, add sufficient IPA to fully dissolve the sample. Dilute to 100 mL with deionized water.
3. Pipette 10 mL of the sample solution into a 100 mL graduated cylinder with stopper. Add 25 mL of chloroform and 15 mL of methylene blue indicator solution to the graduated cylinder. Stopper the cylinder and shake well.
4. Titrate the solution in the graduated cylinder with standardized hyamine solution, beginning with 5 mL additions and lowering to 0.5 and 0.1 mL additions as the endpoint approaches. After each addition, stopper the cylinder, shake well for one minute and allow the two layers to separate completely (**Remark 5**).
5. The endpoint has been reached when the intensity of the blue color is the same in the top and bottom layers after the two layers have separated completely. Record the titrant volume required to reach the endpoint.
6. Using Equation 1 in the Calculations section of this method, determine the percentage of anionic actives in the sample analyzed. Report the results to one decimal place.

Calculations:

Equation 1

$$\% \text{ Anionic Active} = \frac{(\text{mL Hyamine})(\text{N Hyamine})(\text{Anionic Mwt})}{\text{grams of sample}}$$

Safety: Chloroform is a known carcinogen and is toxic by ingestion, inhalation and skin absorption. Use in a well-ventilated area and avoid getting on skin, in eyes or on clothing.

Sulfuric acid is corrosive and can burn. Use caution when handling and avoid getting on skin, in eyes or on clothing.

IPA is flammable. Use in a well-ventilated area and avoid getting in eyes, on skin or on clothing.

Remarks:

1. The methylene blue indicator solution is prepared by adding 0.03 grams methylene blue, 250 mL deionized water, 12 grams

concentrated sulfuric acid, and 50 grams sodium sulfate into a 1,000 mL volumetric flask. Mix well until all components are dissolved and dilute to volume with deionized water.

2. The 0.0033N hyamine solution is prepared by weighing 1.550 grams of hyamine 1622 (Mwt=466) into a beaker. Dissolve the hyamine 1622 in about 100 mL of deionized water. Quantitatively transfer the solution to a 1,000 mL volumetric flask. Dilute to volume and mix well. Standardize the solution against 0.007N sodium lauryl sulfate.
3. The 0.007N sodium lauryl sulfate is prepared by weighing two grams of Stepanol ME dry AW (Stepanol WA-100). Record the weight to the nearest 0.0001 gram. Dissolve the weighed sample in deionized water. Quantitatively transfer the solution to a 1,000 mL volumetric flask. Dilute to volume and mix well. Calculate the normality using the following equation: N=(grams sample x 0.995)/288.
4. If the anionic active is dissolved in a volatile solvent, weigh the sample by difference using a dropping bottle.
5. Placing the stoppered graduated cylinder on its side will decrease the amount of time required to separate the two layers.

References:
1. Hodag Quality Control Manual.
2. Toilet Goods Association, Method 110.

Molecular Weight of Anionic Active	Sample Size in grams (100% basis)
200	0.133
250	0.165
300	0.200
350	0.230
400	0.265
450	0.300
500	0.330

The molecular weights of various products are as follows:

DOSS-70	444
DTSS	749
DHSS	388

ANALYTICAL METHOD

M–017—Sulfite, %

Scope: This test determines the free sulfite content, as Na_2SO_3, in synthetic detergents. It applies to Sole-Terge 8.

Summary: An excess of standard iodine solution is added to an aqueous solution of the sample. The amount of unconsumed iodine solution is back-titrated with standardized sodium thiosulfate solution. The free sulfite content is calculated from the amount of iodine consumed.

Apparatus:
1. Erlenmeyer flask, 250 mL (**Remark 1**).
2. Pipette, 10 mL class A volumetric.
3. Analytical balance, capable of measuring weight to three-decimal-place accuracy.

Reagents:
1. Iodine solution, 0.1N.
2. Sodium thiosulfate solution (0.1N), standardized using LTC-0050.
3. Starch indicator solution, prepared using LTC-0140.
4. Glacial acetic acid, reagent grade.

Procedure:
1. Weigh approximately two grams of sample into a 50 mL Erlenmeyer flask. Record the weight.
2. Add 50 mL of deionized water and 5 mL glacial acetic acid to the flask. Mix well until sample is completely dissolved.
3. Pipette 10 mL of 0.1N Iodine solution into the flask. Mix well.
4. Using 0.1N sodium thiosulfate solution, titrate the sample solution to a pale yellow endpoint. Add about 2 mL of starch indicator solution to the flask and continue titrating until the blue color just disappears (usually a white endpoint).
5. Following steps 2-4, run a blank that contains no sample.
6. Using Equation 1 in the Calculations section of this method, calculate the free sulfite content as Na_2SO_3. Report the results to one decimal place.

Calculations: Equation 1

$$\% \ Na_2SO_3 = \frac{(\text{mL Blank - mL Sample})(N)(6.3)}{\text{Sample wt.}}$$

Safety: Acetic acid is corrosive and toxic. Use caution when handling. Do not get in eyes, on skin or on clothing.

Iodine solution is harmful to organs, especially the thyroid. Do not get in eyes, on skin or on clothing.

Remarks:
1. All Erlenmeyer flasks must be clean and *completely* dry.

References:
1. Hodag QC Manual.

ANALYTICAL METHOD

M–018—Solubility

Scope: This method applies to all products.

Summary: The sample is dissolved in a specified amount of solvent. The solubility of the sample in that solvent is determined by the clarity of the solution.

Apparatus:
1. Beakers, 150 mL.
2. Stir bars.
3. Stir/hot plate.

Reagents:
1. Xylenes, reagent grade.
2. Chloroform, reagent grade.
3. Mineral seal oil, technical grade.
4. Ditridecyl adipate, technical grade.

Procedure:
1. Add sample and the appropriate solvent into a beaker in the proportions stated in the specification (**Remark 1**). Add a stir bar and mix well.
2. Allow the sample solution to settle until all air bubbles are removed. When a sample is completely soluble in the solvent tested, a clear solution results. Report the sample as soluble or insoluble.

Calculations: None required.

Safety: Chloroform is a known carcinogen. Use in a well-ventilated area. Do not get in eyes, on skin or on clothing.

Xylenes are flammable, and the vapors can be narcotic at extreme concentrations. Use in a well-ventilated area. Do not get in eyes, on skin or on clothing.

Remarks:
1. If no proportion is stated in the specifications for the product to be analyzed, prepare a 5 percent solution.

ANALYTICAL METHOD

M–019—Cationic Actives, %

Scope: This method is used to determine the percentage of cationic active in cationic quaternary compounds with known molecular weight using titration with an anionic solution.

Summary: Using an anionic solution, sodium lauryl sulfate and cationic quaternary compounds' different color concentrations of purple in the solvent and aqueous phase, calculate the percentage of cationic active of sample from the Calculations section of this method.

Apparatus:
1. Graduated cylinder, 100 mL with glass stopper.
2. Analytical balance capable of determining weight to four decimal places.
3. Volumetric pipette, 10 mL.
4. Volumetric flask, 100 mL.

Reagents:
1. Chloroform, reagent grade.
2. Isopropyl alcohol, dry and neutralized.
3. Sodium lauryl sulfate (SLS) prepared by weighing out 2.88 grams Stepanol ME Dry AW and diluting it to 1,000 mL with deionized water.
4. Salt buffer (50 g NaCl in 500 mL deionized water).
5. Bromophenol blue indicator solution, 0.1 percent in ethanol.

Procedure:
1. Weigh approximately 1-1.5 grams of sample into a 100 mL volumetric flask. Record weight.
2. Add 21 mL isopropanol and dilute to volume with chloroform.
3. Pipette 10 mL aliquot into stoppered graduated cylinder.
4. Add 20 mL chloroform, 25 mL salt buffer and 1 mL bromophenol blue indicator.
5. Titrate with 0.008N sodium lauryl sulfate solution in 1 mL increments, shaking vigorously after each addition.
6. When the emulsion breaks more readily, add 0.1 mL increments, shaking vigorously after each addition.
7. The endpoint is reached when the solvent phase (bottom layer) is very light purple and the aqueous phase (top layer) is a bright purple.
8. Record the titration volume.
9. Calculate percentage of cationic actives using Equation 1.

Calculations:

Equation 1

$$\% \text{ Active, cationic} = \frac{(\text{mL SLS})(\text{N SLS})(10)(\text{mol. wt})(100)}{(\text{sample wt})(1{,}000)}$$

using the following average molecular weights:
CQ2: 408
CQ9: 388.6
CQ14: 335
Sanitrol: 335
Declor Aid: 335

Safety: Chloroform is a known carcinogen and is toxic by ingestion, inhalation and skin absorption. Be cautious while handling it in the hood.

References:
1. Hodag Quality Control Manual.
2. Toilet Goods Association, Method 110.

ANALYTICAL METHODOLOGY

M–020—Infrared Analysis

Scope: This method applies to all products that are liquid, semisolid or solid.

Summary: An infrared absorbance spectrum of the sample is obtained and compared with an absorbance spectrum of standard material.

Apparatus:
1. Infrared spectrophotometer, continuous scan or Fourier transform, which is capable of obtaining absorbance spectra.
2. Salt plates, KBr.
3. Pellet press.
4. Mortar and pestle.
5. Rubber policeman.
6. Kimwipes.

Reagents:
1. Potassium bromide (KBr), IR grade.
2. Nujol mineral oil.
3. Methanol, reagent grade.

Procedure:

Preparation of Liquid and Semisolid Samples:

1. Sandwich a drop of sample between two salt plates and place the salt plates in the salt plate holder (**Remark 1**).

Preparation of a Solid Sample:

1. Place about 10 mg of sample in a mortar and pestle. Ground into a fine powder.
2. Add about 300 mg of KBr to the mortar and pestle. Mix the KBr and sample well. Place enough of this mixture into the pellet press to make a KBr pellet that allows for an absorbance spectrum to be taken. (**See Appendix III for instructions for using a pellet press.**)
3. Place the KBr pellet on a universal sample holder.

Analysis of Sample:

1. Take a background scan of an empty sample compartment to verify that the instrument is working properly. Compare the background spectrum with a standard background spectrum. They should match very closely. If they do not match, any absorbance spectrum obtained will not represent the sample.
2. If the background spectra do match, place the salt plate holder with sample (or KBr pellet) in the sample compartment. Scan the sample to obtain an absorbance spectrum of the sample. Compare this spectrum with a standard spectrum to determine whether they match. Report the results as "MS" (matches standard) or "not MS" (does not match standard).

Calculations: None required.

Safety: Methanol is flammable and toxic. Use in a well-ventilated area and avoid getting in eyes, on skin or on clothing.

Remarks:
1. Clean the salt plates with an appropriate solvent (Ex. methanol) and Kimwipes before and after using. Allow the solvent to completely evaporate from the salt plates before using.

References:
1. MKP-S10 Pellet Press Instructions, Harrick Scientific Corporation.

Appendix IV

Instructions for Using a Pellet Press

1. Assemble both piston assemblies as follows. Select the appropriately sized die (4 and 7) and secure it in the end bolt (2) by tightening the set screw until snug. Back off the set screw 1/4 turn to ensure free rotation of the die.
2. Take the short neck piston assembly (4 and 2) and place the bolt head down.
3. Seat the collar (5) chamfered side up, on the short neck piston (4). Note: For use of 1mm or 3mm die sets, a smaller collar is used to fit within the collar shown as #5 in the assembly drawing. Both of these collars must be in place to produce small pellets.
4. Fill the collar to the brim with finely ground KBr sample mixture. The ratio of KBr to sample should be approximately 100 to 1. Using a razor blade or straight edge, scrape excess from above the rim. Collar should remain completely full.
5. Slowly screw cell body (6) onto short neck piston assembly (4). Be careful not to disturb the sample.
6. Screw the second piston assembly (2 and 7) onto the cell body (6) to complete construction.
7. For optimum results, evacuation should occur throughout the following procedure. Tighten the assembly with the rods provided (1), except for 10mm and 13mm pellets. For the 10mm and 13mm pellets, common wrenches are all that are necessary to achieve sufficient pressures (about 40 tons per square inch). Use of the rods may lead to bent rods due to excess pressures.
8. Let press stand with pressure applied for a few minutes before disassembling.
9. Pellet may be left in the body or removed for sampling. If the pellet is to be sampled while in the cell body, the Universal Sample Holder (HUS-S1G) is suggested. However, when the pellet is removed for sampling, the Magnetic Sample Holder (HMS-S1G) is suggested. Both sample holders are available from Harrick Scientific Corporation.

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