interpreted as a slight pitch in favor of agri-acids. However, synthetic acids and derivatives are already quite important in the market place and have a chance of breaking through into much larger volumes. Another factor is the effect of TSCA on new product innovation! The latest estimates are that ca. $235,000 of testing will be needed to commercially introduce a brand new product! That's a restraint of large magnitude and will have an effect.

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# Fat-Based Detergent Additives

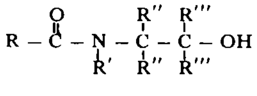
**A. CAHN**, Director of Development, Household Products Division, Lever Bros. Co., Research and Development, 45 River Road, Edgewater, NJ 07020

## ABSTRACT

The function of several of the coco-based alkanolamide additives in detergents today varies depending upon the particular product. It could be foam-boosting, foam stabilization or a variety of other supplementary effects. Tracing the development of the Ninol detergent through to the advent of the "superamides" is illustrative of the kind of progress that has been made in the utilization of this type of fatty acid derivative in the large detergent industry.

The designation additive is a bit diffuse. Whether a given compound is an "additive" or, in fact, a principal component can depend on its function or often on the level at which it is present in a fully formulated product. The compounds discussed here fall into the latter category. They are additives, but at the same time they possess all of the elements which qualify them as surfactants in their own right.

Let us begin with alkanolamides. The general formula for these compounds is:



$$R-\overset{\overset{\textstyle O}{\|}}{C}-\underset{R'}{N}-\overset{R''}{\underset{R''}{C}}-\overset{R'''}{\underset{R'''}{C}}-OH$$

In this general formula, written in a manner suggesting a patent application,

$R$ = alkyl
$R'$ = hydrogen, alkyl or hydroxyalkyl
$R''$ and $R'''$ = hydrogen or alkyl.

There are three important structural elements. First is the acyl group derived from the – long chain – fatty acid, principally coconut fatty acid for our purposes. This places the length of the fatty acid chain at 12-14 carbon atoms. The second is the amide grouping, involving an oxygen, a carbon and a nitrogen atom. Finally, the third element is the presence of at least one 2-hydroxyalkyl group with a backbone where a hydroxyl group is separated from an amide nitrogen by two carbon atoms.

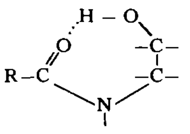
The manner in which all three of the structural elements are combined is of interest and gives us some insight into the special properties of alkanolamides which make them so important as a class of compounds. Not unlike many other commercially important developments, the insight afforded by the consideration of structure should more properly be referred to as hindsight. The first commercial preparation of alkanolamides, as we shall see, was made without benefit of detailed structural considerations.

In examining the structural elements, we note in the first place that the amide linkage is associated with a structural rigidity, as evidenced by relatively high melting points. The framework for this assertion is a consideration of the series of acetic acid, acetyl chloride, acetate esters and acetamide, not to mention other 2-carbon chain derivatives such as ethyl alcohol or the ethyl halides. Except for acetamide, all of the 2-carbon derivatives are liquids or gases.

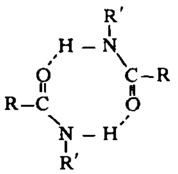
The long carbon chain of the acyl group is also associated with a certain measure of rigidity and elevated melting points, but much less so than the amide group. More importantly, the chain confers a good measure of water insolubility. Two of the three structural groupings, then, would make for a rigid, water insoluble molecule.

With the introduction of an hydroxyl group in the third structural element, water solubility is enhanced. Hydroxyl groups are powerful water-solubilizing groups through hydrogen bonding with water molecules. The ability of hydroxyl groups to confer water solubility through this mechanism is diminished when the possibility exists to form hydrogen bonds *within* the same molecule or with another molecule. When this is possible – and thermodynamically preferred – crystallinity rather than water solubility is promoted. Five- and six-membered ring structures are "thermodynamically preferred," and internal hydrogen bonding often takes place when the resulting structure is a six-membered ring.

Internal hydrogen bonding of alkanolamides would lead to a seven-membered ring, which is difficult to form:



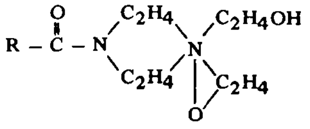
A hydrogen bonding arrangement involving two molecules of alkanolamides leads to an eight-membered ring, also thermodynamically difficult:



Since *intra-* and *inter*molecular hydrogen bonding are not favored, the full water-solubilizing potential of the hydroxyl group is being realized in alkanolamides.

In net, then, we have structural elements that possess opposing water-solubilizing tendencies, the same conflicting elements that are the essentials of the structure of a surfactant. Since alkanolamides do not have ionic groups, we have here, in fact, an example of a nonionic surfactant.

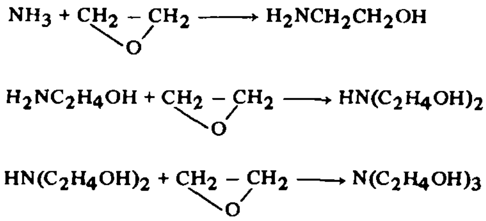
As noted, this analysis of the structure of alkanolamides and the implications for the properties of the molecule is presented with the benefit of 20/20 hindsight. When Kritchevsky first cooked up fatty acids and alkylolamines in the thirties, he postulated a rather complicated structure involving a pentavalent nitrogen and a fancy heterocycle, as shown below:



As a shrewd inventor, Kritchevsky hedged his bets. In U.S. 2,089,212 he says, after having postulated his mechanism: "I do not, however, wish to be bound by these statements since further research may more definitely fix the nature of the reaction products of my invention. For the reasons given, I do not limit my invention to compounds having specific formula but rather to a process for producing improved hydrotropic fats [*sic*] and to products resulting from such a process."

Despite the handicap of early, mistaken structural identity, the alkanolamides managed to sustain a robust development. The 1978 issue of Detergents and Emulsifiers lists some 60 tradenames for commercial product alkanolamides. They represent about 80 million pounds of carboxylic acid amides produced per year, mostly alkanolamides but including also some simple amides. We are dealing with a major chemical.

Before we look at the chemistry of formation of alkanolamides in detail, we must mention the preparation of the alkylolamines which are one of the two precursor compounds. Preparation of these amines from ammonia and ethylene oxide are shown below:



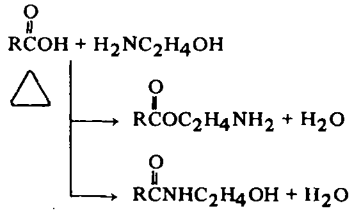
$$NH_3 + \underset{O}{CH_2 - CH_2} \longrightarrow H_2NCH_2CH_2OH$$

$$H_2NC_2H_4OH + \underset{O}{CH_2 - CH_2} \longrightarrow HN(C_2H_4OH)_2$$

$$HN(C_2H_4OH)_2 + \underset{O}{CH_2 - CH_2} \longrightarrow N(C_2H_4OH)_3$$

Mono-, di- and triethanolamines are the principal reaction products, depending on conditions and relative proportions of amine and ethylene oxide. Final purification of the mixture is by fractional distillation. All three materials are high boiling liquids. Di- and triethanolamine are near solids at room temperature.

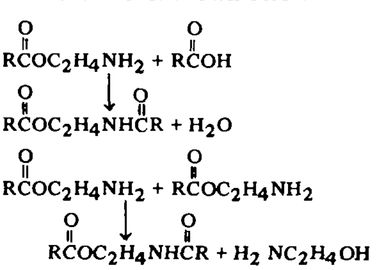
While it is the diethanolamine derivative that is of greatest interest to us, we will take a brief look at the formation of the monoethanolamides. The reaction is shown as



$$R\overset{O}{\overset{\|}{C}}OH + H_2NC_2H_4OH \xrightarrow{\triangle} R\overset{O}{\overset{\|}{C}}OC_2H_4NH_2 + H_2O$$

$$\longrightarrow R\overset{O}{\overset{\|}{C}}NHC_2H_4OH + H_2O$$

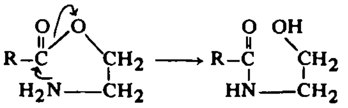
Heating fatty acid and monoethanolamine and distilling off the water formed in the reaction leads to either an aminoester or a hydroxyamide. Both of these have reactive groups which can promote further reaction with more fatty acid, or, in the case of the aminoester with another molecule to form an ester-amide. This is shown below:



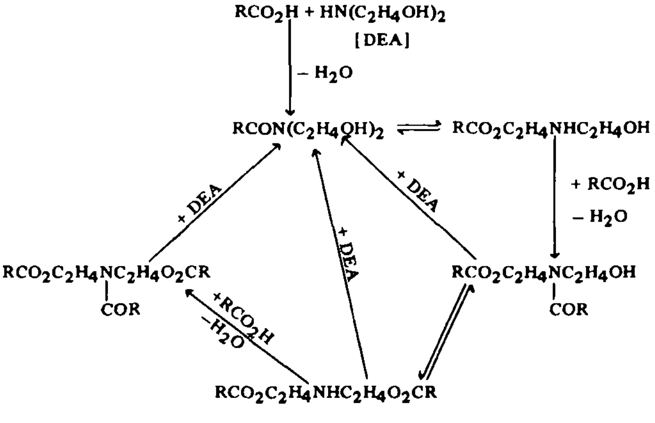
$$R\overset{O}{\overset{\|}{C}}OC_2H_4NH_2 + R\overset{O}{\overset{\|}{C}}OH \longrightarrow R\overset{O}{\overset{\|}{C}}OC_2H_4NH\overset{O}{\overset{\|}{C}}R + H_2O$$

$$R\overset{O}{\overset{\|}{C}}OC_2H_4NH_2 + R\overset{O}{\overset{\|}{C}}OC_2H_4NH_2 \longrightarrow R\overset{O}{\overset{\|}{C}}OC_2H_4NH\overset{O}{\overset{\|}{C}}R + H_2\ NC_2H_4OH$$

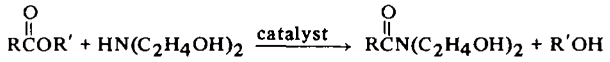
It is the hydroxyamide – the monoethanolamide in this case – which is the desired reaction product. "Aging" the reaction mixture at higher temperatures has been shown to promote the formation of the desired product. The aminoester is capable of an internal rearrangement to form the monoethanolamide. This is shown in the reaction below, which brings out the five-membered ring configuration that facilitates the rearrangement:



If the preparation of monoethanolamides from fatty acids and monoethanolamines proved to be reasonably complicated, the introduction of diethanolamine with an additional function hydroxyl group obviously adds to the complication. Just for the record, the diagram below shows the scheme of possible reactions, equilibria and exchanges first postulated by Kroll and Nadeau in 1957:



Complex though this scheme is, it shows that excess diethanolamine (DEA) ultimately promotes the formation of the diethanolamide reaction product. After holding the mixture at 100 C for several hours, the yield of diethanolamide is maximized. That yield is not 100%, however. A typical composition of the reaction product is 63.5% diethanolamide; 3.5% ester amide; 4.0% fatty acid; and 29.0% diethanolamine. Fortunately, from the point of view of the formulator who wishes to use a reasonably well characterized material, and preferably one without a heavy load of inactive and perhaps detrimental byproduct, another route leading to the preparation of purer alkanolamides is available. This is the route which starts from fatty acid esters shown below:



$$\mathrm{R\overset{O}{\overset{\|}{C}}OR' + HN(C_2H_4OH)_2 \xrightarrow{catalyst} R\overset{O}{\overset{\|}{C}}N(C_2H_4OH)_2 + R'OH}$$

Typically, methyl ester of fatty acid is heated at ca. 100 C with a slight molar excess of diethanolamine in the presence of less than 1.0% of a basic catalyst, such as sodium methoxide and distilling off the methanol which is formed. Reaction time is a few hours, not more than four at atmospheric pressure. Yields are good, much higher in the alkanolamide than provided by the fatty acid route. A typical composition of products made this way from methyl esters is 7.0% DEA; 0.5% fatty acid; 2.5% ester amide; and 90% Diethanolamide. The improvement in purity is significant. Since this improvement was obtained in a commercial context, the designation "superamides" has been applied to the ester-derived mixture.

What might be called "super-super" amides, representing purities of over 90% have been reported using reduced pressure during the reaction. John Monick reported a continuous process for the preparation of alkanolamides which also led to purities in the mid- to high nineties. To the best of my knowledge, neither of the latter two improvements represents a major portion of the current manufacture. Plain heating in the presence of catalyst is too facile a manufacturing process to be easily displaced by improvements.

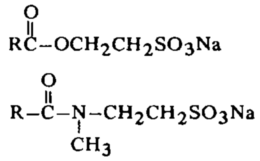
Given a commercially reliable product and the interesting structural elements discussed earlier, the number of uses and applications for alkanolamide is not surprising. For many years, the major end benefit to be derived from the inclusion of alkanolamides into detergent formulations was an increase in the suds levels. That was particularly true in the fifies and early sixties when high suds levels in the washing machine were more of a sine qua non for the formulator than they are at present. Quite possibly the heritage of high suds levels with soap-based laundry products had something to do with the desire to continue to provide such levels with pure detergent products.

While on absolute basis, the need for high suds levels may have diminished somewhat in recent times, nonetheless the presence of sufficient visible foam continues to be an important formulation requirement. Alkanolamides can be helpful here, particularly when the rest of the formulation alone does not produce the needed suds levels. Beyond improving sudsing, alkanolamides have also been shown to affect detergency in a positive manner.

With the spreading of liquid products, alkanolamides have found additional usage as viscosity-controlling agents. They are present also in a number of shampoo formulations, having been recommended for use as lime soap scum dispersants for tallow-derived soaps. Much of the widespread usage is documented in the proprietary and patent literature. Usage as wetting and emulsifying agents was, of course, contemplated in even the early literature. In addition, use of alkanolamides has been reported as plasticizers in resins, and gel formers in specialties.

The widespread usage of alkanolamides, particularly in cosmetics, attests to the innocuous nature of these materials and their good safety with respect to human exposure. Since, in general, they are derived from straight chain, naturally occurring fatty acids, they are also biodegradable, a great plus.

I would now like to discuss briefly another class of fat-derived detergent additives, or anionic surfactants, the acyl isethionates. Historically, these compounds are among the first industrial surfactants. In the 30s, they were first offered by I.G. Farben in Germany under the trade name of Igepon A. The Igepon structural formulas are:



$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2SO_3Na}$$

"Igepon A"

$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{\underset{|}{N}}{-}CH_2CH_2SO_3Na}$$

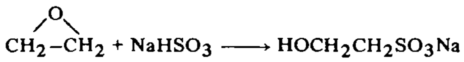
("Igepon T")

The formula for Igepon T is derived from fatty acids and N-methyltaurine. The acyl isethionate is seen to be an ester derived from fatty acid and sodium isethionate. It has also been referred to as sulfoethyl ester of fatty acids.

It is worthwhile to take a look at the structure of the isethionates. The important features are, first of all, the highly polar sulfonate group in the terminal position and an ester group along the chain. The sulfonate group is almost "inorganic" in its highly pronounced ionic character. It is a "rigid" group. The ester group, on the other hand, is characteristically organic in nature. In fact, it is subject to hydrolysis at either extreme of the pH range.

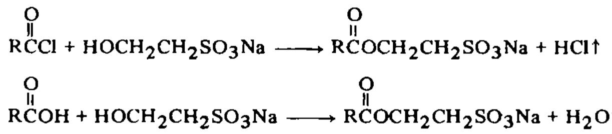
Physical properties of the acyl isethionates follow from the structural elements. The 2-sulfoethyl ester of lauric acid is a solid which melts in the range of 216-218 C. Esters derived from the higher fatty acids melt at somewhat lower temperatures: the stearic ester melts at ca. 170 C.

One can anticipate at once that the preparation of such high melting esters, with almost salt-like character, is not entirely straightforward. It begins with the preparation of sodium isethionate which, like the alkanolamines we discussed earlier, is derived from ethylene oxide. The reaction for this preparation is:



The ethylene oxide ring is opened with sodium bisulfite to yield the sodium salt of isethionic acid.

The first preparation of the 2-sulfoethyl esters involved reaction of sodium isethionate with a fatty acid chloride. This is the first of the two reactions shown below:



$$\mathrm{R\overset{O}{\overset{\|}{C}}Cl + HOCH_2CH_2SO_3Na \longrightarrow R\overset{O}{\overset{\|}{C}}OCH_2CH_2SO_3Na + HCl\uparrow}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}OH + HOCH_2CH_2SO_3Na \longrightarrow R\overset{O}{\overset{\|}{C}}OCH_2CH_2SO_3Na + H_2O\uparrow}$$

As shown, hydrogen chloride is released, with considerable foam formation, and provision must be made to keep up agitation of the reaction mixture as it turns into the solid product in the course of the reaction. The less drastic reaction is shown in the second equation. It is the basis of a commercial process in which zinc oxide is used as a catalyst and in which the final reaction mixture is "diluted" with excess stearic acid which acts as a flux to keep the mixture fluid, or at least plastic. Air is excluded and a partial vacuum is maintained to minimize the formation of off-colors.

The principal large scale application of acyl isethionates is in the formulation of neutral toilet bars. A neutral pH not only prevents the hydrolysis of the sulfoethyl ester but also leads to toilet bar formulation which is extremely mild and can be tolerated by users that often cannot tolerate exposure to the usual bar soap compositions.