Fatty Acid Alkylolamides

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THE ALKYLOAMIDES, or amine condensates as they are often called, have enjoyed perhaps the fastest growth of all detergents in the United States during this decade. From an estimated five million pounds in 1950 they have climbed to an annual volume of more than thirty million pounds today, a growth rate of 25% per year. With a growing list of uses in both household and industrial products, the alkyloamides certainly take their place among the half-dozen major detergent types.


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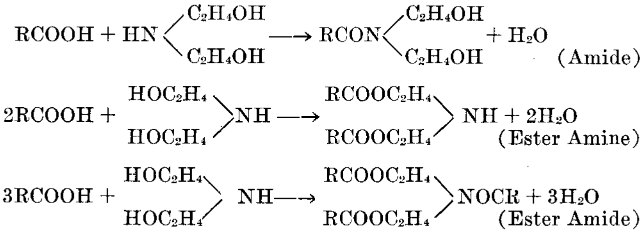
Historically the alkylolamides were first made by condensing 1 mole of lauric or coconut acid with an excess of 2 moles of diethanolamine, as described by W. Kritchevsky (1). These so-called "Ninol-type" 2:1 alkylolamides still account for a large proportion of the total commercial amide production. In addition, there are also large quantities of monoethanolamides and monoisopropanolamides produced which are made simply by reacting 1 mole of fatty acid with 1 mole of the monoalkylolamine. The most recent development in this field of amine condensates has been the so-called "high-activity" alkylolamides made catalytically from 1 mole of methyl laurate with only 1 mole of diethanolamine.

Chemistry

The chemical composition of the alkylolamides has been the subject of considerable study in recent years. When a fatty acid and diethanolamine are heated together, the following reactions can occur:



$$RCOOH + HN\left\langle\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}\right. \longrightarrow RCON\left\langle\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}\right. + H_2O \qquad \text{(Amide)}$$

$$2RCOOH + \left.\begin{matrix}HOC_2H_4\\HOC_2H_4\end{matrix}\right\rangle NH \longrightarrow \left.\begin{matrix}RCOOC_2H_4\\RCOOC_2H_4\end{matrix}\right\rangle NH + 2H_2O \qquad \text{(Ester Amine)}$$

$$3RCOOH + \left.\begin{matrix}HOC_2H_4\\HOC_2H_4\end{matrix}\right\rangle NH \longrightarrow \left.\begin{matrix}RCOOC_2H_4\\RCOOC_2H_4\end{matrix}\right\rangle NOCR + 3H_2O \qquad \text{(Ester Amide)}$$

In addition, there will be some free diethanolamine and unreacted, so-called "free fatty acid," which is actually present as diethanolamine soap.

Trowbridge *et al.* (2) prepared the lauric diethanolamine, the ester amine, and the ester amide in pure form by acylation. They found the ester amine to be quite unstable, reverting in a few days to the lauric diethanolamide, so the amount present in commercial alkylolamides is probably very low. The ester amides were apparently quite stable however. All of the esters exhibited an infrared absorption peak at 575 millimicrons.

Although it is generally agreed that the major component in the Ninol type of alkylolamide is the lauric diethanolamide, the determination of the amount of by-product esters also present has been difficult.

Both Livengood (3) and Kroll (4) have published methods for determining the percentage of ester amine by dissolving the alkylolamide in ethyl ether, washing out diethanolamine with sodium chloride solution and titrating the ester amine left in the ether solution with perchloric acid. The ester amide content is then calculated by finding the ratio of combined fatty acid to combined diethanolamine. In this way a sample of a commercial alkylolamide made from 2 moles of diethanolamine and 1 mole of lauric acid was found by them to contain 9.5% ester amine and 10.5% ester amide.

We believe these results to be in error however, based on infrared determinations made in our laboratory.

By calibrating an I. R. Spectrophotometer with a sample of pure lauric ester amide (made by the acylation method of Trowbridge (2), it becomes a very simple matter to determine the total amount of ester amide plus ester amine since both show the same ester carbonyl absorption peak at 575 millimicrons. By using this technique, the following total ester contents (expressed as ester amide) were found in some of our commercial alkylolamides: lauric diethanolamine condensate (2:1 Ninol type), 1.2%; lauric diethanolamine condensate (1:1 activity type), 3.4%; lauric monoethanolamine condensate (1:1 reaction), 4.6%; lauric monoisopropanolamine condensate (1:1 reaction), 5.1%.

It would therefore seem that the very high concentrations of esters found in the diethanolamides by the above authors must result from errors in the analytical methods used, magnified by the subsequent step of using ratios of these values in the calculations. Hence the true lauric diethanolamide content of the Ninol type of alkylolamides is actually considerably higher than indicated by them.

The most reliable procedure for determining true lauric diethanolamide content is the following.

a) Find "free fatty acid" (really amine soap) by titrating a sample in ethanol with KOH to the phenolphthalein end-point.

b) Saponify another portion by boiling with 0.1N KOH in alcohol, then back titrate with HCl to thymolphthalein-D.C. Red end-point to find total fatty acid.

c) The difference is combined fatty acid, which must all be present as lauric diethanolamide except for the amount of total ester amide found by infrared.

By this method the amount of lauric diethanolamide in a 2:1 Ninol type of lauric diethanolamine condensate is found to be 63% rather than the 49% reported by Kroll.

In the case of the monoalkylolamides, agreement between the analytical and infrared determinations of the ester content is better since Livengood found about 5% of ester in a 1:1 lauric isopropanolamide condensate (using a saponification method), which agrees well with our infrared findings.

In recent years a group of alkylolamides made from methyl laurate has appeared on the market, with the unusually high lauric diethanolamide content of about 92%. These are 1:1 lauric-diethanolamine condensates. It is rather surprising that simple heating of 1 mole of lauric acid with 1 mole of diethanolamine produces a product so high in ester amide content that it is unsuitable for detergent uses. On the other hand, if 1 mole of diethanolamine is heated with 1 mole of methyl laurate (plus a catalyst), the reaction goes smoothly to yield a product of very high lauric diethanolamide content which is eminently suitable for use in detergent systems. These are the so-called "high-activity" alkylolamides. A reaction of this kind is described by Meade (5). The composition of a high-activity lauric alkylolamide of this type made by our company would be 92% lauric diethanolamide, 3% ester amide, 4% free diethanolamine, and 1% sodium laurate.

It is interesting to note that the ester content is somewhat higher than this figure, immediately after reaction is completed, but drops slowly on storage, apparently because of rearrangement of ester amine to lauric diethanolamide, as noted by Trowbridge (2).

Properties

The alkylolamides exhibit a number of unusual properties which have accounted for their rapid growth, but, before describing these, a brief tabulation of the physical appearance of several different members may be of interest, as shown in Table I.

Viscosity. One of the unique properties of the alkylolamides is their ability to thicken aqueous solutions. Figure 1 presents the viscosity curves for two coconut diethanolamides (2:1 type), showing that viscosities of several hundred centipoises can be reached with less than 10% alkylolamide in solution. While it is true that the ethylene oxide type of nonionic also gives viscous solutions in water, concentrations of 40–50% are required. The reason for this thickening action is not well understood but is probably caused by an association of some kind with water molecules to form complexes. This thickening action does not occur in other solvents, such as alcohol.

The thickening action of the alkylolamides can also be used to increase the viscosity of other detergent solutions. In Figure 2 are shown blends of a lauryl sulfate with two high activity 1:1 diethanolamides and a conventional 2:1 type. As can be seen, the viscosity of the lauryl sulfate solution is increased from 3 cp. to more than 1,000 cp. by admixture with these alkylolamides. The 1:1 high activity types are more effective thickeners than the 2:1 alkylolamides.

Water-insoluble products like lauric monoethanolamide and lauric isopropanolamide also make excellent thickeners. Even though they are not soluble in water alone, they can be dissolved in the detergent solution.

Foam Stabilization. Another very important property of the alkylolamides, particularly in connection with dishwashing and laundry detergents, is the ability to stabilize the foam of other detergents. For

TABLE I

Appearance of Alkylolamides

Composition		Ratio of amine to acid	Appearance
Fatty base	Alkylolamine		
Lauric acid	Diethanolamine	2:1	Soft white paste; water-soluble
Coconut acid	Diethanolamine	2:1	Yellow liquid; water-soluble
Methyl laurate	Diethanolamine	1:1	High-activity type is a white wax; moderately water-soluble
Coconut acid	Diethanolamine	1:1	Amber liquid; soluble in kerosene
Lauric acid	Monoethanolamine	1:1	White wax; insoluble in water
Lauric acid	Isopropanolamine	1:1	White wax; insoluble in water
Oleic acid	Diethanolamine	2:1	Amber liquid; kerosene-soluble
Stearic acid	Monoethanolamine	1:1	Hard white wax; water-insoluble

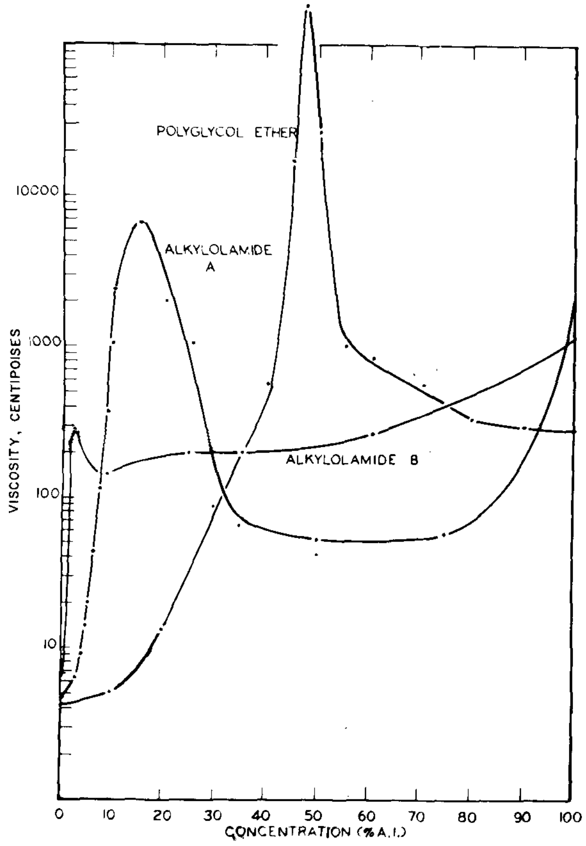


FIG. 1.

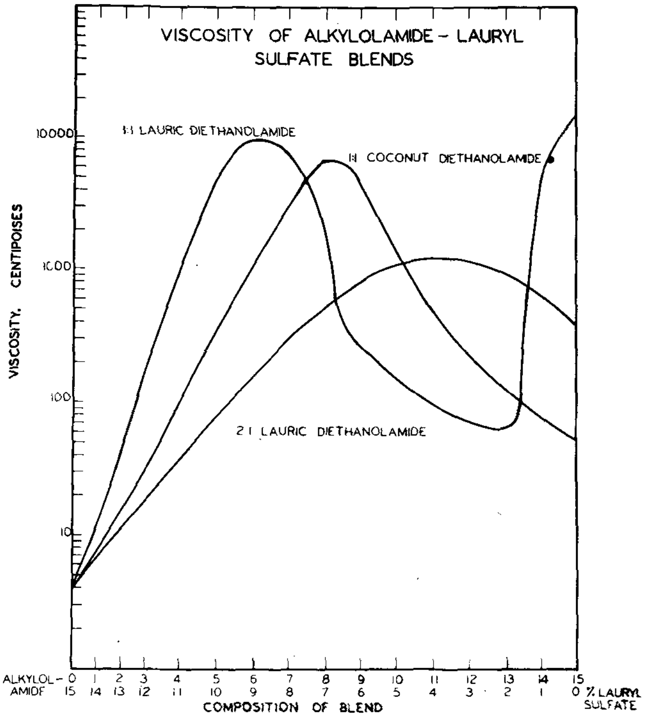


FIG. 2.

example, when alkyl aryl sulfonates are used to wash dishes, the high initial foam rapidly collapses as the water becomes greasy. This foam collapse can be greatly retarded by addition of alkylolamides. In Figure 3 is shown graphically the results of a dishwashing test in which the number of soiled dishes that can be washed before disappearance of the foam are counted. As can be seen, about 50% more plates can be washed by blending the sulfonate with a lauric alkylolamide; the high-activity type is the most effective.

The effect that the type of fatty acid in the alkylolamide has on this stabilizing action was studied in a slightly different type of dishwashing test. Here a fixed number of soiled plates were washed and the residual foam heights were then measured. The results are given in Table II where a series of 2:1 type diethanolamides were made up with different fatty acids and then blended 1:1 with sodium alkyl aryl sulfonate for this test. As can be seen, the foam-stabilizing action is most effective for the laurate and drops off rapidly as the molecular weight increases.

The water-soluble dialkylolamides also exhibit good foam stability in combination with soaps. Whereas most nonionic detergents greatly decrease the foaming power of soaps, the amides have no adverse effect and often result in increased foam volume.

Rusting. Another interesting property of the alkylolamides is their rust-inhibiting action. Although the majority of surfactants increase rusting rates, even dilute solutions of the diethanolamides will prevent corrosion of iron or steel. This property is of considerable commercial importance as it permits shipment of liquid cleaners in unlined steel drums.

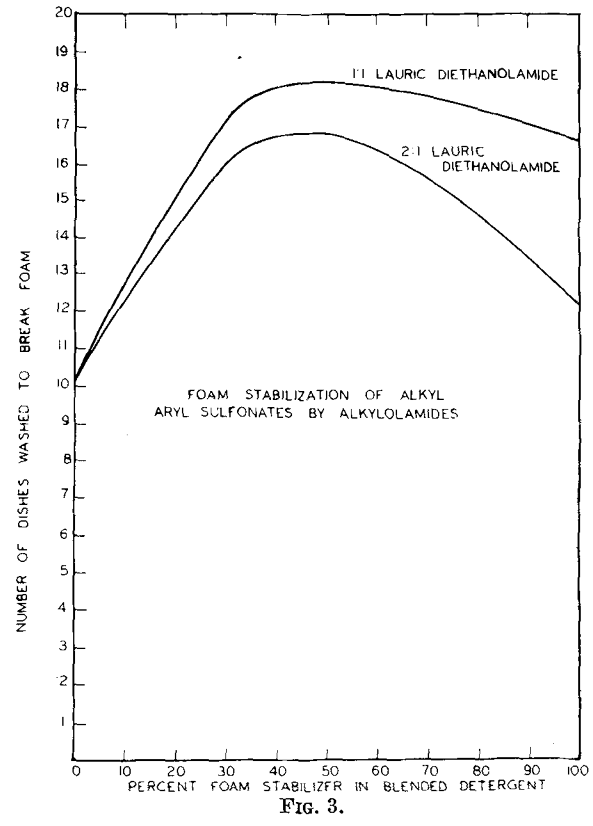


FIG. 3.

TABLE II
Effect of Fatty Acid Base on Foam Stabilization by Alkylolamides

Fatty acid base used in 2:1 diethanolamide	Foam weight of blended detergent	
	Initial	Final
............(Sulfonate used alone)......................	48	2
Capric	49	11
Lauric	48	16
Myristic	40	6
Palmitic	33	3
Oleic	29	2
Stearic	26	0

Detergency. It should also be emphasized that the lauric or coconut alkylolamides are excellent detergents; their cleaning power is intermediate between the alkyl aryl sulfonates and the ethylene oxide type of nonionic. The water-soluble diethanolamides are widely used as scouring agents for removing greasy soils in the textile industry (6). Richardson has pointed out (7) that even the water-insoluble lauric monoethanolamides improve the cotton detergency of alkyl aryl sulfonates when used in blends. In addition, a number of investigators (8, 9) have found the alkylolamides to possess outstanding soil-suspending properties, which help prevent redeposition in laundering. Table III shows the improvement in detergency which results when an alkylolamide is added to a built alkyl aryl sulfonate (ACH114 soiled cloth used).

TABLE III
Detergency-Boosting Effect of Alkylolamides

Composition (%)			Detergency (%)
Amine condensate	Alkyl aryl sulfonate	Phosphate and sulfate	
0	25	75	32.9
5% 2:1 Lauric diethanolamide	20	75	42.2
5% 1:1 Lauric diethanolamide	20	75	40.4
5% 2:1 Coconut diethanolamide	20	75	40.0
5% 1:1 Coconut diethanolamide	20	75	43.0
Hot water alone	....	....	17.9

Like all classes of surfactants, the alkylolamides have their limitations as well as their strong points.

For one thing, the water-soluble types are sensitive to salts so that they are thrown out of solution by even small concentrations of electrolytes. This is the reason that dilute solutions in tap water are cloudy; the hardness causes an incipient salting-out. Fortunately this problem can be overcome by adding anionic surfactants, such as alkyl aryl sulfonates, which act as couplers. Alcohol or urea can also be used.

Similarly, water solutions of alkylolamides are sensitive to acids. The natural pH of these solutions is about 9 because of the diethanolamine present. Addition of any acid to a pH under 8 will cause clouding and gelling, probably because of liberation of some free fatty acid and the formation of salts. Again this can be overcome by the addition of anionics so blends can readily be adjusted to neutrality if desired.

Extremely high alkalinity, such as free caustic, will slowly saponify the diethanolamide types hence formulations should not exceed pH 12 for stability.

Applications

The largest volume of alkylolamide is used in the household detergent field. For example, a simple liquid dishwashing detergent formula is 30% sodium alkyl aryl sulfonate, 10% lauric-diethanolamine condensate, 10% alcohol, and 56% water.

The function of the amide is mainly to improve the foam stability in the dishpan, but it also contributes to detergency and skin emolliency. As already pointed out, the "high-activity" 1:1 diethanolamide is somewhat superior to the 2:1 condensates, but they are less soluble so have a greater tendency to freeze out. The monoalkylolamides can also be used here, but again cold solubility is a problem unless large percentages of alcohol are used.

Spray-dried, beaded detergents of the light-duty and heavy-duty types usually incorporate about 2 or 3% of alkylolamide for foam and detergency improvement. The monoethanolamides or isopropanolamides are generally used here because a liquid type of alkylolamide would make the product too sticky and reduce tower through-put. Since hundreds of millions of pounds of spray-dried detergents are produced annually, this represents a large outlet for alkylolamides.

In the restaurant field a large quantity of low-priced, hand dishwashing powder is used, consisting of dry-mixed phosphates and alkyl aryl sulfonates. A liquid coconut or lauric diethanolamide is often sprayed onto the powder while mixing. The waxy monoalkylolamides cannot be used for they do not become intimately associated with the sulfonate in dry-mixing and would not dissolve in water during use.

In the cosmetic field, shampoo products utilize large quantities of alkylolamides to stabilize lather on the hair, thicken the product, and impart emolliency. A simplified formulation for a pearly, lotion type shampoo is 15% sodium lauryl sulfate, 4% coconut diethanolamide, 3% stearic diethanolamide, and 78% water.

The water-soluble coconut (or lauric) amide improves body while the stearic amide imparts pearlescence and opacity. For extremely viscous liquid shampoos the 1:1 high activity diethanolamide can be used. Wool-washing detergents and carpet shampoos are formulated along similar lines.

A special use of alkylolamides in the cosmetic field is as a lipstick base (10). It has been found that the fluorescein dyes (such as eosin) used in these products are soluble in monoalkylolamides and impart rapid straining action and indelibility.

Shampoos based on coconut soaps can also be improved by the addition of alkylolamides which act to improve the foam and also help to disperse limesoap curds so that they can be rinsed away instead of adhering to the hair. In addition, the amide will improve clearity of the shampoo by dispersing higher fatty acids, such as stearic, that may be present.

Synthetic liquid floor cleaners have largely displaced the conventional potash scrub soaps for institutional cleaning, largely because of the excellent properties of certain special coconut alkylolamides. A general formula for a floor cleaner of this type is 10% coconut diethanolamide (2:1 type), 5% phosphates, 2% alkyl aryl sulfonates, and 83% water.

The coconut amide used gives a product with good cleaning action, high viscosity, and nonrusting properties which permit it to be shipped in plain steel drums. Foam is only moderate, which is desirable for high-speed cleaning techniques.

As mentioned previously, some of the alkylolamides are oil-soluble, for example, the condensate made by heating 1 mole of coconut fatty acid and 1 mole of diethanolamine. Such a product, which is essentially an ester amide, is used in the dry-cleaning industry as a water-in-oil emulsifier for carrying water into the wash wheel. A special oleic diethanolamide is being used to emulsify water into petroleum for ointment bases.

These oil-soluble amides exhibit good corrosion inhibition in oil systems and can be used in crankcase lubricants, slushing oils, and other applications where protection against moisture is required.

In the textile-processing field, alkylolamides are used in a variety of applications ranging from wool scouring to cotton finishing. Softeners and plasticizers for sizings are made from stearic diethanolamides, which are sometimes treated with acetic acid to make them cationic and substantive to the fibers.

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