necessary for any shampoo if it is to obtain and hold any significant portion of the market.

Textile Auxiliaries. The fatty alcohol sulfates are not widely used as textile auxiliaries but are used in some places for kier-boiling of cotton. The C_4–C_{10} alcohol sulfates are sometimes used as wetting agents in the mercerizing of cotton. The alcohol sulfates are used as levelling and suspending agents in the dyeing of mixed wool and acetate rayon fabrics.

Electroplating. The alcohol sulfates are used in electroplating. In nickel plating baths they reduce the crystal size of the nickel plated on the metal; consequently the porosity of the film is reduced.

Ulcer Remedies. The decyl and lauryl sulfates are used for treatment of stomach ulcers. The exact reason for their effectiveness is not known, but tests have indicated their usefulness.

Toothpastes. Lauryl sulfates for use in toothpaste have long been known to be very effective and advantageous. The foaming characteristics and clean feel left in the mouth are their main reasons for use.

Rug and Upholstery Cleaners. The sodium lauryl sulfates are widely used for on-location rug and upholstery cleaning. Their detergency properties are excellent for this purpose, yet they do not wet through the rug or upholstery, which would often cause mildew. The sodium salt is used so that it can be picked up by a vacuum cleaner after the item is dry. Where detergents are used which are not dry powders when dehydrated, the detergents themselves cause rapid resoiling of the item cleaned.

Miscellaneous Uses. The fatty alcohol sulfates are also used in alkaline metal cleaning baths, in detergent bars, and as emollients and emulsifiers for cosmetics. Combinations of alcohol and alcohol sulfates or C_{16}–C_{18} chain length yield stiff, stable emulsions for creams and similar preparations. An example of this is the use of cetyl alcohol in a cream brilliantine formula.

The lauryl sulfates are used for washing the felts used on paper machines. Surprisingly this same detergent has been shown to be effective against aphids and soft-bodied insects.

A recent patent indicates that hexyl sulfate is useful as a coupling agent for higher alkyl sulfates in liquid, heavy-duty detergent formulations.

The list could continue as the alcohol sulfates have found wide and varying usage. However there is one derivative of the fatty alcohols which should be mentioned, even though not alcohol sulfates but the fatty alcohol ether sulfates. These materials are just being introduced in the American market and are prepared from fatty alcohols by addition of ethylene oxide, followed by sulfation. They have many of the good properties of the fatty alcohol sulfates yet allow for greater variation in their properties through change in the length of the ether chain between the alkyl radical and the sulfate.

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The Alkylolamides

JEROME KRITCHEVSKY, Ninol Laboratories, Chicago, Illinois

AS WITH SO MANY DISCOVERIES, the Ninol alkylolamides originated as a by-product of an entirely different line of investigation. Sometime in the late '20's Wolf Kritchevsky began a study of methods for transforming water-soluble dyestuffs into oil-soluble types and observed that acidic dyes containing carboxyl groups could be precipitated by basic dyes containing amine groups. By then treating water-soluble acid dyes with various amines, he found that esters made from alkylolamines and fatty acids, such as oleyl ethanolamine, could convert water-soluble dyes to oil-soluble types.

In the course of preparing these ester amines Dr. Kritchevsky made a significant observation. He noted that, by heating one mole of coconut fatty acid with one mole of diethanolamine, a water-insoluble condensate was produced as expected; surprisingly however, the presence of an extra mole of diethanolamine seemed to modify the reaction to give a product completely soluble in water. This new material foamed and wetted well and showed good resistance to hard water. Recognizing the importance of this development, Dr. Kritchevsky filed patent applications, which resulted eventually in issuance of U. S. Patent 2,089,212 in 1937, covering what has been described as the first American detergent.

Chemistry

In spite of the great commercial importance these alkylolamides (referred to as the "2:1 Type") have since achieved, their chemistry has never been fully elucidated. It is known that merely mixing an extra mole of diethanolamine (DEA) at room temperature with a 1:1 coconut diethanolamide will not impart water solubility since heating for several hours at about 140–150°C. is required.

U. S. Patent 2,089,212 speculates that the first mole of diethanolamine reacts with the coconut fatty acid during heating to form an amide, and the second mole of DEA then reacts further with a terminal hydroxyl to form a quaternary ammonium compound. This is not too probable however, in view of the fact that the alkylolamides do not exhibit definite cationic behavior and are not as highly alkaline as a quaternary base would have to be.

Furthermore the fact that the second mole of DEA is so weakly held that it can be titrated or distilled off would indicate it is physically rather than chemically combined. One possibility might be that the second mole of DEA is hydrogen-bonded to the diethanolamide in some way, thus imparting water solubility to the otherwise sparingly soluble amide.

Although these water-soluble coconut alkylolamides have become the most important type commercially, derivatives made from other fatty acids and two moles of DEA have also been used quite extensively in cosmetics, textiles, and other applications. In addition, alkylolamides of a simpler type, made by reacting equimolar quantities of fatty acids and monoalkylolamines, such as monoethanolamine or isopropanola-

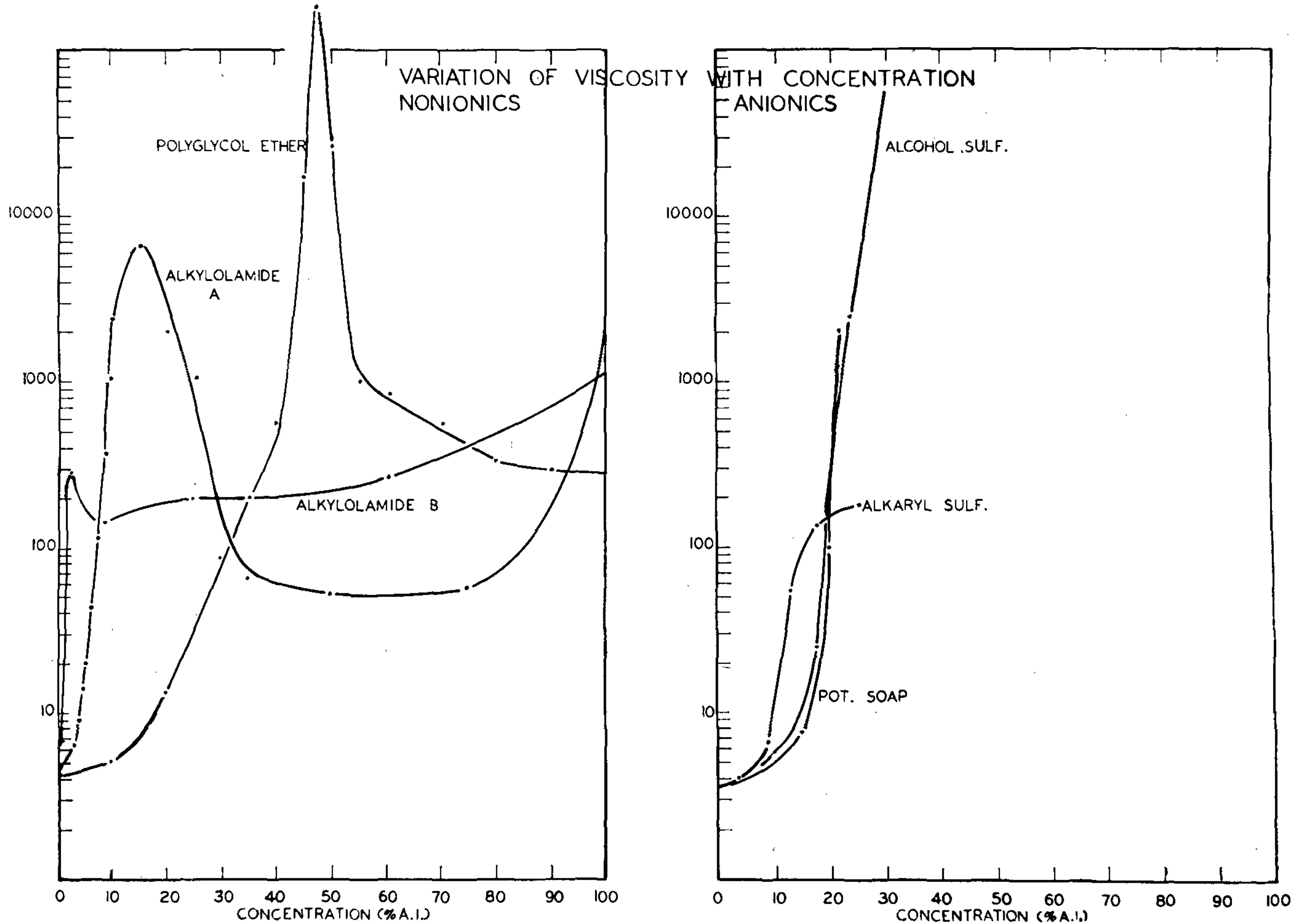

FIGURE 1

mine, are also in wide use. Depending on the fatty acids and the amines used, the alkylolamides vary considerably in physical form, as can be seen from Table I. In general, the highest fatty acids and the monoalkylolamines tend to give the hardest waxes.

TABLE I
Types of Alkylolamides

Ingredients		Properties
Fatty acid	Hydroxyamine	
Lauric	Diethanolamine	Water-soluble liquid
Lauric	Monoethanolamine	Insoluble wax
Lauric	Isopropanolamine	Insoluble wax
Oleic	Diethanolamine	Water-dispersible liquid
Stearic	Diethanolamine	Dispersible paste
Stearic	Monoethanolamine	Very hard wax

The properties of the alkylolamides are somewhat dependent on the exact grade of raw materials used and the nature of the heating cycle. For example, the viscosity in water will depend on whether a whole coconut fatty acid or a stripped acid is used and on exactly how far the condensation is carried.

To some extent this results from the fact that these amine condensates are rather complex mixtures. Both ester amines and ester amides as well as amides can be formed, and cyclization to form piperazines is also a possibility. In practice however a 2:1 type of lauric diethanolamine condensate, when properly prepared, is found to contain about 65% of true diethanolamide, and practically no ester amine or piperazine, though there may be a few per cent of ester amide.

Recently a new process for producing alkylolamides by ester interchange has come into use. This involves reacting 1 mole of a fatty acid methyl ester with only 1 mole of diethanolamine under special conditions. These products, which can be described as the "1:1 Type," contain very little excess of diethanolamine and have true amide contents of over 90%. As might be expected, they are not very water-soluble but can be used in blends with other detergents where they become solubilized.

Properties

Type. The water-soluble alkylolamides can be considered essentially nonionic in behavior. Where the condensation has been carried close to completion, these products appear entirely compatible with both cationic and anionic surfactants over a wide pH range.

If the condensation reaction is not carried all the way, then a certain amount of amine soap is present, and this destroys compatibility with cationics.

Solubility. The only truly water-soluble members of the series are the condensation products of C_{10} or C_{12} fatty acids with 2 moles of diethanolamine. All the other possible combinations using monoethanolamine, isopropanolamine, and various fatty acids are not water-soluble. Most of the alkylolamides are soluble in ethanol although some types, such as monoethanol stearamide, are not, except in the hot.

Several of the higher fatty acid amides are soluble in kerosene, particularly the oleic derivatives. Surprisingly the condensation product made by heating equimolar amounts of coconut fatty acid and DEA is kerosene-soluble whereas the corresponding ones made from monoethanolamine and isopropanolamine are not. This is believed to be caused by a high degree of ester amide formation under these conditions in the case of DEA. Such products make excellent water-in-oil emulsifiers.

Viscosity. One of the outstanding properties of the alkylolamides is their viscosity in fairly dilute, aqueous solutions. Thus 2% or 3% solutions of the 2:1 type coconut diethanolamide in distilled water have viscosities of 200 cp. or more. No other commercial surfactant exhibits this behavior, which is limited to the C_{12} diethanolamides. Capric diethanolamide is not as viscous, and the higher amides are insoluble. Figure 1 shows the viscosity curves of several different surfactants in water. Below 10% only the two alkylolamides (A and B) give appreciable viscosity. Both of these are 2:1 types based on coconut fatty acid and DEA, but B is condensed farther.

As might be expected, the alkylolamides can also be used to thicken solutions of other surfactants, and, in fact, this is an important commercial application of these products. In Figure 2 the thickening action of two lauric alkylolamides on lauryl sulfate is shown. As can be seen, the 1:1 type alkylolamide thickens more than the regular 2:1 type. Since the former contains a higher proportion of the active amide, this is not surprising.

Foam Stabilization. It is now well known that alkyl aryl sulfonates and even lauryl sulfates produce foams that are very unstable in the presence of greasy soils. The addition of alkylolamides has been found greatly to increase the foam stability of these products, with the lauric diethanolamides being probably the most effective. Figure 3 compares the foam-stabilizing action of a conventional 2:1 lauric diethanolamide (NINOL AA-62) with that of a 1:1 lauric diethanolamide made *via* the methyl laurate route (NINOL AA-62 EXTRA). As can be seen, the higher amide content of the 1:1 Type gives superior foam-stabilization, as judged by a dishwashing test, to a dead foam end-point.

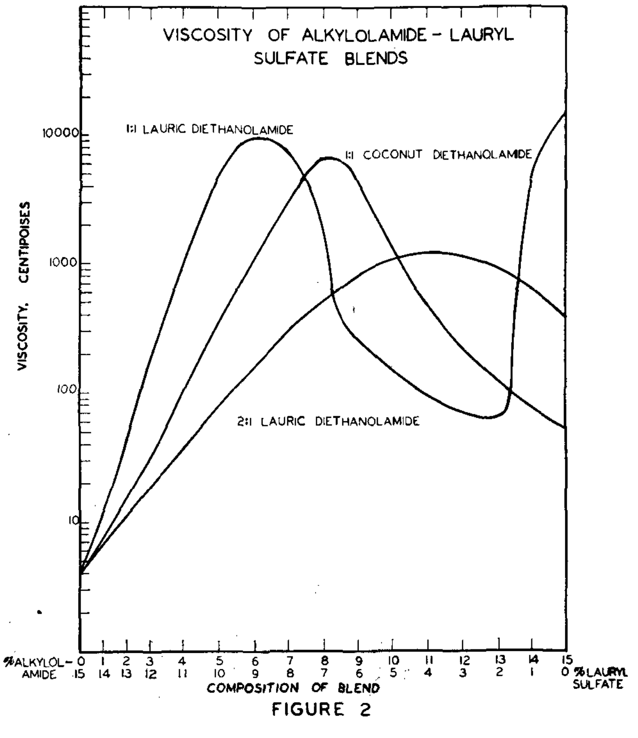

FIGURE 2

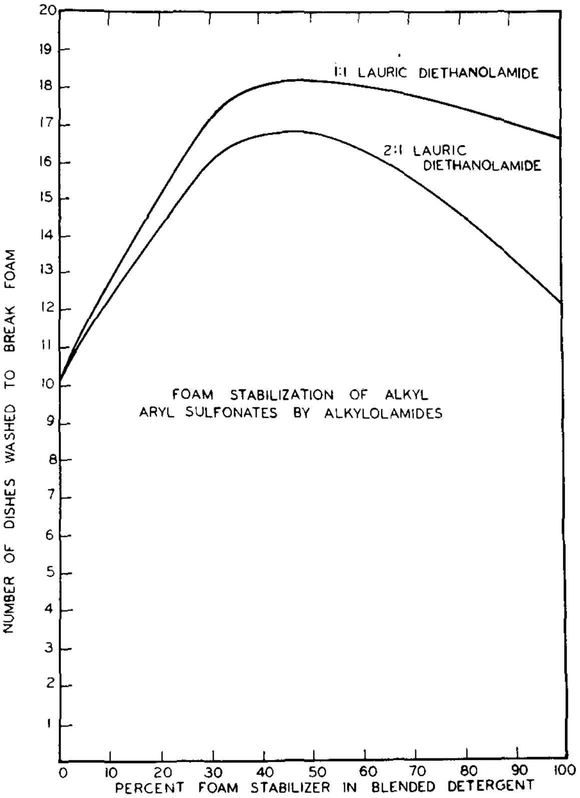

FIGURE 3

As the molecular weight of the fatty acid increases, the foam-stabilizing action of the diethanolamides decreases, and some of the amides of higher acids can even act as foam depressants, as shown by Table II in which eight soiled dishes were washed with mixtures of lauryl sulfate and various 2:1 Type alkylolamides and the residual foam was measured.

Detergency. The unusual properties of the alkylolamides, such as their thickening, foam stabilizing, and rust-inhibiting action, have tended to divert attention from their detergent properties.

Actually the water-soluble alkylolamides are excellent detergents and exhibit much better cleaning action than the alkylaryl sulfonates, for example. This is illustrated by Table III, which gives the results of laundering tests on soiled cotton. As can be seen, addition of an alkylolamide to the alkyl aryl sulfonate enhances detergency considerably.

Applications

While the total quantity of the various alkylola-

TABLE II
Effects of Diethanolamides on Dishwashing Foam

Concentration in dishpan		Foam height (mm.)	
% Lauryl sulfate	% Diethanolamide	Initial	Residual
0.025	......	51	13
0.0125	0.0125 capric	49	15
0.0125	0.0125 lauric	50	19
0.0125	0.0125 myristic	43	10
0.0125	0.0125 palmitic	40	6
0.0125	0.0125 oleic	38	5
0.0125	0.0125 stearic	30	2

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

mides used today is not definitely known, a reasonable estimate would place the figure at about 25 million pounds.

More than half of this is probably going into powdered and liquid household detergents for dishwashing and laundering, where they are used to improve the action of the alkylaryl sulfonate base. In fact, the outstanding foam-stabilizing action of the lauric amides has helped to make the use of the low cost alkylaryls possible in this field. Without them, the rapid collapse of suds in the presence of soil would make the retail products unacceptable to the housewife.

In addition to boosting suds, the alkylolamides markedly increase the cleaning action of the alkyl aryls since these nonionic detergents possess excellent soil-removal properties. Numerous studies have demonstrated the value of the alkylolamides for scouring wool or washing cottons in textile plants.

Textile finishes are another important outlet for alkylolamides, where certain stearic derivatives are used as softening agents for a variety of fibers. Antistatic compounds and dye-levelling agents are also based on alkylolamides in many cases.

The cosmetic industry is another large user of alkylolamides. Several different types are used as thickeners for the popular lauryl sulfate synthetic shampoos to produce the desired viscosity. In addition, they improve flash foam and impart a degree of hair conditioning. Other amides are used in liquid cream shampoos as opacifying and pearlescing agents and in clear coconut soap shampoos to improve the rinsability. The addition of alkylolamides to aerosol shave creams appears to lend crispness to the lather produced.

Certain oil-soluble alkylolamides form very stable water-in-oil emulsions and are therefore used in such items as pharmaceutical absorption bases, dry-cleaning soaps, and fuel-oil additives.

The water-soluble amides are also widely used in industrial liquid cleaners for floors, equipment, and other maintenance jobs. In such products the high viscosity, rust inhibition, and detergency of the water-soluble alkylolamides lend just the right combination of properties to the cleaners.

Miscellaneous applications cover a wide range of uses from rust-inhibiting, protective oils to latex stabilizers, and the list is growing constantly.

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Nonionic Surfactants[1]

C. E. STEVENS, Antara Chemicals, Division of General Aniline and Film Corporation, New York, N. Y.

SYNTHETIC NONIONIC SURFACTANTS were invented in 1930 in the Ludwigshaven Laboratory of the I. G. Farben industries by Conrad Schoeller and Max Wittwer (1). Commercial production started almost immediately, and the new products were quickly introduced into a wide variety of textile processes. Importation to the United States started in 1932, and domestic manufacture was initiated prior to World War II.

The growing technical and commercial importance of the nonionics has been reported in numerous articles (2, 3, 4, 5, 6). Insofar as possible this paper supplements rather than repeats the subject matter covered in the more recent reviews. It is limited in scope to those materials which derive an important portion of their hydrophilic properties from a linear polyoxyethylene chain. Included are compounds prepared by reaction of ethylene oxide with hydrophobic molecules containing an active hydrogen atom as well as compounds prepared by reaction of hydrophobic molecules with preformed linear polyoxyethylene chains, *i.e.*, polyglycols. Nonionic surfactants in which the hydrophilic portion of the molecule is a polyhydroxy group have been omitted. Also omitted are compounds containing amide nitrogen or amine nitrogen atoms as the connecting link to a polyoxyethylene chain.

Manufacture of Nonionic Surfactants

Most of the important nonionic surfactants are synthesized in an anhydrous environment in the presence of an alkaline catalyst by the reaction of ethylene oxide with hydrophobic compounds containing an active hydrogen atom (7). To be suitable for ethoxylation, hydrophobes should melt below 110°C. so that they are fluid liquids at the reaction temperature, which is in the range of 120–200°C. Ethoxylation of hydrophobes in solvent systems is difficult and is not common practice.

Ethoxylation is usually carried out as a batch process although continuous reactors have been designed and operated. Careful control of experimental variables, such as catalyst, concentration of catalyst, reaction temperature, and rate of ethylene oxide addition, permit the preparation of essentially equivalent products in ethoxylation reactors of quite different design characteristics. Consequently reactor designs and reaction conditions vary markedly among the different nonionic manufacturers.

In carrying out ethoxylations, the hydrophobe is charged into the reactor and heated to the reaction temperature. Ethylene oxide addition is then started. The polymerization is exothermic, and cooling is required. Careful maintenance of reaction temperature is essential to the manufacture of products to close specifications. For many types of nonionics the speed of reaction depends to a large degree on the cooling capacity of the system and the maximum rate at which ethylene oxide can be charged into the reaction mixture.

Satisfactory ethoxylation catalysts include: a) sodium or potassium salts of the hydrophobe; b) sodium