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]

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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 or potassium methoxide or ethoxide; and c) sodium or potassium hydroxide. The best catalyst and the optimum concentration of this catalyst are variables which must be determined experimentally for each product. Generally speaking, 0.3% by weight of anhydrous catalyst, calculated on the weight of the starting hydrophobe, is a good approximation when planning experiments of this type. In the production of many of the commercial nonionic surfactants the catalyst residue is neutralized with an organic or inorganic acid after the reaction is completed.

Mole-Ratio Distribution

The polyoxyethylation of a hydrophobic base is an addition polymerization (8). The rate of addition of the first ethylene oxide to the hydrophobe is dependent upon the reactivity of the active hydrogen atom of the hydrophobe. After the first addition of ethylene oxide, increase in polyoxyethylene chain length is through reaction of ethylene oxide with the hydroxyl group of an oxyethanol compound. Since polyoxyethylene chain length does not appreciably influence the reactivity of the terminal hydroxyl group in the chain, increase in chain length is random and subsequently yields a closely related mixture of polyoxyethylene compounds.

Flory has shown, for the addition of ethylene oxide to ethylene glycol, that the distribution of molecular sizes is represented by Poisson's distribution formula. Mayhew and Hyatt studied the mole-ratio distribution of typical polyoxyethylated nonylphenols and concluded that distribution of molecular species in these materials also follows the Poisson formula in a manner analogous to that of the polyethylene glycols (9). Figure 1, taken from their work, shows the mole-ratio distribution for nonylphenol plus 6 moles of ethylene oxide as compared with that of ethylene glycol plus 10 moles of ethylene oxide as determined by Flory.

It is generally accepted that commercial ethoxylated nonionics are mixtures which under optimum reaction conditions can approach the relatively narrow mole-ratio distribution of the Poisson formula. However it does not follow that a narrow mole-ratio distribution is associated with the most desirable properties in a commercial nonionic. In fact, reaction conditions are often established to obtain a product of wide mole-ratio distribution in order to obtain certain desired performance characteristics. Nonionics of relatively narrow mole-ratio distribution are frequently lower-melting and have sharper and higher cloud points than materials of the same gross composition with a broader mole-ratio distribution.

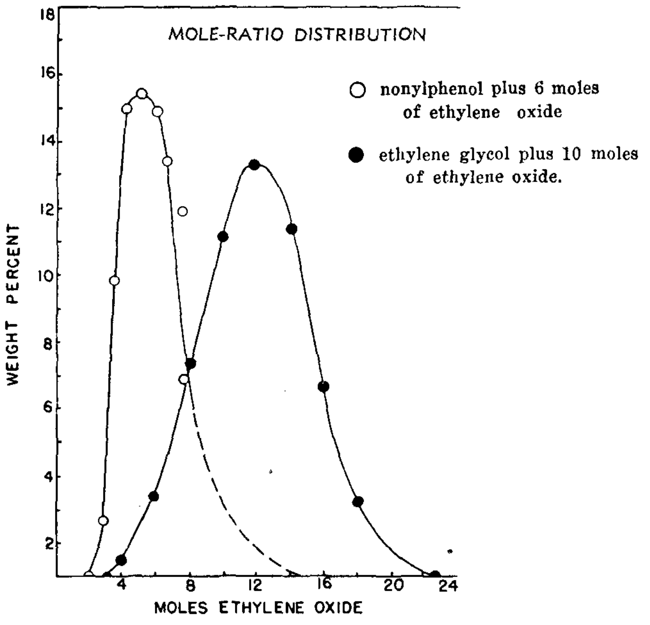

FIG. 1.

Mole ratio (*i.e.,* the average number of moles of ethylene oxide per mole of hydrophobic base) is the term generally used to specify the ethylene oxide content of nonionics. However "weight percentage of ethylene oxide" has several practical advantages over mole ratio as a means of describing nonionics. It is unfortunate that the latter term is not more widely used. The advantages of using the expression "weight percentage of ethylene oxide" are illustrated in Table I. The "weight percentage of ethylene oxide" in the three compounds of Table I is approximately equal. This indicates that they have approximately the same hydrophobic-hydrophilic balance even though their respective mole ratios vary from 10 to 44.

TABLE I

Wt. % Ethylene Oxide *vs.* Mole Ratio

Hydrophobe	MW base	MW cpd.	Mole ratio	% EtO
1. Nonylphenol	220	704	11	68.7
2. Dinonylphenol	346	1,094	17	68.4
3. Triolein	885	2,821	44	68.6

Compounds 1, 2, and 3 have a similar hydrophobic-hydrophilic balance.

Advantages and Disadvantages of Nonionic Surfactants

Nonionic surfactants have certain advantages as compared with anionic compounds. As is implied by the name, the performance properties of the nonionics are less affected by the nature and concentration of electrolytes in dilute aqueous solutions than are those of the anionics.

Another advantage of ethylene oxide in conferring water solubility on hydrophobes is that any desired degree of solubility can usually be attained. In contrast the solubilizing power of the sulfate or sulfonate group is fixed, and the molecular weight of the hydrophobe must be modified in order to obtain sulfates or sulfonates with a specifically desired solubility in water.

Another advantage of ethylene oxide as a hydrophile is that the product obtained in the reaction vessel is essentially 100% active, salt-free, and lighter in color than the starting base. Consequently there is no need for relatively expensive purifying and drying operations.

One disadvantage of nonionics as compared with anionics is that a full range of hydrophobic-hydrophilic balances is not available as 100%-active solids.

Another disadvantage of the presently available nonionic surfactants is that none of them form copious and stable foams as compared with the better-foaming anionics. Neither is it possible to build the foam of nonionics as easily as it is to build the foam of anionics.

Hydrophobic Bases

A wide variety of satisfactory hydrophobic bases for manufacture of nonionic surfactants is available at a reasonable cost. These include alkyl mercaptans, octylphenol, nonylphenol, dinonylphenol, tetradecylphenol, dimerized alkylphenols, lauryl alcohol, oleoyl alcohol, tallow alcohol, tridecyl alcohol, castor oil, soybean oil, oleic acid, tall oil, stearic acid, lauric acid, polyoxypropylene, and hexitol esters. Considerable research effort is being directed to the development of new hydrophobic bases.

Each of the hydrophobes listed above is used commercially as the base for manufacture of a homologous series of nonionics of different mole ratios by at least one of the more than 17 manufacturers of nonionics. The total number of nonionics on the market is certainly in excess of 100 significantly different chemical compounds. An accurate estimate of this number must be deferred until a majority of the manufacturers disclose the compositions of their products.

Nonionic Surfactants as Chemical Intermediates

Nonionic surfactants are used extensively as intermediates for the syntheses of anionic surfactants (7). In part this is a matter of using a relatively short ethylene oxide chain to increase the solubility in water of a hydrophobe over that which can be obtained by monosulfation—or sulfonation. However a polyoxyethylene chain in compounds of this type contributes other desirable properties in addition to increasing water solubility. The two nonionics shown in Figure 2 are useful as chemical intermediates and, in addition, have surface-active properties which also warrant their manufacture and sale as surfactants.

NONIONIC SURFACTANTS AS CHEMICAL INTERMEDIATES

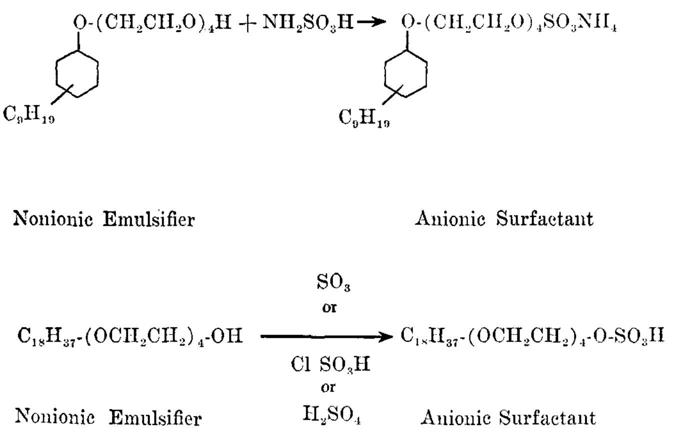

FIG. 2.

Some hydrophobes, *e.g.*, lauryl alcohol, are ethoxylated with 1 to 3 moles of ethylene oxide for use as intermediates for sulfation. These very low mole-ratio products are not widely used as surfactants *per se*.

Ethoxylated alkylphenols may also be converted to anionics by ring sulfonation. These sulfonates are useful specialties. Various types of nonionic surfactants are used as intermediates for the preparation of iodophors (11). The mechanism of the solubilization of iodine in these compounds has not been well explained.

Uses of Nonionics as Surfactants

Nonionic surfactants are being used in an increasing variety of industrial processes as well as in a wider range of consumer products. Most of these uses have been described in the technical and trade literature. Present usage of nonionic surfactants is primarily in aqueous solution and utilizes the wetting, detergent, foaming, dispersing, or emulsifying properties of these products. In many instances it is advantageous to use nonionics in combination with anionic, cationic, or amphoteric surfactants. The brief discussion which follows merely indicates the general areas in which nonionics are now used without attempting to correlate these uses with the specific surfactant properties involved.

Basic manufacturing industries which use substantial quantities of nonionics in their processes include the petroleum, pulp, paper, textile, leather, and paint industries; polymer and synthetic-fiber manufacturing; metal processing; and agriculture.

Household products which contain appreciable percentages of nonionics include heavy-duty detergents, light-duty detergents, shampoos, cosmetics, pesticide sprays, rug and upholstery shampoos, waxes, polishes, paints, and special-purpose cleaners.

Industrial products containing nonionics are used as wall and floor cleaners and finishes, food and dairy detergents, laundry and dry-cleaning detergents, metal cleaners and finishes, and sanitizers.

Classes of Nonionic Surfactants

In describing, by chemical classification, the various types of nonionic surfactants, it is difficult to know where to draw the line with respect to technical interest *versus* commercial importance. The lack of adequate production and sales statistics by chemical classification complicates the evaluation of the importance of certain categories of materials.

Again, with the intention of supplementing previous publications, easily available data have been treated in less detail in order to permit reference to less well known nonionics. "Specialty products" in the following discussion are either designed for a single use or else are believed to total less than 5 million pounds annual production per product.

Carboxylic Acids as Hydrophobes

Fatty acid esters may be prepared either by direct reaction of ethylene oxide with a fatty acid or by mono- or di-esterification of a preformed polyoxyethylene chain with a fatty acid. Wrigley *et al.* have recently studied the mechanism and rate of reaction of ethylene oxide with fatty acids and have correlated surface-active properties with chemical composition (12). The products in this category vary in commercial importance from low-volume, textile specialties to heavy-duty detergents for the household market.

The largest volume products in the carboxylic ester class are polyoxyethylated tall oils. These materials are used to some extent as industrial and textile detergents. However their principal volume use is in a low-foaming, heavy-duty, household detergent designed especially for automatic clothes-washing machines. Although the polyoxyethylated tall oils are esters and subject to hydrolysis in hot alkaline media, this does not interfere with their use in low-foaming, built formulations. On the contrary, it is probable that the small amount of hydrolysis which occurs in their manufacture and/or use contributes to their performance because the soap which is formed *in situ* functions as an anti-foamer. The soap also contributes to the detergency of the formula while the nonionic present is an excellent lime-soap dispersant and prevents curd formation in hard water.

One product, stearoyloctaoxyethylene ethanol, has attracted considerable attention because of its use in foods for human consumption. It is too soon to attempt to predict the eventual extent of this market.

Higher Alcohols and Thio Alcohols as Hydrophobes

Ethyoxylated fatty alcohols were also among the early commercial types of nonionics. They have continued to grow in volume and importance but at a moderate rate and primarily for specialty uses, such as textile and paper processing auxiliaries, cosmetic emulsifiers, latex stabilizers, etc.

Tridecyl alcohol, which recently became available from the oxo process, also shows promise as a hydrophobic base for a homologous series of nonionics which could very quickly grow to rival the fatty alcohols as a hydrophobe.

As a type, the nonionics derived from alcohols have excellent surfactant properties and chemical stability. Probably the greatest deterrent to growth of these products has been the relatively high cost of suitable alcohols as compared with that of other hydrophobic bases.

Ethoxylated fatty alcohols contain appreciable amounts of unreacted hydrophobe. Since the unreacted alcohol is solubilized by the nonionic, it does not usually interfere with surfactant performance and in many uses actually contributes desirable properties. This is especially true in the case of low moleratio, ethoxylated alcohols which are used as intermediates for sulfation. Because of the relatively high content of unethyoxylated hydrophobe in commercial grades of polyethoxylated alcohols, there is some question as to the validity of using Poisson's formula for estimating the distribution of molecular species in products of this type. Wrigley and his co-workers have recently studied the reaction of ethylene oxide with fatty alcohols and the properties of the products from this reaction (12).

Dodecylmercaptan has been used for several years as the base for an homologous series of nonionics. These products have excellent surface-active properties which are essentially similar to their analogues containing oxygen except that odor and sensitivity to oxidation preclude them from some uses. The polyoxyethylated mercaptans will probably continue to have a valid place in specialty markets.

Alkylphenols as Hydrophobes

Ethyloxylated alkylphenols were invented by Steindorff *et al.* of the I. G. Farben industries in 1934 (13). They were originally imported into the United States from Germany. Domestic manufacture was started in this country in 1937. The ethoxylated alkylphenols are probably the most versatile and eventually could become the largest tonnage products in the nonionic class. Chemically these compounds are ethers which are stable to hydrolysis by acids and alkalies and to many oxidizing agents in dilute aqueous solutions. Their surface-active properties include good detergency, wetting, emulsification, and moderate foaming.

The variety of olefin alkylating stocks now available makes possible the manufacture of a wide range of mono-, di-, and trialkylphenol hydrophobes which on ethyoxylation can yield products especially designed for specific application. The alkylphenol-based nonionics are not as yet as big a factor in the heavy-duty household detergent field as the tall oil-based products. However their use in this field is growing rapidly.

The reaction of an alkylphenol with ethylene oxide takes place more readily than the subsequent reaction of the alkylphenoxyethanol with ethylene oxide. Consequently ethyoxylated alkylphenols are virtually free of unreacted alkylphenol.

Esters of Polyhydroxy Compounds as Hydrophobes

Carboxylic acid esters of aliphatic and cyclic polyglycols are widely used as bases for ethoxylation. Because the fatty acid used, the degree of esterification, and the degree of ethoxylation are all variables, the number of compounds in this category is quite large (14). The composition and properties of these products are well described in trade literature. However the volume of many of these items is believed to be quite small. Slightly higher chemical costs and the sensitivity of the ester linkage to hydrolysis limit the use of these compounds more than their surfactant properties, which are excellent. In general, these products find more use in emulsification and specialty uses than in detergent applications.

Polyoxypropylene as a Hydrophobe

Linear propylene oxide polymers with molecular weights of 800 and greater were recently described by Vaughn *et al.* as hydrophobic bases for an homologous series of nonionics (15, 16). Nonionics from this base have grown fairly rapidly to commercial importance in a variety of specialty uses and possibly also in household detergent formulations. In many cases, where highly efficient wetting or detergency is required, the polyoxypropylene ethoxylates will probably be used in conjunction with other surfactants.

As shown by Schuette and Wittwer in 1934, propylene oxide polymerizes under the same conditions as ethylene oxide, and polypropyloxylations can be carried out prior to, during, or subsequent to addition of ethylene oxide (17). Products of this type will eventually be more thoroughly investigated and should become quite commonly used materials.

Glycerides as Hydrophobes

Several million pounds a year of ethylene oxide are used in the manufacture of a group of nonionic surfactants which are complex mixtures prepared by the reaction of glycerides, such as castor oil or soybean oil, with ethylene oxide or alternatively by reaction of these glycerides with polyoxyethylene and/or polyoxypropylene. The products are principally used as de-emulsifiers in the production of petroleum, as textile assistants, and as emulsifiers and stabilizers for synthetic latices.

Even though the chemistry of the reaction of glycerides with ethyleneoxide is not clean-cut and easy to describe in equations, these products can be manufactured reproducibly to specifications. It is possible that the effectiveness of the polyoxyethylated glycerides may lie in the complexity of the mixtures which are obtained in the synthesis.

Future Developments

Detergency, emulsification, wetting, and foaming are composite properties derived from the more fundamental surfactant properties of surface-energy lowering, adsorption, solubility, etc. Present uses for nonionics are principally in aqueous systems and utilize the composite properties just referred to. It is anticipated that new inventions will disclose many new uses for nonionic surfactants which will require different composites of properties, including more extensive use of these compounds in non-aqueous systems. Cases in point are the recent description of a process for using nonionic surfactants as flocculating agents for clays in oil-well-drilling fluids, and the discovery of iodophors (18).

In the near future nonionics will be generally recognized as comprising two major categories of products. The larger tonnage items will become staple commodities manufactured to standard specifications and available from two or more producers. Specialty items and patent-protected inventions are expected to increase in number of products and in total volume. In most cases these latter types of materials will be sold by companies specializing in technical service to specific industries.

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Sugar Esters[1]

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Previously reported studies (1) with polyoxyethylene condensates have demonstrated that optimum surfactant properties require the presence of about two ethylene oxide units for every three carbon atoms in the alkyl chain. One could hope that sucrose with 11 oxygen atoms would contribute about the same hydrophilic effect as a polyoxyethylene containing an equal number of oxygen atoms. An effective surfactant derived from sucrose would then require an alkyl group containing about 16 or 17 carbon atoms.

The usual range of carbon atoms in the alkyl chain of a surfactant is 12 to 18. Consequently this would fit into the well-established framework, and it might be expected that useful surfactants would result from the chemical combination of fatty acids and sucrose. This has been demonstrated (3). Glucose and sorbitol, on the other hand, contain an insufficient number of oxygen atoms per molecule. It is necessary to add oxyethylene groups to obtain sufficient water-solubility, with an alkyl chain of adequate size for surface activity.

The physiological properties of the sucrose esters are unique. Sucrose monostearate is nontoxic, odorless, and tasteless. Its solutions do not sting the eyes or cause allergic response when injected intravenously. When ingested, the sugar esters hydrolyze to form normal food products. Not only are these esters assured of a favorable position in food and medicinal applications, but they will create new markets in those industries where none previously existed for synthetic surfactants.

Sucrose is the least expensive material commercially available for use as the hydrophilic portion of a nonionic surfactant. When combined with tallow fatty acids to form sucrose monotallowate, the resulting product is certainly based on low-cost raw materials. If the manufacturing process is also inexpensive, the sugar esters will be competitive in applications where their special physiological properties are not important. Consequently our major effort has been directed toward developing and improving the method of manufacture.

Alcoholysis Reaction

As previously described (4), the reaction between sucrose and fat to form a sucrose ester is a straightforward alcoholysis reaction. However there are numerous complications. Sucrose cannot be heated for prolonged periods at temperatures exceeding 100°C. without caramelizing. At safe operating temperatures the solubility of sucrose in fat is negligible. It is necessary to employ a neutral solvent, one which does not decompose or enter into the reaction. Dimethylformamide and dimethylsulfoxide proved to be suitable solvents.

To effect at least 90% conversion of one of the reactants to the sugar ester, it is necessary to employ either a very large excess of the second reactant or to remove one or more of the products from solution. The use of a large excess of one reactant would require relatively large equipment in relation to product yield and would not be economical. The solubility characteristics of the sugar esters are intermediate between sucrose and fat. There is little likelihood of finding a solvent for sucrose and fat from which the sucrose ester will precipitate. Similarly glycerine will not separate from a solvent for