Nonionic Surfactants

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ABSTRACT

Over one billion pounds of nonionic surface-active agents are produced per year in the U.S. alone. The oxyethylene derivatives of alcohols and alkylphenols account for 71% of this production. Methods of making these surfactants, along with descriptions of their properties and main uses in various detergents, are described.

INTRODUCTION

Nonionic surfactants comprise a broad group of over 250 types of surface-active molecules. These products find use in many commodity applications as well as in a broad array of highly fragmented and specialized low-volume uses. As a category, they encompass fatty acid amides and esters, alcohol, amine, and phenol alkoxylates, fluorinated alcohols, organic polymers, and organo-silicone copolymers.

U.S. production of nonionic surface-active agents in 1975 amounted to 1,047 million pounds or 24.1% of the total surfactant output reported (Table I). The nonionic surface-active agents most commonly selected for use in formulated systems with a cleaning or detergency function are the oxyalkylene derivatives, particularly the ethoxylated alcohols and alkylphenols. Together these two surfactant categories accounted for 71% of U.S. production of all nonionic surfactants in 1975. Since the primary interests of this conference are detergents and detergency, attention will be focused principally on these particular derivatives. The commercial routes to their production will be reviewed first, followed by a description of their key physical properties, and finally, a review of the principal areas of their application and consumption.

SYNTHESIS OF ALCOHOL AND PHENOL ETHOXYLATES

Alcohol Ethoxylates

Surfactant-Range Alcohols: The straight-chain alcohols employed in nonionic surfactant manufacture today range in chain length from 8 to 18 carbon atoms. Until the early 1960s, these alcohols were made, almost exclusively, from natural sources by the saponification of waxes or by the reduction of long-chain acids derived from oils and fats, such as coconut oil, tallow, and palm kernel oil. Beginning in 1960, the production of straight-chain, detergent-range alcohols by synthetic routes starting from petroleum sources began on a large scale in the U.S. By 1976, detergent range alcohols were being prepared via four principal routes. These four basic commercial processes are:

(a) *Ziegler process:* This sequence to straight-chain primary alcohols, illustrated in Figure 1, was introduced first on a commercial scale by Continental Oil Company. In this process, ethylene is allowed to react with triethyl aluminum to yield a high molecular weight trialkyl aluminum which, in turn, is allowed to oxidize with air to form an aluminum alcoholate. The alcoholate is hydrolyzed to yield straight-chain primary alcohols.

(b) *Oxo process:* In the oxo process, carbon monoxide and hydrogen are allowed to add to an olefin, to yield an aldehyde which contains one carbon more than the starting unsaturated hydrocarbon (Fig. 2). This reaction, referred to as hydroformylation, yields the two structural isomers expected from a Markownikoff addition across the olefin group. The resulting aldehydes then are reduced to the corresponding alcohols.

(c) *Natural sources:* Surfactant-range primary alcohols also may be recovered from naturally occurring vegetable and animal sources, most notably coconut and palm kernel oils and animal fats. These natural triglycerides normally are transesterified with methyl alcohol and the methyl esters, in turn, are reduced to the corresponding alcohols by hydrogenation (Fig. 3).

(d) *Paraffin oxidation:* The air or oxygen enriched oxidation of linear paraffins, in the presence of boric acid, leads to a random mixture of secondary alcohol structural isomers (Fig. 4). Some small portion of the alcohol may be further oxidized to the corresponding ketone during the reaction sequence. Any ketones formed are, in turn, reduced to alcohol functionality by standard procedures.

Alcohol Ethoxylation: Surfactant-range alcohols are converted into nonionic surface-active materials by reaction

TABLE I

Nonionic Surface-Active Compounds
1975 U.S. Production[a]

Surfactant type	Amount (MM lbs)
Carboxylic acid amides	82.21
Carboxylic acid esters	222.35
Alkylphenol ethoxylates	179.45
Nonbenzenoid ethers	562.82
Total	1,046.83

[a]U.S. International trade commission, September 1976.

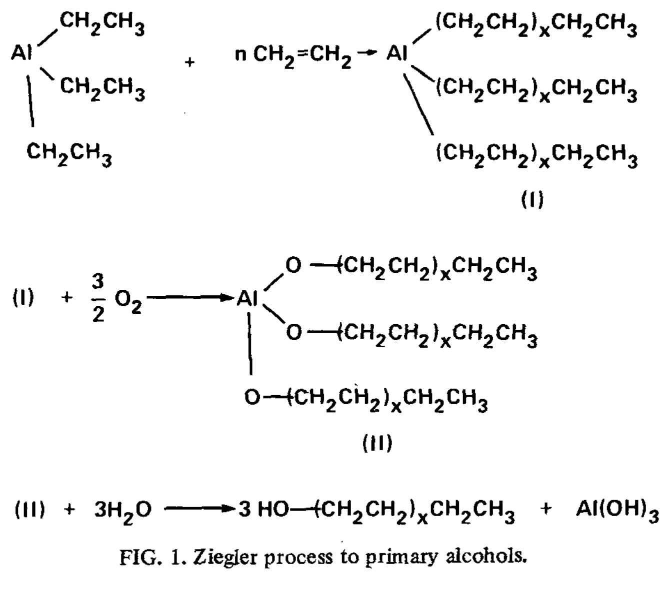


FIG. 1. Ziegler process to primary alcohols.

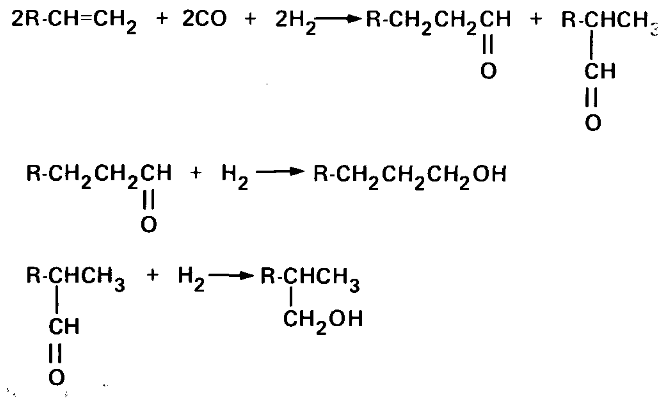
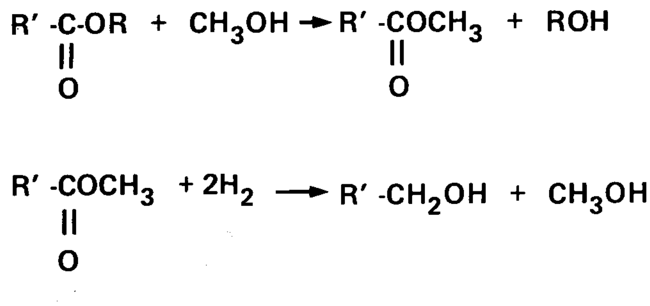


FIG. 2. Oxo process to primary alcohols.



R AND R' ARE ALKYL GROUPS

FIG. 3. Primary alcohols from natural sources.

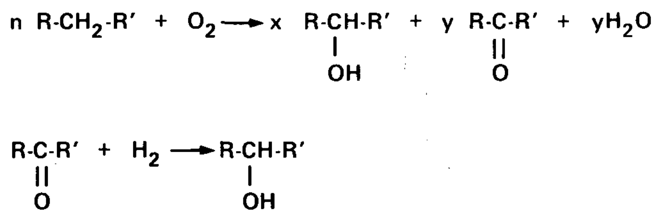


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FIG. 4. Paraffin oxidation to secondary alcohols.

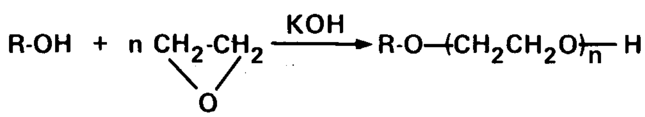

FIG. 5. Alcohol ethoxylation.

with ethylene oxide in the presence of a base catalyst, like potassium hydroxide (Fig. 5). A typical product distribution, formed by the addition of seven moles of ethylene oxide to a primary alcohol, is shown as an example in Figure 6.

Alkylphenol Ethoxylates

The second major category of nonionic surfactant used in detergency and cleaning applications is the alkylphenol ethoxylates. The principal alkylphenols used are the octyl, nonyl, and dodecyl derivatives. The nonylphenol ethoxylates account for ca. 55% of the total category's tonnage while the octyl derivative accounts for about 30%. These surfactants are prepared by the ethoxylation of the starter alkyl-substituted phenols.

Alkylphenols: The alkylphenols are made commercially via two principal routes (Fig. 7). The first involves chlorination of linear paraffins to yield randomly

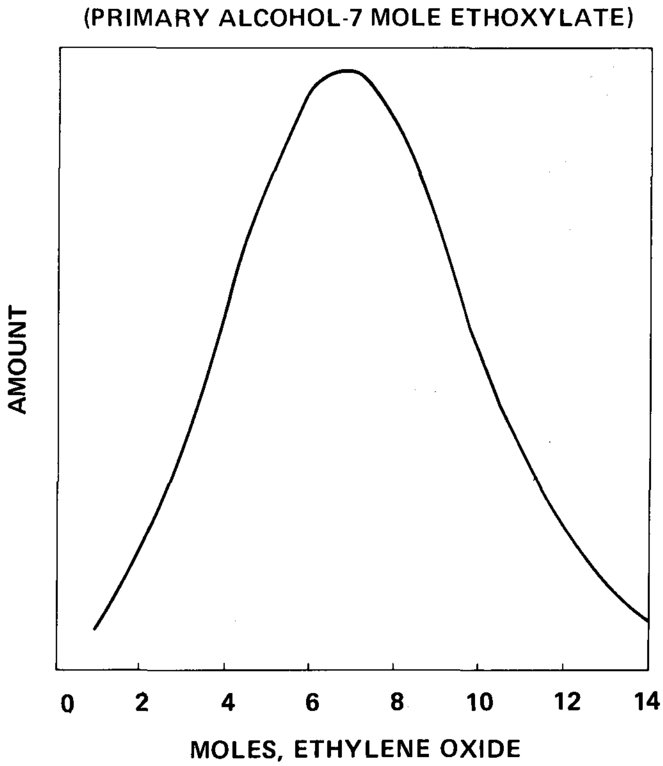

FIG. 6. Ethylene oxide distribution.

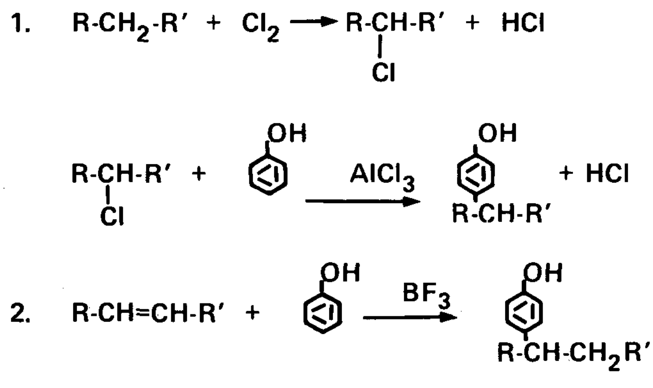

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FIG. 7. Routes to alkylphenols.

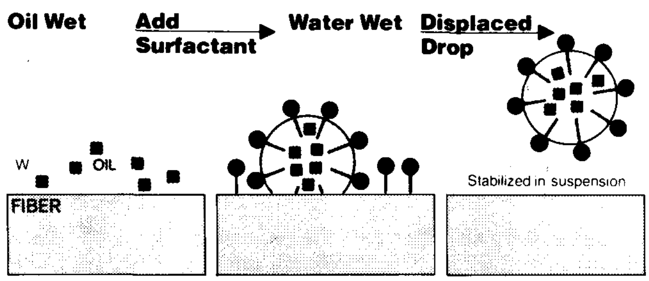

FIG. 8. Surface activity.

substituted isomeric chlorocarbons. The chlorocarbons, in turn, are allowed to condense with phenol in the presence of a Lewis acid. This sequence is depicted as Route 1 in Figure 7.

The second route involves the addition of an olefin directly onto phenol in the presence of a Lewis acid, as shown in Route 2.

Alkylphenol Ethoxylates: The alkylphenol ethoxylates

TABLE II

Cloud Points of Nonionic Surfactants

Primary alcohol ethoxylates[a]		Alkylphenol ethoxylates[b]	
Moles of ethylene oxide	Cloud point, °C	Moles of ethylene oxide	Cloud point, °C
5	<0	7	<5
7	50	9	53
9	60	15	96
12	90	20	>100

[a] C_{12} to C_{15} alcohol started.
[b] Nonylphenol started.

react readily with ethylene oxide, under base-catalyzed conditions, to yield the desired molecular weight range nonionics. Commercially, products are available with average numbers of moles of ethylene oxide ranging from ca. 4 to over 40, although 8 to 12 moles of ethylene oxide are generally selected for applications in the detergency area.

PHYSICAL PROPERTIES

In order to understand the physical chemistry of nonionic surfactants in aqueous solution, it is necessary to dwell for a moment on their general molecular structure. All nonionic surfactants are composed of two connected but distinctly different portions. One end of the molecule is hydrophobic in nature, or water disliking, and is strongly attracted to oily or hydrophobic substrates. The other end is hydrophilic in type, or water liking, and is strongly attracted to hydrophilic substrates or to water itself. The hydrophobe segments in the nonionic surfactants emphasized here are the alkyl or alkylphenyl groups derived from the starting alcohols or alkylphenols, whereas the hydrophile entity is the polyoxyethylene chain. Nonionic surfactants then, because of this dual character, are especially efficient in concentrating (absorbing) at interfaces between water and air or water and hydrophobic phases.

These molecules also orient themselves in and around an insoluble oil phase in water, as depicted in Figure 8. By enveloping the outer surface of the droplet, the surfactant renders it hydrophilic in nature, thereby preventing recombination of the droplets into a continuous hydrophobic layer. This duality of functionality, characteristic of nonionic surfactants, and, indeed, of all surfactants, accounts for their observed high surface activity in dilute water solution. This surface activity is readily measured via surface tension methods and is exploited, in a practical way, in the detergency process.

Solubility Characteristics

The polyoxyethylene nonionic surfactants range in solubility over a spectrum from complete oil compatibility to complete water solubility. This property is dependent upon the number of moles of ethylene oxide present on the hydrophobe selected. In general, the addition of 1 to 4 moles of ethylene oxide to a conventional hydrophobe yields oil-soluble products. As the mole ratio is increased to 5 to 6 oxyethylene groups, water dispersibility is observed, and with a mole ratio of about 7, complete water solubility at room temperature is realized. Conversely, solubility in hydrocarbon solvents, like normal paraffins, decreases as the mole ratio of ethylene oxide increases above about 3.

Cloud Point

A very important factor in making the most efficient use of nonionic surfactants in aqueous systems is an understanding of a property called cloud point. Ethoxylates, in general, exhibit an average solubility in water which is inversely related to temperature, i.e., as the temperature of an aqueous solution increases, the intrinsic solubility of dissolved nonionic surfactants progressively decreases. The temperature at which any given ethoxylate begins to come out of solution and cloud the liquid phase is characteristic and is called the cloud point for that particular surfactant. Table II provides typical data. It should be noted, and expected, that as the mole ratio of ethylene oxide increases in any nonionic family, water solubility also increases and, therefore, so too the cloud point.

TABLE III

Ross–Miles Foam Test[a]

Nonionic surfactant	Cloud point (°C)	Initial foam height (mm)
Primary alcohol[b]		
7 Moles EO	52	80
9 Moles EO	59	130
12 Moles EO	91	155
Secondary alcohol[c]		
7 Moles EO	37	65
9 Moles EO	60	165
12 Moles EO	90	175
Alkylphenol[d]		
7 Moles EO	5	33
10 Moles EO	63	172
15 Moles EO	96	190

[a] Test conditions: ASTM D1173-53, temperature 50 C, concentration 0.2%.
[b] C_{12}-C_{15} alcohol.
[c] C_{11}-C_{15} alcohol.
[d] Nonylphenol.

Wetting

Nonionic surfactants are among the most powerful wetting agents available. The same molecular interactions that promote efficient surface tension lowering at interfaces, also concomitantly foster enhanced wetting. Thus, nonionics with a low ethylene oxide content have been found to be the most efficient wetting promoters. Maximum wetting efficiency of any given surfactant often is observed at or somewhat above its cloud point temperature. In this temperature range, partially soluble surfactant migrates readily to the various interfaces to lower surface tension and promote efficient wetting.

Foaming

In general, as a class, nonionic surfactants tend to be low foamers. Some specific data on foaming are presented in Table III. It can be seen that materials with lower cloud points and lower moles of ethylene oxide exhibit less tendency to promote foaming in aqueous solution than those of higher cloud points and ethylene oxide contents. A word of caution in reading and predicting the foaming propensity of nonionic surfactants is necessary. The temperature at which foaming is measured is very important. Measurements at temperatures significantly above the cloud point of the material used, yield sharply reduced values. The partially insoluble surfactant migrating to the air/water interface can act, in essence, as a foam-control agent.

Biodegradation

Primary and secondary alcohol ethoxylates readily undergo primary biodegradation. In the laboratory and under field conditions, these materials seem to cleave first into hydrophobe and polyethylene glycol fractions, both of which subsequently degrade further into carbon dioxide and water. The alkylphenol ethoxylates, on the other hand, appear to be somewhat more resistant to biologically induced degradation. There is much controversy in the technical literature as to the extent, rate, and mechanism of the degradative process with this surfactant class.

TABLE IV

U.S. Surfactant Usage by Major Type

Surfactant	Use in 1976 (%)	Use in 1981 (%)
Anionics	70	65
Nonionics	25	29
Cationics	5	6

TABLE V

Household Consumption of Ethoxylated Surfactants

Type	In 1976 (%)	In 1981 (%)
Heavy duty liquids	20	35
Laundry powders	37	26
Light duty liquids	29	24
Household specialties	14	15

TABLE VI

Industrial/Institutional Consumption of Ethoxylated Surfactants

Use	In 1976 (%)	In 1981 (%)
Industrial process cleaning	43	46
Textile maintenance	18	17
Food service	17	16
Janitorial and housekeeping	22	21

A host of analytical procedures has appeared in the technical literature for detecting the presence and level of nonionic surfactants in dilute aqueous solution. The OECD expert panel on the biodegradation of nonionic detergents (1975) has recommended adoption of Wickbold's iodobismuthate (BIAS) method as the official procedure for the determination of nonionic surfactants in water and sewage. This procedure seems to provide a sensitivity of ca. 0.01 mg/liter for both alcohol and alkylphenol ethoxylates with chain lengths between 6 and 30 ethylene oxide units.

An improved cobalt thiocyanate (CTAS) procedure reported by S.L. Boyer in 1976 for the determination of nonionic surfactants in aqueous systems recently was adopted by the SDA. Results comparable to those achieved with the Wickbold method were found when this improved procedure was tested in a variety of biodegradability studies as well as on environmental samples.

Other even more selective and analytical methodology can be expected to evolve in the future which will provide still greater sensitivity for nonionic surfactants.

APPLICATIONS

Nonionic surfactants, being efficient wetting agents, low foamers, and effective emulsifiers, find utility in a broad array of home and industrial application areas. The U.S. surfactant usage by major surfactant type is shown in Table IV. In an overall product segment forecast by Union Carbide to grow by almost 25% over the next 5 years, the nonionic portion will increase from the present 25% share to 29% share by 1981. It is projected that in household applications, consumption will increase most profoundly in the heavy duty liquid (HDL) detergency category, as shown in Table V. In the industrial and institutional sphere, the respective use categories are forecast by Union Carbide to remain relatively constant through the 5 year period, as shown in Table VI.

The specific market segments encompassed by the broad use categories shown above are presented in Table VII. Many of the segments focus on the cleaning or treatment of yarns and fabrics. Although it is not possible within the time allotted to characterize each of the segments cited, several of the major areas are particularly worthy of comment here.

TABLE VIII

Surfactant Consumption in Household Laundry (Liquids and Powders 1980)

Surfactant	MM
Alkylbenzene sulfonates	453
Alcohol ethoxylates	260
Alcohol ethoxylates sulfate	130
Amides	50
Alcohol sulfates	25
Alpha olefin sulfonates	20
Soaps	70
Total	1008

Laundry Detergents – Liquids and Powders

The consumption of nonionic surfactants in the household laundry detergent category is increasing dramatically and is expected to continue this growth over the next 5 years. In the U.S., the growing popularity of HDL detergents is most responsible. Unbuilt liquid products normally contain between 30 and 40 wt % nonionic surfactant. The surfactants of preference in the U.S. are the biodegradable ethoxylates containing from 7 to 9 moles of ethylene oxide. Whether dissolved in a liquid product or formulated into a dry laundry powder, nonionics provide excellent oily soil removal, low sensitivity to hard water ions, and desirable controlled-foaming properties.

The overall potential for nonionic surfactants in the U.S. household detergent category is projected by Union Carbide to be ca. 500 million pounds per year by 1981. This demand will be for both the nonionic surfactants themselves and for the sulfates produced from these nonionics. The breakdown projected in 1980 between nonionic and anionic usage in household detergent liquids and powders is shown in Table VIII.

Dishwashing Detergents

Automatic dishwasher detergents are buffered alkaline formulations containing small amounts of surfactants, normally 1 to 3 wt %, together with an active chlorine compound. These surfactants generally are nonionic in type and are prepared from a mixture of ethylene and propylene oxides. These copolymers exhibit good stability to chlorine and have effective foam-controlling properties, even in the presence of proteins and the soaps formed during the

TABLE VII

Nonionic Ethoxylated Surfactant Consumption by Major Market Segment

Household products	Industrial and institutional products	Textile mill products
Laundry detergents	Laundry detergents	Scouring agents
Dishwashing detergents	Food service products	Spin finishes
Laundry aids	Janitorial cleaners	Coning oils
Misc. hard-surface cleaners	Transportation cleaners	Warp sizing agents
	Metal cleaners	

saponification of greasy soils in the washing action. These surfactants also promote good drainage from dishes and glassware, an action which is necessary to achieve acceptably low water spotting and surface haze.

In hand dishwashing products, alcohol or alkylphenol oxyethylene nonionics generally are used in combination with an anionic surfactant, like sulfated nonionic or alkylbenzene sulfonate, and a foam stabilizer, such as an amine oxide or a coconut diethanolamide. The nonionic component provides grease cutting efficiency while the anionic material imparts the desired flash-foaming properties and an enhanced cleaning activity.

Laundry Aids

Laundry aids encompass a broad array of products including detergency boosters, fabric softeners, bleaches, prespotters, and presoak compositions. The spray-on prewash spotter category has had a particularly favorable growth in the U.S. over the past 5 to 6 years. The trends toward polyester fabrics, low and no phosphate detergents and cool water washing combine to favor the perceived contributions achievable from this type of product. These spray-on products normally contain about two thirds to three quarters organic solvent, the remaining portion being nonionic surfactant. The organic solvent usually is paraffinic in type and is used to dissolve hydrophobic soils like human sebum, vegetable and mineral oils, etc. The surfactant, on the other hand, emulsifies the paraffin/oil combination and facilitates its removal during the subsequent laundering sequence. It is projected by Union Carbide that ca. 35 million pounds of nonionic surfactant will be consumed annually in this product category by 1980. In laundry presoak and fabric softener systems, the nonionic ethoxylates function primarily as wetting agents or emulsifiers. In laundry boosters, they bring an extra dosage of cleaning to the washing medium.

Hard-Surface Liquid Cleaners

There are two important types of liquid hard-surface cleaners marketed commercially in the U.S. The first, product concentrates, contain normally 5 to 30 wt % nonionic surfactant along with grease-cutting solvents and compatible builders. Such formulations are designed to be diluted with water before use. The second type, spray-on formulations, are offered at their intended use concentration and are formulated primarily for cleaning walls and tiling. In these products, the nonionic level is held to about 1 to 2 wt %, along with ca. 2 to 5 wt % water-soluble solvent and an appropriate level of builder. In both types of products, the nonionic surfactant is added to provide efficient greasy or oily soil removal. Approximately 20 million pounds of nonionic surfactants are consumed annually in the U.S. in this product category.

Industrial and Institutional Cleaning Products

The industrial and institutional markets in the U.S. consume ca. 120 million pounds per year of ethoxylates in an array of laundry, dishwashing, transportation, janitorial, and food service cleaning applications (see Table VI). The types of surfactants used are similar to those reviewed above in the household products area. The individual materials preferred, however, may be somewhat different because the laundering and washing conditions currently employed often are not the same as those used in the home. The trend to cooler wash temperatures and the growing use of synthetic fabrics and reduced phosphate cleaning systems are combining now to bring the choice of surfactants in this market segment closer to those preferred in the household products sphere. Although the demand for surfactants in the industrial and institutional area is growing only at about a 4% annual rate, the demand for nonionic alkoxylates is expected to grow by almost twice this figure.

Textile Mill Treatments

Nonionic surfactants are widely used in the textile industry as scouring agents, yarn preparation spin finishes, coning oils, warp sizing, alkaline scouring, and fabric finishing agents and as wetting agents and emulsifiers in dyeing and printing operations. Used at a 0.05 to 0.1 wt % concentration, alkylphenol and alcohol ethoxylates exhibit excellent degreasing and cleaning properties. The choice of nonionic surfactant is dependent on the use and temperature in the mill application of interest. Currently, around 100 million pounds of nonionic surfactants are used annually in all textile mill applications in the U.S.

Miscellaneous

Various nonionic surfactants find significant usage in a host of other highly fragmented application areas. The alcohol and alkylphenol ethoxylates are formulated into a wide range of metal cleaners, carpet shampoos, agricultural products, leather processing aids, drilling fluids, and water flooding packages in petroleum recovery. They, and others, also are used as dispersants for dyes and pigments, as stabilizers in latex paints, as defoamers, deinkers, and leveling aids in papermaking and as emulsifiers and wetting agents in personal care products. Certain amine ethoxylates are used in the preparation of asphalt compositions and metal corrosion inhibitors, and the glyceryl and sorbityl monostearates find wide application in food products as anti-staling agents and as emulsifiers for water-in-oil dispersions.