The Use of Biodegradable Linear Alcohol Surfactants in Textile Wet Processing[1]

HARRY T. ZIKA, Union Carbide Corporation, Research and Development Department, South Charleston, West Virginia 25303

ABSTRACT

Highly biodegradable linear alcohol surfactants have proven to be efficient wetting and scouring agents for use in all phases of textile wet processing. The linear alcohol surface active agents can be directly substituted for the conventional alkylphenol-based materials, which have previously been shown to be resistant to biodegradation. No loss in performance or handling characteristics are encountered by changing the surfactant hydrophobe from alkylphenol to linear alcohol. Surfactants based on the linear primary alcohols, which are widely used in biodegradable household detergents, are somewhat less desirable for use with textiles due to generally higher solidification points and less efficient wetting ability. Replacement of branched chain alkylphenol nonionics by more biodegradable linear alcohol ethoxylates has proceeded rather slowly in the textile industry. This is due to various factors, one of which is the reverse relationship between low five-day biochemical oxygen demand (BOD) requirements for industrial waste streams and the higher five-day BOD of the linear alcohol ethoxylates. Continued use of slower degrading alkylphenol ethoxylates is not, however, a satisfactory solution to the problem of the best choice of surfactant. Longer range oxygen demands on receiving waters are shown to exist as a result of such slower biodegradation of these alkylphenol nonionics.

INTRODUCTION

The use of nonionic ethoxylates as wetting and scouring agents by the textile industry is a well established fact, for reasons which will subsequently be presented. An estimated 10 billion pounds of textile fibers are currently being consumed each year, and most of these end up in textile wet processing operations. As in the soap and detergents industry the availability of the highly biodegradable linear alcohol ethoxylates held promise for a quick changeover from the less degradable alkylphenol ethoxylates. For a number of reasons, however, the switch has occurred much more slowly than in the soap and detergents industry. Not the least among these reasons is the definition and measurement of nonionic biodegradability.

The determination of the biodegradability of nonionic surfactants has been the subject of considerable investigation during the past decade. Schick provided a review of recent literature (1), which suggests that biodegradation of the hydrophobic group can occur in all nonionics except those having highly branched carbon chains. Conway and Waggy (2) employed a variety of laboratory experimental procedures to show rapid biodegradability of linear alcohol ethoxylates. Conway et al. (3) reported that linear secondary alcohol surfactants were destroyed in an active sludge plant during a field study. Patterson et al. (4) explained the rapid biodegradation of the linear alcohol ethoxylates as being due to fission of the molecule into hydrophobic and hydrophilic entities, with rapid oxidation of the hydrophobic group. No fission occurs in the case of the alkyl phenol ethoxylates, with slow biodegradation simultaneously occuring via oxidation and hydrolysis of the alkyl groups, the aromatic ring and the ethoxy chain. A massive three-year round-robin investigation of nonionic biodegradability was performed by 17 laboratories of detergent manufacturers and detergent intermediates suppliers, together with one FWPCA laboratory, under the auspices of a subcommittee of the Soap and Detergent Association (SDA) (5). The report concludes that "primary and secondary alcohol ethoxylates, alkyl ethanolamides, and alkylamine oxides are all highly biodegradable... and can readily be removed under conditions of normal secondary sewage treatment." The use of linear alcohol ethoxylates for textile wet processing has previously been reported by Rein (6) and by this author (7). This investigation extends the previous work and explores the question of biodegradability vs. five-day biochemical oxygen demand (BOD).

EXPERIMENTAL PROCEDURES

Foam performance was determined using the Ross-Miles foam test (ASTM Test Method D1173-53).

Wetting ability was determined by the Draves wetting test (AATCC Method 17-1952), using 5.0 g cotton skeins and a 3.0 g hook.

The surface tension of aqueous surfactant solutions was determined by ASTM Test Method D1331-56, using a du Nouy tensiometer.

The cotton scouring ability was measured by washing F.D. Snell carbon soiled cloth in a Terg-O-Tometer. Four 4 in. x 4 in. swatches were scoured for 15 min at 140 F in 1.0 liters of surfactant solution (unbuilt) with a hardness of 50 ppm as $CaCO_3$. Agitator speed was set at 100 rpm. The scoured swatches were rinsed under running tap water at about 100 F, ironed dry and evaluated with a Photovolt reflectometer.

Determination of freezing range was performed by a modification of standard cooling curve techniques, observing the discontinuity in a time vs. temperature curve. Viscosity was determined by the capillary method, using Cannon-Fenske viscometers. Gel ranges were determined by observation of sharp discontinuities in viscosity-composition curves of aqueous surfactant solutions. Cloud points were determined on a 1.0% aqueous solution of the nonionic as the temperature at which the first swirl of cloudiness appears upon stirring the solution during a slow temperature traverse.

Five-day BOD tests were performed using the standard biochemical oxygen demand test (8) in synthetic river water to which surfactant has been added. The biological seed consisted of acclimated bacteria from laboratory activated sludge units. The River Dieaway test results were data which were submitted by the Research and Development Laboratory, Union Carbide Corporation, South Charleston, W. Va., to the SDA round robin investigation previously described (5). The river water, from the Elk

[1]One of eight papers being published from the Symposium, "Surface Active Agents in the Textile Industry," presented at the AOCS Meeting, New Orleans, April 1970.

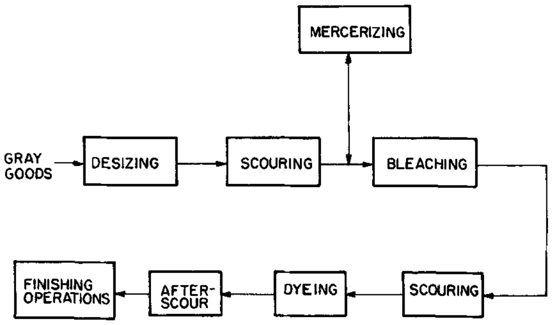

FIG. 1. Textile wet processing: cotton, synthetic-cotton, synthetics.

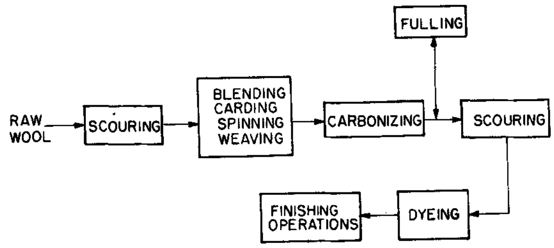

FIG. 2. Textile wet processing: woolen fabrics.

River, was modified by addition of a small amount of acclimated organisms from laboratory activated sludge units.

DISCUSSION

Textile Wet Processing

The application of surfactants in textile wet processing is more readily understood with inclusion of a brief description of the various process operations. A typical flow diagram for cotton or cotton-synthetic fabrics is shown in Figure 1. Each of these operations will normally be performed in the presence of wetting and scouring agents, or both. Thorough, fast wetting of the fabric is required for successful processing, particularly at the higher and higher speeds employed in continuous operation.

The first of these operations is desizing. Starch sizing, used in the largest volumes, is usually removed by enzymatic action, or, less frequently, by the use of sodium bromite. Nonionics are preferred wetting agents in the desizing bath because of their ability to quickly wet, their excellence in emulsification of any sizing waxes used in combination with the starch, and because they exhibit a minimum effect on heat stability of the enzyme.

The hydrolyzed starch is then extracted by scouring, usually in the presence of about 4-6% caustic soda. Starch dialdehyde is more soluble in alkaline solution and thereby may be more completely removed. The alkaline scour may include some emulsified hydrocarbon solvent, and frequently is performed under pressure. A wetting-scouring agent is always used. A high cloud point nonionic can be used at caustic concentrations below 4%; at higher alkalinities, the use of an anionic surfactant is desirable to avoid insolubility problems.

Mercerizing of cotton is performed using 18% to 30% of caustic solution. No nonionics and very few anionics are effective wetting agents in such solutions. Generally cresols are used as penetrants, but certain organic phosphates have also been used.

Bleaching operations may or may not require a wetting agent, depending on the fabric and the method of bleaching; a nonionic ethoxylate would be the surfactant of choice.

Wetting agents are used in all dyeing operations, as there exists a critical need for thorough, even wetting in order to afford even dyeing. Nonionic surfactants also act as leveling agents in these operations. A leveling agent acts by preferential and quick complexing with dye sites on the fibers; as the dyeing operation continues they are slowly replaced by the dye, with consequent even dyeing. Anionics are also useful in dyeing operations as dispersants for certain insoluble dyes and as emulsifiers for some dye carriers.

Wetting agents are required in most finishing operations, except in the application of waterproofing agents. These operations include permanent press treatment, flame-proofing, mildew-proofing, insect-proofing and application of soil release agents and softeners.

Processing of woolen goods (Fig. 2) begins with raw wool scouring, where up to 35% of the weight of the raw wool is removed by the scouring. Nonionic ethoxylates are widely used for removal of dirt, burrs, perspiration salts and for emulsification of wool grease.

Processing of woolen fabrics includes carbonizing, i.e., treatment with a 5% solution of mineral acid to destroy remnants of burrs and other cellulosic impurities. Once again, the nonionic serves as the wetting agent.

Fulling, or felting, of many types of woolen fabric is performed using a surfactant solution to provide lubricity, as well as cleansing, during the mechanical fulling operation. Fatty acid amide nonionics or soaps are commonly used in this operation.

Scouring, dyeing and finishing operations are generally similar to those described earlier.

Surfactant Uses in Textile Processing

It is already apparent that nonionic ethoxylates are the workhorse surfactants of textile processing. This is true for many reasons. They are, first, excellent wetting, emulsifying and scouring agents. They exhibit complete stability at low pH conditions. They show compatibility with other types of surfactants, dyes and other processing additives. They are excellent lime soap dispersants. They demonstrate outstanding economics on a price-performance basis; they are sold as high quality products with 100% activity. They exhibit great versatility and are useful from beginning to end of the wet processing operations. They are significantly lower foaming than other types of surfactants, and they exhibit lower substantivity.

Anionic surfactants also demonstrate utility in certain operations. They are useful in highly alkaline solutions. They are good dispersants for insoluble dyestuffs. They are good emulsifiers for textile lubricants, and they are used in certain dyeing applications.

Cationics are used for the same purpose as in the soap and detergents industry, as textile softening agents.

Performance Comparisons

In keeping with the title of this paper, the performance of biodegradable linear alcohol nonionics in textile wet processing operations is next considered. The paramount factor is wetting ability. In this parameter, as well as in the others, the cloud point, or effective solubility, of the nonionic is of utmost importance. The examination of wetting, therefore, was grouped into low, medium and high cloud point nonionics, with corresponding test temperatures. Nonionic cloud point and hydrophobe similarity were closely matched, where these were commerically available.

Wetting performance of low cloud point nonionics by the Draves test is shown in Figure 3. These are seen to be extremely fast wetting agents at 77 F, with very low 20 sec wetting concentrations. The linear alcohol nonionics, both primary and secondary, are seen to be roughly equivalent. [The linear primary alcohol ethoxylates included the Alfonic series, manufactured by the Continental Oil

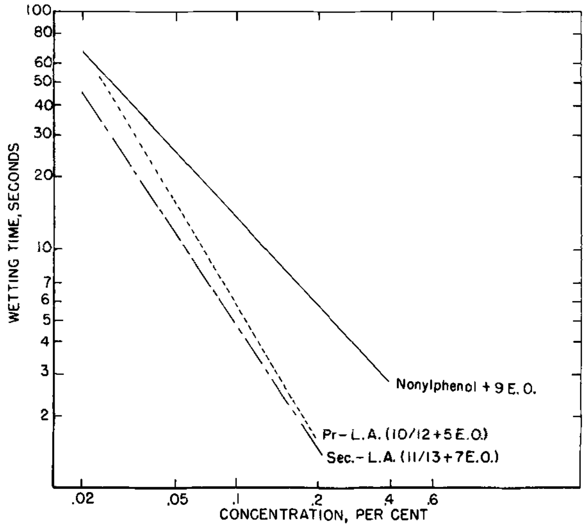

FIG. 3. Draves Wetting Test at 77 F: low cloud point nonionics, 95-100 F.

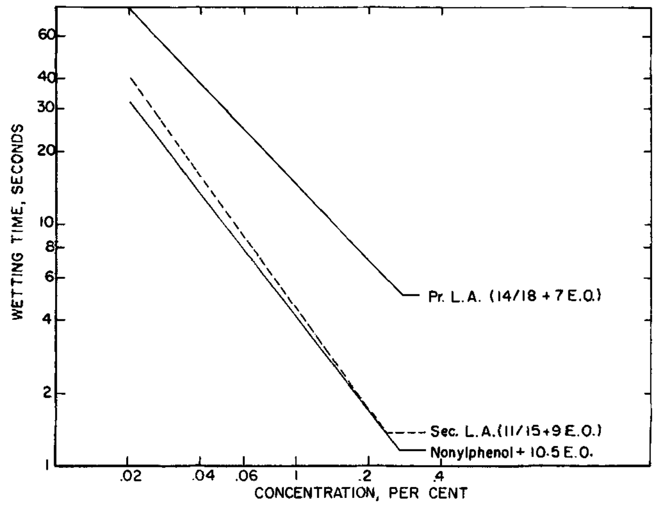

FIG. 4. Draves Wetting Test at 140 F: medium cloud point nonionics, 140-150 F.

Company, and the Neodol series, products of the Shell Chemical Company. The linear secondary alcohol ethoxylates, the Tergitol S series, are made by the Union Carbide Corporation. The numbers in parentheses in each label denote the carbon number range of the linear alcohol and also show the number of moles of ethylene oxide.]

Equivalent performances were shown by medium cloud point linear secondary alcohol and nonylphenol nonionics in Figure 4 at a test temperature of 140 F (60 C).

At high temperatures, (Fig. 5) the linear secondary alcohol nonionic showed somewhat better wetting at lower concentrations, while the linear primary and the branched chain nonylphenol ethoxylates were virtually identical in performance.

In each cloud point category, therefore, the linear alcohol nonionics are seen to be at least adequate replacements for the conventional alkylphenol nonionics as wetting agents.

An interesting compilation of wetting performance curves is shown in Figure 6. Here the wetting curves of several nonionics is plotted versus a temperature traverse, with concentration held constant. As expected, high cloud point nonionics performed best at the higher temperatures and somewhat less efficiently at low temperatures. It is interesting to note that one of the linear alcohol nonionics of lowest cloud point surprisingly retained good wetting characteristics about 70 F above its nominal cloud point. This same material exhibited the best wetting at the low temperatures.

Good performance in cotton scouring was demonstrated by all three classes of nonionics in Terg-O-Tometer testing of F.D. Snell cotton soil cloth, with the linear alcohol surfactants showing slight superiority to the alkyl phenol ethoxylate. The tests were performed at 140 F in unbuilt solutions over a range of concentrations, in water of 50 ppm hardness (Fig. 7).

All of the three classes of nonionics will satisfactorily reduce the surface tension of aqueous solutions, even at very low surfactant concentrations. The two linear alcohol nonionics exhibit identical performance curves, showing surface tension values of 29 dynes/cm at a concentration of 0.01% (Fig. 8).

Somewhat different Ross-Miles foaming characteristics are shown by the three nonionics being compared (Table I). The linear primary nonionic has the lowest initial foam but a relatively high 5 min foam height. The branched chain octylphenol ethoxylate, on the other hand, has the highest initial foam and a low 5 min foam. The linear secondary

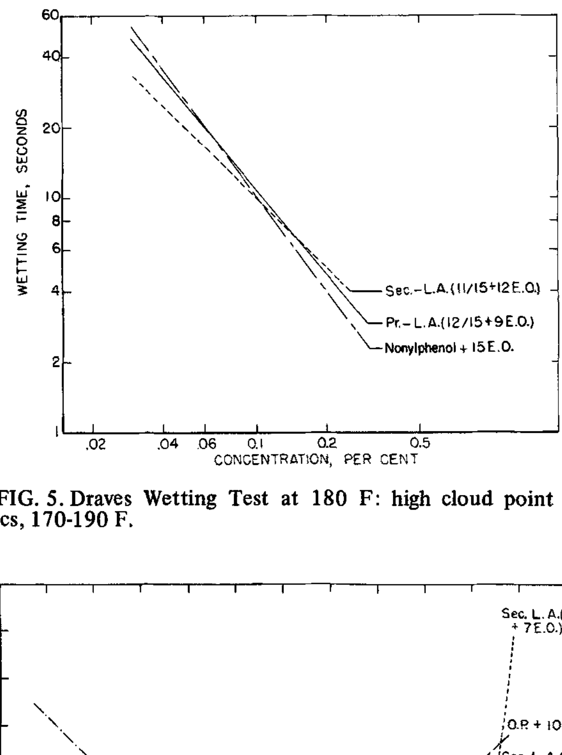

FIG. 5. Draves Wetting Test at 180 F: high cloud point nonionics, 170-190 F.

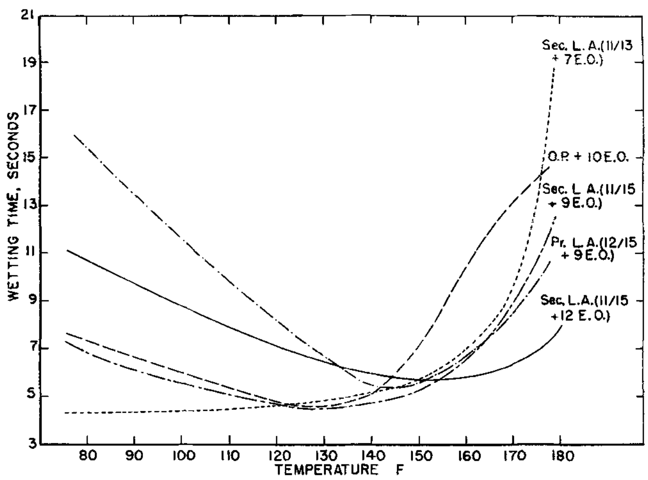

FIG. 6. Effect of temperature on wetting performance: Draves Wetting Test, concentration: 0.1%.

alcohol nonionic demonstrates an intermediate initial foam and the lowest final foam. Low foaming qualities are highly desirable in almost all textile processing applications.

Low foam modified nonionics can readily be prepared from the biodegradable linear alcohol ethoxylates. These

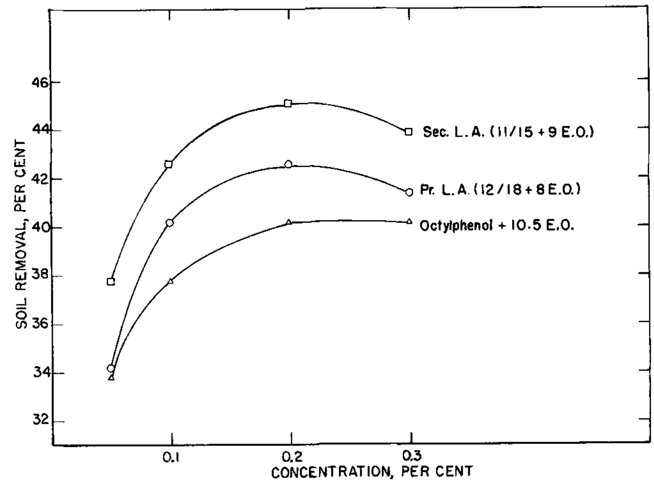

FIG. 7. Effect of concentration on cotton scouring: Terg-O-Tometer Test at 140 F, medium cloud point nonionics, 140-150 F, F.D. Snell Soil Cloth.

perform similarly to equivalent products based on branched chain alkylphenol, as illustrated in Table II. Such products are usually made by "capping" of the terminal hydroxyl of the polyoxyethylene chain.

Because of space limitations, it is not possible to compare performance characteristics of linear alcohol-based anionics with those based on alkylphenol. Such anionics, the ethoxysulfates, the sulfates and the phosphates, are easily prepared and are currently being used in the textile industry as biodegradable equivalents of earlier products based on alkylphenols.

Physical Property Characteristics

In an industrial operation, where materials must be pumped or mixed, physical handling characteristics assume considerable importance. Some of these characteristics are presented in Table III. The freezing range of the linear secondary alcohol and the nonylphenol ethoxylate are within 6.0 F of one another, at 45 to 51 F. The freezing range of the primary ethoxylate, however, is 30 to 35 degrees higher.

The lowest overall viscosity measurements are shown by the linear secondary alcohol nonionic. This fact can offer some advantage in handling of the product, particularly in cold weather. The primary alcohol ethoxylate is seen to be a solid at 68 F (20 C); at the same temperature the nonylphenol adduct is quite viscous, and the secondary alcohol ethoxylate shows a relatively low viscosity of 78 centistokes.

One of the handling problems which all users of nonionic ethoxylates must learn to overcome is concerned with

TABLE I

Foam Performance Comparisons[a]

Hydrophobe	Initial foam height, mm	5 min foam height, mm
Linear primary alcohol ethoxylate, 12/15 - 9 EO[b]	130	60
Linear secondary alcohol ethoxylate, 11/15 - 9 EO[b]	165	10
Branched octylphenol ethoxylate, 9 EO[b]	180	15

[a]Ross-Miles Foam Test: 0.2% concentration at 122 F (50 C) in distilled water.

[b]Moles of ethylene oxide.

avoidance of the nonionic's gel range in aqueous solution. For the nonylphenol and primary alcohol ethoxylates the gel ranges are from 40% to 70% nonionic. A considerable handling advantage is shown by the linear secondary alcohol nonionic with two limited gel points, at 50% and 70%, with a clear solution in between at 60%.

Biodegradability/BOD Relationship

The acceptance of linear alcohol ethoxylates by processing industries has been much less rapid than that shown by the soap and detergents industry. A number of reasons exist to explain this factor. (a) The suppliers and users of surfactants in the textile industry are legion in number. Industrial users are more fragmented, thereby harder to reach with an industry-wide message. (b) The textile industry is vitally concerned with waste pollution control, as exemplified by the recent expenditure of millions of dollars in building disposal facilities. Expenditures for pollution control in this industry are now consuming 15% of all capital budgets. Effluents contain a wide range of chemicals, and resultant disposal problems are complex. To add to this complexity, there still exist differences of surfactant manufacturers' claims as to what constitutes true biodegradability, even after publication of the SDA report on the biodegradability of nonionics. (c) Perhaps the most important reason is that there are many interpretations of what constitutes pollution. In the minds of many, the chief criterion of pollution is the measurement of the BOD imposed upon the receiving water by any given chemical. This attitude is encouraged by the fact that in many areas BOD and suspended solids are the chief parameters which are evaluated by pollution control authorities. This partial view recently resulted in a news story in one of the prominent textile industry papers announcing that a synthetic sizing agent for textiles was "not a pollutant, that it showed

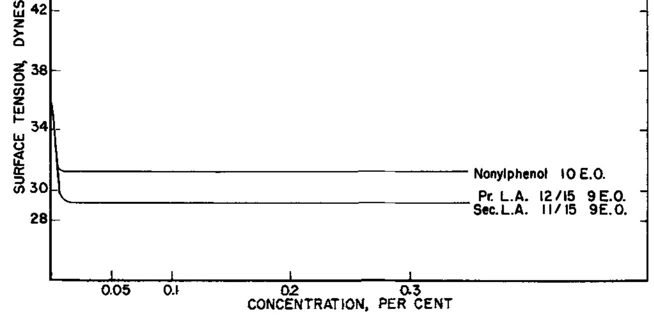

FIG. 8. Surface tension: duNouy tensiometer determination at 77 F.

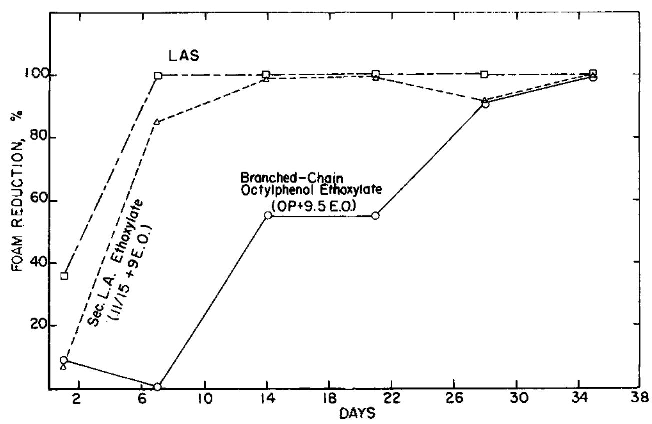

FIG. 9. River Dieaway Biodegradability Test: effect of reaction time on biodegradability; data for SDA round robin study.

TABLE II

Low-Foaming Modified Nonionics

Hydrophobe	Cloud point, C	Ross-Miles Foam, mm[a] Initial	Final	Draves wetting, conc. %[b]
Linear primary alcohol	16	15	Nil	0.09
Linear secondary alcohol	21	Nil	Nil	0.10
Alkylphenol	23	15	3	0.07

[a]Temperature at 50 C, 0.2% concentration.
[b]Temperature at 25 C, 20 sec wetting.

no BOD." No consideration is given to the eventual fate of the "nonpolluter" in the receiving waters after removal from the fabric by the scouring process.

This same line of reasoning has been applied to the use of low BOD surfactants, particularly if a mill is under orders to immediately reduce the BOD load of its effluent. The commonly accepted BOD value is a measurement of the ability of the organic compound to be degraded by the action of microorganisms in a five-day period, as measured by the amount of oxygen consumed. As the reaction proceeds, the oxygen necessary for these aerobic micro-organisms to function will be taken from the water, thus reducing the dissolved oxygen content. The test is one means of characterizing a readily biodegradable compound from one that is more resistant to microbic attack. Within the limits of this five-day test, the conventional branched-chain alkylphenol nonionics are essentially unattacked, so the five-day BOD is only 0.06 lb oxygen/lb nonionic. A linear secondary alcohol ethoxylate (11/15 + 9 EO), on the other hand, shows a five-day BOD of 0.44 lb oxygen/lb product. This is one of the confirmatory tests indicating that the linear alcohol nonionic should rapidly biodegrade in a typical disposal plant; the lack of any appreciable five-day BOD for the alkylphenol ethoxylate, conversely, presages difficulty in its adequate biodegradation in the average disposal system.

The no-BOD rating of the alkylphenol ethoxylate often appeals to the mill superintendent who is harassed to lower his effluent BOD. But what are the possible ramifications of this alternative procedure? One distinct probability is illustrated in Figure 9. This is a portrayal of a laboratory technique as to what may happen to a surfactant molecule which finds its way to a river. In the River Dieaway test the surfactant, together with necessary nutrients, is added to river water and allowed to remain quiescent for days or weeks. The organisms present are largely or entirely those which are already present in that sample of river water but may include small amounts of acclimated microorganisms. This graph shows complete foam reduction in 7 to 14 days for linear alkylate sulfonate and linear secondary alcohol ethoxylate (11/15 + 9 EO). This foam test was the only test used by the SDA Subcommittee in the last three of the four round-robins as a measure of residue surface activity. In this particular sample of river water, 35 days were required for complete disappearance of foam caused by a branched chain octylphenol ethoxylate.

Given enough weeks, then, the alkylphenol ethoxylate can apparently degrade in the natural waters. And thereby one can see the other side of the no-BOD coin. If this molecule can pass through the disposal system largely unchanged, due to its slow biodegradability, it can be expected that over longer time periods it will continue to slowly degrade and continue to utilize the dissolved oxygen in the river. Meanwhile the slowly degrading surfactant will retain some of its foaming characteristics; it may also show undesirable effects on aquatic life. Should the passage time to the sea be sufficient, the 30- or 60-day oxygen demand is therefore likely to be a value far greater than the insignificant five-day BOD.

The definition of pollutant therefore enlarges beyond tne scope of the BOD_5 value. Perhaps the mill superintendant must also seek the answer to another question: Is it possible to adequately dispose of all constituents of our mill waste on our property (e.g., in our disposal plant)?

TABLE III

Nonionic Ethoxylates: Physical Property Characteristics

Physical properties	Linear secondary alcohol, 11/15 + 9 EO[a]	Linear primary alcohol, 12/15 + 9 EO[a]	Nonylphenol, + 10.5 EO[a]
Freezing range, F	50-52	77-82	45
Viscosity, centistokes			
68 F (20 C)	78	Solid	318
104 F (40 C)	33	32	105
212 F (100 C)	6.5	8	13
Gel Range			
Nonionic concentration, % at 77 F (25 C)			
30	Clear solution	Clear solution	Clear solution
40	Clear solution	Rigid gel	Rigid gel
50	Rigid gel	Rigid gel	Rigid gel
60	Clear solution	Rigid gel	Rigid gel
70	Rigid gel	Soft gel	Rigid gel
80	Clear solution	Clear solution	Clear solution

[a]Ethylene oxide.

REFERENCES

1. Schick, M.J., "Nonionic Surfactants," Vol. 1, First Edition, Marcel Dekker, Inc., New York, 1967, p.971-996.
2. Conway, R.A., and G.T. Waggy, Amer. Dyest. Rep. 55(17):33-40 (1966).
3. Conway, R.A., C.A. Vath and C.E. Renn, Water Works Waste Eng. 1965:28-31.
4. Patterson, S.J., C.C. Scott and K.B.E. Tucker, JAOCS 47:38-41 (1970).
5. Mauser, M., J.H. Benedict, K.A. Booman, T.E. Brenner, R.A. Conway, J.R. Duthie, L.J. Garrison, C.D. Hendrix and J.E. Shewmaker, Ibid. 46:432-440 (1969).
6. Rein, B.B., Amer. Dyest. Rep. 56(24):55-61 (1967).
7. Zika, H.T., Text. Chem. Color. 1(15):26-31 (1969).
8. American Public Health Associatiion, Inc., "Standard Methods for the Examination of Water and Wastewater," 11th Edition, New York, 1960).

[Received June 23, 1970]