

Block Polymer Nonionic Surfactants in Textiles

IRVING R. SCHMOLKA, BASF Wyandotte Corporation, Wyandotte, MI 48192

ABSTRACT

Block polymer surfactants have wide acceptance in the textile industry. These products are characterized by low-to-moderate foam, low levels of toxicity, and a variety of other desirable physical properties. This paper reviews their use as lubricants, texturizers, antistats, softeners, dyes, rayon processing agents, emulsifiers, defoamers and bleaching agents.

A block polymer nonionic surfactant has been defined (1) as "a surface active agent prepared by the sequential addition of two or more alkylene oxides to a low molecular weight water soluble organic compound (initiator) containing one or more hydrogen atoms." An examination of the published literature, including articles in journals, chapters in books, and U.S. and foreign patents, discloses many reports on the preparation and use of a great variety of these block polymer surfactants in the textile and in other industries. These surfactants are the result of using a combination of various alkylene oxides and permutations in the order of addition of these oxides.

The monomers which can be used include 1,2 propylene oxide, 1,3 propylene oxide, 1,2 butylene oxide, 2,3 butylene oxide, 1,3 butylene oxide, 1,4 butylene oxide, also known as tetrahydrofuran, isobutylene oxide, amylene oxide and other similar higher molecular weight alkylene oxides, epichlorohydrin, butadiene monoxide, styrene oxide, cyclohexene oxide, glycidyl alkyl ethers, ethylene oxide, glycidol and butadiene dioxide.

A surface-active agent, whether it is nonionic, anionic or cationic, must have both a water-soluble group and a water-insoluble group. The hydrophobe in a true block polymer nonionic surfactant must be derived from an alkylene oxide or a mixture of alkylene oxides which possesses a maximal oxygen-to-carbon atom mole ratio of 0.4. Propylene oxide, butylene oxide and epichlorohydrin are examples of such monomers. The hydrophile, on the other hand, must be derived from an epoxide or mixture of epoxides with a carbon-to-oxygen atom mole ratio of 0.5 or greater. This group includes monomers such as ethylene oxide and glycidol. The methods of manufacturing the block polymer surfactants involve a synthesis done in the presence of an alkaline catalyst under essentially anhydrous conditions and elevated temperature and pressure, and have been described previously (2). Several types of block polymer surfactants are commercially available. These include the poloxamers (trade name PLURONIC), the structure of which is shown in Figure 1. The hydrophobe consists of a polyoxypropylene

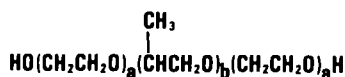


FIG. 1. Poloxamer.

lene group derived from the polymerization of propylene oxide, surrounded by 2 polyoxyethylene hydrophiles that are derived from the addition and subsequent polymeriza-

tion of ethylene oxide.

By using the reverse order of addition, the meroxapols are obtained (see Fig. 2 for structure). The proprietary



FIG. 2. Meroxapol.

name for this group of products is PLURONIC R. In these products, the central polyoxyethylene hydrophile, prepared by the polymerization of ethylene oxide, is surrounded by 2 hydrophobic groups that are derived from the subsequent addition and polymerization of propylene oxide.

The structure of the third group of products, the poloxamines, known commercially as TETRONIC, is illustrated in Figure 3. These resemble the poloxamers only in that they

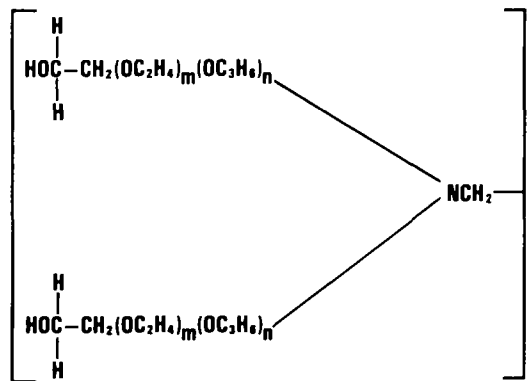


FIG. 3. Poloxamine.

have a central polyoxypropylene hydrophobic area surrounded by a polymer of ethylene oxide. These surfactants differ from the poloxamers in several ways: (a) they have 4 chains because the initiator, ethylenediamine, has 4 active hydrogen atoms. The initiator for the poloxamers, propylene glycol, has only 2 active hydrogen atoms. (b) They have higher molecular weights—up to 30,000—compared to only 14,000 for the poloxamer surfactants. (c) They exert a slight cationic effect due to the 2 pairs of unshared electrons on the 2 nitrogen atoms. (d) They have greater thermal stability than the poloxamers due to the amine nitrogen forming an amine oxide upon oxidation (Fig. 4).

The data are derived (3) from thermograms obtained by heating a 100-mg sample in a platinum crucible in air at the rate of 8 C/min, using a Mettler thermoanalyzer, under a dynamic atmosphere of 8 L/min. The temperatures shown are those at which a 1% weight loss occurs. Obviously, the higher the temperature, the more thermally stable is the surfactant. These data are useful in selecting polymers for

POLYOL	MW	% EO	T, °C*
POLOXAMER 401	4,400	10	194
POLOXAMINE 701	3,400	10	225
POLOXAMER 402	5,000	20	187
POLOXAMINE 702	4,000	20	241
POLOXAMER 124	2,200	40	191
POLOXAMINE 304	1,650	40	236
POLOXAMINE 504	3,400	40	230
POLOXAMER 407	12,500	70	201
POLOXAMINE 707	12,000	70	213

* TEMPERATURE AT WHICH A SAMPLE LOSES 1% OF ITS WEIGHT IN AIR.

FIG. 4. Comparative TGA of poloxamer vs poloxamine.

fiber lubricants because, in the spinning operation, high thermal stability is a prerequisite.

A fourth group of commercially available block polymer surfactants is the minoxapols, also known by the proprietary name TETRONIC R. These surfactants are the reverse of the poloxamines and their structure is shown in Figure 5. These polymers exhibit slightly higher thermal stability than their poloxamine counterparts. The thermogravimetric analysis data to show this are seen in Figure 6 and were obtained in a similar manner as the data shown previously (BASF Wyandotte Corp., private communication).

A fifth type of surfactant is the hetomers, also known by the commercial name PLURADOT polyols. As shown in Figure 7, these products are derived from a triol to which 2 different blends of propylene oxide and ethylene oxide are added. The initial mixture is richer in propylene oxide to form the hydrophobe, but the second mixture is richer in ethylene oxide and forms the hydrophile.

However, a search of the literature has revealed that several other monomers have been used to prepare still other block polymer surfactants which are reported to have unusual, unexpected or superior properties when applied to textiles or when used in the textile industry.

Block polymer surfactants have wide applicability in the textile industry because of the versatility permitted by innumerable variations in their composition. Organic synthesis chemists have been able to take advantage of these permutations to provide tailor-made molecules for specific applications. As many of the specific details are proprietary information, this presentation must deal largely in the generalities provided by published information, principally U.S. and foreign patents. Block polymer surfactants have application in the textile industry in the areas of lubricating, texturizing, softening, antistat, dyeing, process improvement, bleaching, emulsifying, dispersing, wetting and cleaning, among others. Some of these applications will be reviewed more extensively than others.

LUBRICANTS

Symm and Barron have reported (4) that block polymers of oxybutylene, preferably 1,2 or 2,3, or mixtures thereof, and oxyethylene are useful fiber lubricants. The preferred compounds contain 40-60% by weight of a predominantly 1,2 oxybutylene and have a hydrophobe molecular weight range of 500-3,000, with the balance of oxyethylene. The structure of the compounds based on a polymer of 1,2 butylene oxide (I) or 2,3 butylene oxide (II) as a hydrophobe is shown in Figure 8. Apparently, these block poly-

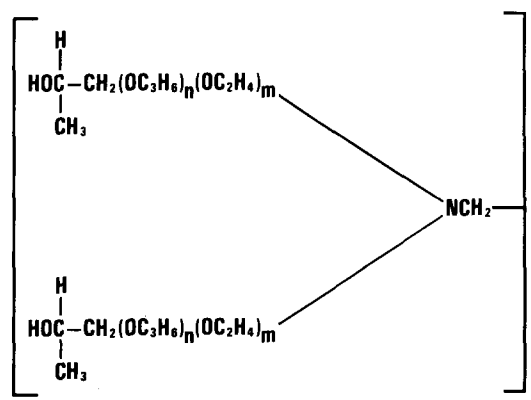


FIG. 5. Minoxapol.

POLYOL	MW	% EO	T, °C*
POLOXAMINE 504	3,400	40	230
MINOXAPOL 50R4	4,000	40	255
POLOXAMINE 701	3,400	10	225
MINOXAPOL 70R1	3,400	10	250

* TEMPERATURE AT WHICH A SAMPLE LOSES 1% OF ITS WEIGHT IN AIR.

FIG. 6. Comparative TGA of poloxamine vs minoxapol.

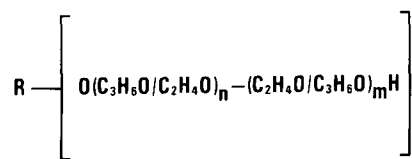
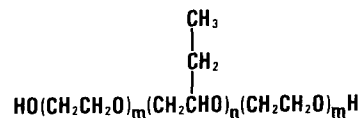
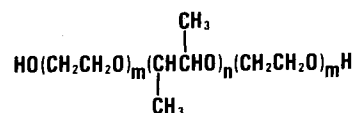


FIG. 7. Hetomer.



I



II

FIG. 8. Ethoxylated polyoxybutylene glycols.

mer surfactants currently are not commercially available, but they have been offered on an experimental basis (BASF Wyandotte Corp., private communication).

More recently, Login and Newkirk have reported (5) that block polymer surfactants derived from tetrahydrofuran (tetramethylene oxide or 1,4 butylene oxide) and ethylene oxide provide lubricity for synthetic textile fibers, especially polyester, polyamide and their mixtures. The structure for these block polymer surfactants (TMO EO) is shown in Figure 9.

A standard test procedure was used to measure the lubricity of these fiber lubricants—i.e., determination of the coefficient of friction using a Rothschild F meter. Figure 10 is a comparison of the data for several poloxamers vs analogous block polymer surfactants of this type. Apparently, these surfactants currently are not commercially available, although they have been offered on an experimental basis (BASF Wyandotte Corp., private communication). The lower the coefficient of friction value, the greater is the lubricity provided by the polymeric surfactant.

These tetrahydrofuran-ethylene oxide block polymers were also shown to possess significantly better thermal stability than the poloxamers. This was shown by measuring the temperature at which a 1% weight loss occurs in air. The data obtained are shown in Figure 11.

TEXTURIZING

In the spin-texturizing of synthetic fibers such as polyester or polyamide, in which the fibers are passed over a heated plate maintained at 190-250 C, a stabilized liquid nonionic surfactant or blend of surfactants is used as a lubricant. A small amount of lubricant is needed on the surface of the fiber to make it less prone to static, snarls and breakage in subsequent processing steps. A heat-stable lubricant is needed that will not decompose during processing to result in a build-up of decomposition products or soil on the machinery which can contaminate the textile fibers. Rather, it must depolymerize at about 250 C without leaving a residue. The compositions must also have high wetting and spreading and fiber-sealing capacities and form uniform coatings, thereby yielding constant friction coefficients. These compositions generally contain (6) a substantial proportion of a block polymer surfactant, especially a poloxamer, although the use of a merxapol or a poloxamine has also been indicated as being beneficial in these finish compositions (7,8). The compositions are claimed to be especially useful in high-speed texturizing and bulked continuous filament production, in addition to draw-texturizing. Block polymer surfactants, such as the poloxamers or the heteromers, containing up to 2% of an alkali or alkaline earth salt of a saturated carboxylic acid effectively improve (9) the handling of synthetic textile fibers in the spin-finishing operation. Addition of the salt substantially increases the amount of lubricant remaining on the fiber by retarding decomposition and the formation of deposits on the machinery.

SOFTENER

Block polymer nonionic surfactants have also been reported (10) to be useful as components of a liquid textile conditioner. Either a water-insoluble poloxamer or poloxamine is useful in the final rinse after a washing operation. Block polymers function as emulsifying agents and also provide a reduced, but constant, viscosity for these compositions without phase separation.

A solid softening and conditioning composition designed for automatic laundry dryers is reported (11) to contain as one of its ingredients a nonionic softening agent such as a

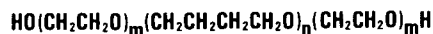


FIG. 9. Ethoxylated polyoxytetramethylene glycols.

LUBRICANT 1% BY WT ON YARN	SPEED METERS/MIN.	COEFFICIENT OF FRICTION
POLOXAMER 108	100	0.93
	200	0.97
TMO EO ANALOG 108	100	0.89
	200	0.93
POLOXAMER 212	100	0.90
	200	0.94
TMO EO ANALOG 212	100	0.75
	200	0.82
POLOXAMER 217	100	0.90
	200	0.95
TMO EO ANALOG 217	100	0.78
	200	0.83

FIG. 10. Lubricity of fiber lubricants.

MOLECULAR WEIGHT	HYDROPHOBE	% ETHYLENE OXIDE	T, °C*
1100	PO	10	185
1190	THF	10	203
1900	PO	50	198
2080	THF	50	226
2750	PO	20	180
2840	THF	20	203
6600	PO	70	201
6050	THF	70	220

* TEMPERATURE AT WHICH A SAMPLE LOSES 1% OF ITS WEIGHT IN AIR.

FIG. 11. Fiber lubricant oxidation stability.

poloxamer.

Aqueous solutions of reaction products of acid anhydrides, preferably maleic, phthalic and succinic, and poloxamine are reported (12) to have excellent fabric softening properties and to be mild on both the skin and clothes. At least 60% of the terminal hydroxyl groups of the poloxamine should be reacted with the acid anhydride. The structural formula for a typical product is shown in Figure 12. The resulting products were evaluated for their softening and antistatic properties by adding a 0.3% water solution of these products to the rinse cycle of an automatic home washing machine containing 65/35 polyester cotton, 150 denier broad woven cloth. The wash was then dried for 45 min in an automatic clothes dryer and tested for static cling and rated subjectively for softness.

The Static Charge Rating (SCR) is determined by brushing each cloth sample 10 times with a nylon felt and placing the brushed cloth sample against an aluminum plate inclined from the horizontal by 60° with the cloth sample on the underside of the plate. The time for each cloth sample to separate from the plate was measured in seconds. A completely untreated fabric of 100% nylon would cling to the

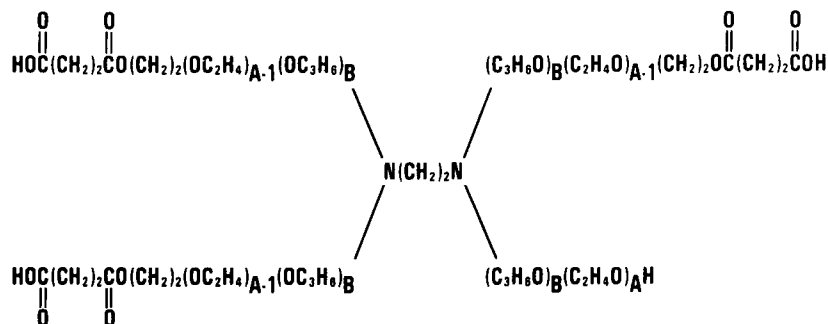


FIG. 12. Typical fabric softener.

COMPOUND	SOFTNESS RATING g/8 LB. LOAD		SCR, SEC TO SEPARATE g/8 LB. LOAD	
	1	3	1	3
UNTREATED POLOXAMINE 908	P	G	110	10
S.A. MODIFIED POL. 908	G	E	10	1
S.A. MODIFIED POL. 707	G	E	4	1
S.A. MODIFIED POL. 1508	G	E	15	2
M.A. MODIFIED POL. 707	G	E	4	1
P.A. MODIFIED POL. 707	G	E	15	3
S.A. MODIFIED PEG 4000	P	G	125	10
DIFATTY QUATERNARY SULFATE	P	G	95	10

P = POOR G = GOOD E = EXCELLENT

FIG. 13. Drying and static test on novel fabric softeners.

aluminum plate for several hours whereas a well treated fabric separated after a few seconds or would not cling at all. The results of the drying and static tests are summarized in Figure 13.

ANTISTAT

The antistatic properties of high ethylene oxide-containing block polymer surfactants alone or their chemical derivatives have been widely recognized. The first recorded use of a block polymer surfactant in a composition to combat static effects was noted in 1958 (13). Bacon used an amine soap together with a water-soluble poloxamer to prevent static build-up on sweaters of nylon, cellulose acetate and polyester, and found the resulting antistatic ratings of the sweaters were greatly improved over those of untreated sweaters.

The use of poloxamers 182 and 184 has been reported to be suitable for providing temporary antistatic protection to acrylan fabrics, whereas poloxamer 144 gave durable antistatic protection as shown after 5 washings at 130 F (14).

The addition of water-soluble ethylene oxide/propylene oxide, or ethylene oxide/butylene oxide block copolymers of high molecular weight to melt spun drawn polyamide filaments was reported (15) to provide permanent antisoiling and antistatic properties to the fibers. The polyethers had to be incompletely soluble in the polyamide and not appreciably decompose or volatilize during the spinning operation. Fabric made from the finished filament had a high de-

gree of silk-like resilience and was designed for use as a heavy denier-prefilament pile carpet.

The higher molecular weight poloxamers, i.e., those with a molecular weight greater than 4,000, have been reported to have much superior permanent antistatic properties than their lower molecular weight homologs, as well as to other higher molecular weight alkoxyated amines which lack the tetrafunctionality of a poloxamine. This was found to be true for both polyamide (16) and polyester (17) fibers. This was demonstrated by evaluating the antistatic property by an AATCC standard procedure 115-1969 "The Electrostatic Clinging of Fabrics, Fabric to Metal Test." The production of hydrophobic fibers having antistatic properties made by incorporating an ester of a dibasic acid or acid halide with a poloxamer containing up to 30% propylene oxide and a molecular weight of less than 10,000 into the spin bath prior to spinning the fiber has been described (18). When this fiber and a similar fiber without antistat were spun into yarn and then evaluated for antistatic activity, the control was found to lack activity whereas the pieces containing the antistat dissipated half the charge in 2-14 sec.

When a nonwoven polyester fabric containing a poloxamer was treated with an aqueous alkali to extract up to 20% of the fiber and from 30-95% of the polyol, a soft, antistatic, nonwoven fabric with good bulk was produced (19). A more effective nylon antistatic agent was reportedly obtained (20) by chain extending a poloxamine with a di-epoxide or a compound yielding a diradical such as a diester or diisocyanate. Another improved polyamide antistatic agent is reportedly (21) obtained by use of a reaction product of a poloxamine and a sulfur-containing compound which is soluble in the poloxamine. As a result of condensing the 2 chemicals together, the melt viscosity of the original poloxamine is greatly increased at 100 C. This eliminates the occurrence of drips which are otherwise encountered in the molten polyamide as it emerges from the spinneret in the melt-spinning operation.

The antistatic properties of polyamide fibers were also improved (22) by uniformly dispersing the condensation product of a poloxamine and a phenolic compound in the fibers, to eliminate or reduce the occurrence of nubs in the subsequent melt spinning process.

DYEING

One of the major uses for the block polymer surfactants in the textile industry today (1981) is the field of dyeing. These unique surfactants may serve as dispersing, leveling, thickening, penetrating, emulsifying, spreading, antimigration, antifoaming and wetting agents. Because they are non-ionic in nature, the block polymers are not precipitated or

inactivated by hard water ions. They can improve dye leveling for synthetics as well as for the natural fibers, like cotton and wool. The poloxamines and other block polymers can also function as effective solubilizing agents for water-insoluble dyes. Those surfactants with a high ethylene oxide content (70-80%) and with a high hydrophobe molecular weight appear to be the most effective for this function. Their generally very low-to-moderate foaming action, coupled with their ability to disperse dyes, pigments, lime soap curd, and other types of soil, together with their ready rinsing ability, are partly responsible for the widespread use of the block polymer surfactants in the textile industry.

Because of their higher molecular weight and greater thermal stability than many other nonionic surfactants, the block polymers can be used in high-temperature dye leveling operations and at ambient temperatures, as well. The foam problems that often develop in incorporating dye into a dyeing adjuvant have been reported (23) to be controlled by use of a low-foaming block polymer surfactant which acts not only to improve the uniformity of dyeing and the tensile strength of the fiber, but also serves to enhance wetting of the textile and to function as the anti-foam agent. The dyeing ability of vinylidene cyanide copolymers was improved by modification of the coagulation bath by means of addition of a poloxamer. The fibers that coagulated in the bath (24) increased pick-up of the dispersed dye, pink BA.

One of the first dyeing compositions to be reported (25) that used a block polymer surfactant was a vat dye adapted to home use. The dye composition used a poloxamer or a poloxamine, preferably one containing 80% by weight of ethylene oxide and was suitable for use on cellulosic fibers, nylon, or silk.

It has been reported (26) possible to dye nitrogen-containing fibers, such as wool or nylon, at a pH of 4-6 with an anion disperse dye using a composition which contains a poloxamer.

A clear concentrate composition for use as a print paste on fibrous articles by screen printing may have (27) as one ingredient a nonionic surfactant such as a poloxamer. The block polymer is used to enhance the thickening capabilities of a polyurethane thickener. The print paste may be used with various fiber types, including both synthetic and natural fibers and their blends, including wovens and non-wovens.

Dye solutions which are characterized by excellent Kusters dye bath stability have been developed (28) by use of an ethylene oxide/propylene oxide block copolymer such as poloxamer 161 as one of its components. The compositions maintain their storage stability even at high concentrations and do not separate out under normal storage or use temperatures.

CELLULOSE PROCESSING

A study on the application of surface-active agents to viscose processing has revealed (29) that of all the surfactants evaluated for adding to the cellulose prior to steeping, in order to provide uniform distribution in subsequent processing operations, the block polymers of ethylene and propylene oxides appeared to be the most suitable.

In the slurry steeping step, the prior addition of either a poloxamer or a poloxamine has been reported (30) to cause a marked decrease in clumping, foaming and floating of the cellulose. The amount of surfactant needed to obtain this effect varied from 0.02 to 0.25%, based on the dry weight of the pulp. In the shredding operation, which follows next, the cellulose which had been steeped in the

presence of the block polymer surfactants exhibited a noticeable reduction in time and power requirements (31), indicating an ease in shredding as a result of the surfactant addition.

Another positive gain was the finding (29) that the shredded pulp, which had been exposed to the block polymer surfactant, had improved porosity. This was shown as the alkali cellulose crumb was more accessible to the carbon disulfide vapors. In addition, the viscose filtration was improved and the rate of acetylation of high α -cellulose pulp was increased (31). The surfactant-treated cellulose exhibited increased absorptivity as a result of more thorough penetration, which caused more effective mercerization.

It has been further shown (32) that treatment of a high α -cellulose pulp with a poloxamine or a poloxamer improved the viscose processing. After coagulation, filaments having improved fatigue life in high-tenacity tire yarn were obtained.

Addition of only 0.02-0.5% of a poloxamine to a coagulating bath in viscose processing gave filaments with a thicker skin and a more diffuse boundary between the skin and core, and which had a noncrenulated surface (33).

BLEACHING

Peroxygen bleaching agents are widely used in the textile industry for removal or reduction of undesirable natural color bodies from new fabrics, as well as to whiten fabrics and remove stains. However, because peroxides react slowly with color bodies, they must be applied frequently at elevated temperatures to be effective, thus limiting their usefulness. One approach to this drawback has been the use of activators. However, this has presented many new problems and, in general, this approach with polyester/cotton blends has been inadequate. It has been reported (34) that this has been overcome by coating the textile fabric surface with an adherent layer of viscous, water-soluble composition comprising a peroxide activator dispersed in a block polymer surfactant, such as poloxamer 403 or poloxamer 235. A specific weight ratio of activator to surfactant from 1:10 to 10:1 is used. The coated fabric is immersed in water containing at least 5 ppm by wt of active oxygen, of a peroxygen compound, until the water-soluble, coated layer has disintegrated.

It has also been reported (35) that the poloxamers may be used in a process to extend the storage stability of active oxygen-containing aqueous concentrates used as bleaching agents in textile finishing operations. The concentrated peroxide solution has a pH of 2.5-6 and a peroxide content between 2.5 and 75%, with a surfactant content between 1 and 20%.

EMULSIFYING

Block polymers of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide, as well as the poloxamines, have been reported (37) to be useful as emulsifying agents for the preparation of conditioning agents on lint cotton fibers prior to spinning. These surfactants have the added advantage of not imparting substantial wetting ability to the branched-chain, monohydric, primary fatty alcohol used as the conditioning agent. The formulation generally is composed of 25-75 wt % fatty alcohol containing 25-75 wt % water and 0.05-10 wt % nonionic emulsifying agent based on the weight of water.

DISPERSING

The dispersing properties of the poloxamer surfactants have

been reported (37) useful for water-insoluble copolymers prepared from an unsaturated monomeric acid, such as acrylic or itaconic, in an organic compound containing a single vinylidene group (e.g., esters of acrylic acid and monohydric alcohols such as butyl and other similar compounds). These products are used as auxiliary agents for enhancing the crease resistance of cellulosic fabrics, especially cotton and rayon, for hand building, for increasing tear strength or for improving abrasion resistance, and are applied in aqueous media.

WETTING

Organic detergents are frequently used as wetting agents in the textile industry for a variety of textile processing steps, such as bleaching, dyeing, desizing, mercerizing and finishing. They promote fast wetting of the textile as it passes through the various treating baths. Unfortunately, the surfactants which provide the fastest wetting time tend to be the highest foamers. The presence of foam can become serious, especially if the volume of foam produced exceeds the capacity of the vessel in which the fabric is being treated. In the dyeing operation, the presence of foam can cause "specking" due to the presence of undissolved particles. In the finishing operation, the foam may result in uneven application of the finishing agent due to prewetting of the fabric by the foam. Thus, it is highly desirable, if not absolutely necessary, to use only nonfoaming or low-foaming wetting agents. Among the hundreds of commercially available nonionic surfactants, the block polymers are well known for their low foaming or defoaming properties. Thus, it has been reported (38) that 50-99 parts of a blend of a tris(butoxyethyl) phosphate and 1-50 parts of a nonionic surfactant, such as a poloxamer or poloxamine, will provide a nonfoaming wetting composition suitable for use in many textile processing steps.

In the course of repeatedly washing the same fabrics, such as sheets or shirts, a graying or dullness of color develops. Incorporation of optical brighteners to improve brightness has numerous objections—they are expensive and are largely rinsed away. Bleaching has been used, but it does not impart brightness. However, it has been claimed (39) that the use of an aqueous solution of sodium hypochlorite with pH > 10 and a nonionic surfactant such as a poloxamer may be used to lower the surface tension to < 45 dynes/cm at 25 C and suspend in it 0.1-5.0% of an insoluble styrene polymer with a particle size of 0.5-5.0 μ . This is deposited on the fabrics permanently, thereby increasing the fabric brightness by increasing the light reflection from the fabric. The fabrics that are amenable to this treatment include natural products such as cotton and silk, and synthetics such as polyamides and polyesters.

CLEANING

This review would be incomplete if it overlooked the many U.S. and foreign patents issued in which the property of the block polymers of ethylene oxide and propylene oxide to remove soil from fabric or their ability to provide some ancillary property is described. Thus, a heavy-duty liquid detergent stabilized by polymerizing a monomer to a poly-

mer, and built with tetrapotassium pyrophosphate, reports (40) the potential use of poloxamers or poloxamines as the organic surfactants. Solid grades of both poloxamers and poloxamines reportedly (41) are useful in a granular, heavy-duty, soap-based detergent composition. Controlled foam heavy-duty detergent compositions based on nonionic surfactants such as the poloxamers for soil removal have been described (42). These are only three of the many examples that could be cited to illustrate the usefulness of the block polymer surfactants in this application area.

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