A Review of Block Polymer Surfactants

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ABSTRACT AND SUMMARY

A brief historical review of four series of commercially available block polymer surface-active agents—the PLURONIC^R, TETRONIC^R, PLURADOT^R, and PLURONIC^R R polyols—is presented. A comparison is made of the physical properties within each series, in the form of trend lines. These parameters encompass solubility, rate of solubility, wetting, foaming, defoaming, emulsification, thickening, cleansing, and toxicity. The physical property relationships which depend upon variation in the hydrophobe molecular weight and variation in the hydrophile hydrophobe balance are shown to be similar in each series of surfactants. Differences among the four series of polymers, where they exist, are seen to vary from little to significant. The many controversial articles on the micellar nature of the block polymers and their critical micelle concentrations are examined. Considerations of the important physical properties which lead to practical applications are discussed. Some of the more important newly developed potential uses of these polymeric surfactants are then described in various application areas, including the cosmetic, medical, paper, pharmaceutical, and textile industries.

INTRODUCTION

A block polymer nonionic surfactant is a surface active agent prepared by the sequential addition of two or more alkylene oxides to a low molecular weight water-soluble organic compound containing one or more active hydrogen atoms. It is the purpose of this review to compare the physical properties of four different groups of commercially available block polymer surfactants and to discuss some of their most recent industrial applications. The block polymer surfactants to be reviewed include the PLURONIC^R, PLURONIC^R R, TETRONIC^R, and the PLURADOT^R polyols. The corresponding nonproprietary names of the first three are poloxamer, meroxapol, and poloxamine, (1) respectively.

SYNTHESIS

The poloxamers are synthesized (2) by the sequential addition first of propylene oxide and then ethylene oxide to a low molecular weight water-soluble organic compound, propylene glycol. The hydrophobe is the inner polyoxypropylene glycol which changes from a water soluble- to a water insoluble- polymer as the molecular weight goes above 750. The addition of ethylene oxide in the final step provides water solubility to the molecule. In this series, as in all other syntheses to be presented, the oxyalkylation steps are carried out in the presence of an alkaline catalyst, generally sodium or potassium hydroxide. The alkaline catalyst is then neutralized and usually removed from the final product. The equations representing this synthesis are shown in Figure 1.

When the order of addition of the alkylene oxides is reversed, the meroxapol series is produced (3), as shown by the equations in Figure 2.

In this series, ethylene glycol is the initiator. It is informative to note the essential important differences between the poloxamer and the meroxapol structures. This should be kept in mind when physical properties of the two series are compared with each other. The poloxamer structure is terminated by two primary hydroxyl groups, while the meroxapol series has secondary hydroxyl groups at the ends. In the poloxamer series the hydrophobe is on the inside, while the corresponding meroxapol has the hydrophobe split in two, each half of which is on the outside of the surfactant. This is illustrated in Figure 3.

A slightly different structure is exhibited by the poloxamines, which are prepared (4) from an ethylenediamine initiator. These resemble the poloxamers in having the same sequential order of addition of alkylene oxides. Their synthesis is shown in Figure 4.

Structurally, the poloxamines differ from the other polymers in that they have four alkylene oxide chains, rather than two, since four active hydrogens are present in the initiator. These surfactants also differ from the other polymers in that they contain two tertiary nitrogen atoms, at least one of which is capable of forming a quaternary salt (5). These polymers are also terminated by primary hydroxyl groups.

The fourth series of surfactants to be discussed are the PLURADOT polyols. Currently there is no nonproprietary name assigned to this family of polymers. These surface active agents can be prepared (6) from a low molecular weight trifunctional alcohol, such as glycerine or trimethyl-

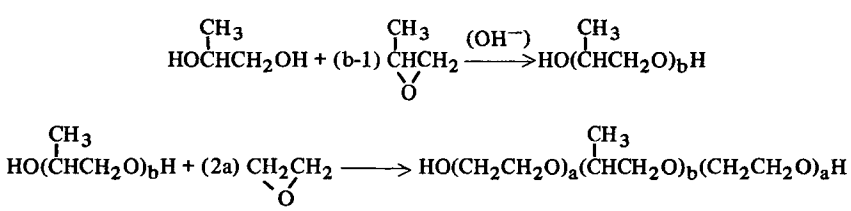

FIG. 1. Poloxamer Synthesis

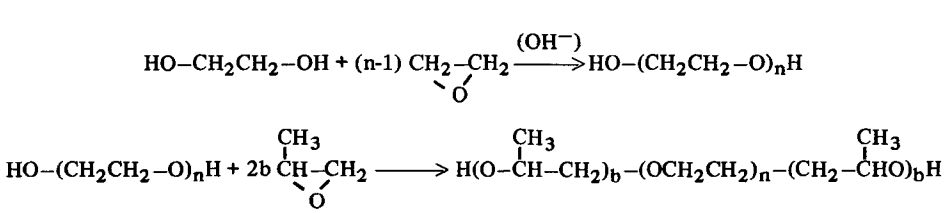

FIG. 2. Meroxapol Synthesis

Meroxapol

P. O.	E. O.	P. O.

Poloxamer

E. O.	P. O.	E. O.

FIG. 3.

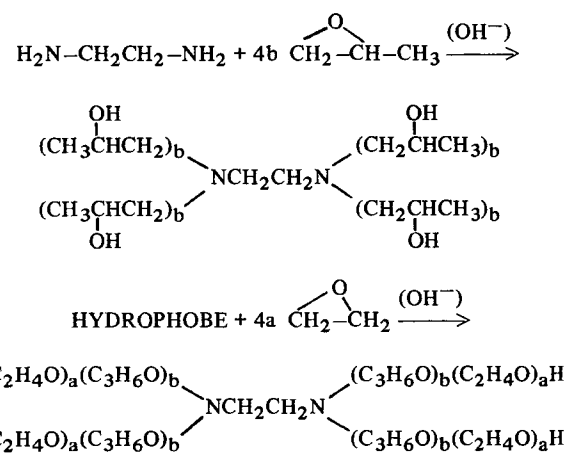

FIG. 4. Poloxamine Synthesis

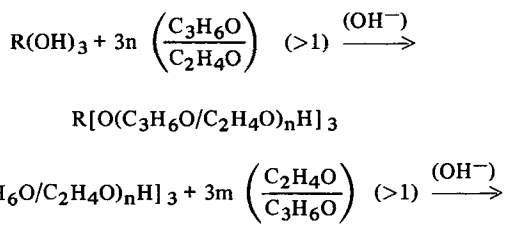

FIG. 5. Pluradot Polyol Synthesis

olpropane, which is oxyalkylated initially with a blend of propylene and ethylene oxides, but mostly with propylene oxide, to form the hydrophobe. This is followed by oxyalkylating with a blend of ethylene and propylene oxides, but mostly with ethylene oxide, to form a hydrophile. This synthesis scheme is shown in Figure 5.

This group of surfactants has three chains, one more than the poloxamer and meroxapol series, but one less than the poloxamine polymers. Because of the slower rate of reaction of propylene oxide, compared to ethylene oxide, it is suggested that the terminal hydroxyl group is composed primarily of secondary hydroxyl groups rather than of primary hydroxyl groups.

Obviously there are no chemical differences within any one series of polymeric surfactants. Among the four series, there are two differences. (1) The presence of the two tertiary nitrogen atoms in the poloxamines and their absence in the other polymers, and (2) the terminal secondary or primary hydroxyl groups, as mentioned previously.

NOMENCLATURE

Since there are more than seventy-five different polymeric surfactants, the nomenclature of each system will be explained. As seen in Table I, which illustrates the poloxamer series, the first two digits of a poloxamer, when multiplied by 100, indicate the approximate hydrophobe molecular weight. The last digit, when multiplied by 10, gives the percent of ethylene oxide in the molecule, the balance being propylene oxide.

The meroxapol series is shown in Table II. The first two digits, when multiplied by 100, give the total molecular weight of the two polyoxpropylene glycol hydrophobes. The last digit, multiplied by 10, gives the percent ethylene oxide in each polymer. In this respect the meroxapol nomenclature system resembles the poloxamer system.

The poloxamine series is described in Table III. The same system is used with the poloxamines as with the previous two series. The last digit, multiplied by 10, gives the percent ethylene oxide in the final molecule, while the first two digits are indicative of the hydrophobe molecular weight. The zero was included so as to minimize confusion with the poloxamer numbering system.

The last series, the PLURADOT polymers, is shown in Table IV.

The exact relative percentages of ethylene and propylene oxides in the hydrophobe and the hydrophile in this series are proprietary information. However, from physical property data, specifically cloud points, it can be seen that the larger the second digit, the greater is the total percent of ethylene oxide in the molecule. As seen in the table, the larger the first digit, the greater is the hydrophobe molecular weight.

PHYSICAL PROPERTIES

Cloud Point

Major differences in physical properties are seen to exist within any one series. In addition, when one compares one series with another, some differences and some similarities are readily apparent. All four nonionic series are alike in that they derive their solubility in water from hydrogen bond formation between the many ether oxygen atoms present and protons in the water. When the temperature of a solution of a nonionic surfactant is raised, the hydrogen bond is broken and the nonionic clouds out of solution. This is known as the cloud point. For poloxamers, the 1% cloud point ranges from a low of 14 C to a high of 100 C. This latter figure is for the most hydrophilic polymers containing 80% ethylene oxide. In contrast, the meroxapols have a narrower cloud point range. The important difference would be the lowered cloud point with the most hydrophilic members, those that contain 80% ethylene oxide. The poloxamines resemble the poloxamers in this property, since they are structurally similar. The PLURADOT polymers have the lowest maximum cloud point primarily because the most hydrophilic members have a lower ethylene oxide content than the 80% exhibited by the other series, and perhaps, partly due to the presence of some propylene oxide in the terminal hydrophile. These data are shown in Table V.

Water Solubility

Within any one series, as the percent of ethylene oxide increases, or the molecular weight of the hydrophobe decreases, the solubility in water increases. This is true for all four series.

Within any one series, the rate of solubility of a polymer in water decreases as the hydrophobe molecular weight increases. In a comparison of the rate of solubility in water of two similar polymers, one with the hydrophile on the outside, poloxamer 188, and the other with the hydrophile on the inside, meroxapol 17R8, the latter had a faster rate of solubility than the former.

In another comparison between two polymers with a

TABLE I

Poloxamer Series

Hydrophobe molecular weight	10	20	30	40	50	60	70	80
4000	401	402	403	-	-	-	407	-
3250	331	-	333	334	335	-	-	338
2750	-	282	-	284	-	-	-	288
2250	231	-	-	234	235	-	237	238
2050	-	212	-	-	215	-	217	-
1750	181	182	183	184	185	-	-	188
1200	-	122	123	124	-	-	-	-
950	101	-	-	-	105	-	-	108

% Ethylene oxide

TABLE II

Meroxapol Series

Hydrophobe molecular weight	10	20	30	40	50	60	70	80
3100	31R1	31R2	-	31R4	-	-	-	-
2500	25R1	25R2	-	25R4	25R5	-	-	25R8
1700	17R1	17R2	-	17R4	-	-	-	17R8
1000	-	-	-	-	10R5	-	-	10R8

% Ethylene oxide

TABLE III

Poloxamine Series

Hydrophobe molecular weight	10	20	30	40	50	60	70	80
6750	1501	1502	-	1504	-	-	-	1508
5750	1301	1302	-	1304	-	-	1307	-
4750	1101	1102	-	1104	-	-	1107	-
3750	901	-	-	904	-	-	-	908
2750	701	702	-	704	-	-	707	-
1750	-	-	-	504	-	-	-	-
750	-	-	-	304	-	-	-	-

% Ethylene oxide

similar molecular weight and the same ethylene oxide/propylene oxide ratio, the tetrafunctional polymer, poloxamine 707, was found to dissolve more rapidly than the difunctional polymer, poloxamer 407. This suggests that the length of the polymer chain has an effect on the rate of solubility.

This is substantiated when one compares the rate of solubility, within any one series, of a group of polymers with the same ethylene oxide/propylene oxide ratio, but of varying molecular weight. It has been found that the larger the molecular weight of the hydrophobe, the slower is the rate of solubility.

No solubility rate comparisons have been carried out with the PLURADOT polymers.

Oil Solubility

None of the poloxamers is soluble is mineral oil. However, by placing the polypropylene glycol hydrophobe on the outside of the molecule, it is of interest to note that many of the meroxapol polymers do exhibit moderate solubility in this lipophilic solvent. The poloxamine and PLURADOT polymers are also insoluble in mineral oil. This is to be expected, since they more closely resemble the poloxamer than the meroxapol structure.

The solubility characteristics of the four series of polymers in an organic solvent, such as propylene glycol, are quite similar. The higher the hydrophobe molecular weight, the less soluble is the polymer. Also, those polymers with a high percentage of ethylene oxide or a high percentage of propylene oxide, everything else being equal, are less soluble in propylene glycol than those polymers which have an ethylene oxide content of between 40 and 60%.

TABLE IV

Pluradot HA Series

Increasing hydrophobe molecular weight ↑	Low				High
	510	520	530	540	550
	410	420	430	440	450

% Ethylene oxide

TABLE V

1% Cloud Point, °C

Surfactant	Minimum	Maximum	Δ
Poloxamer	14	100	86
Meroxapol	25	99	74
Poloxamine	15	100	85
Pluradot	25	77	52

TABLE VI

Poloxamine Wetting Times,[a] Sec.

Hydrophobe molecular weight	10	20	30	40	50	60	70	80
6750	-	51	-	84	-	-	-	>360
5750	-	30	-	48	-	-	-	-
4750	-	15	-	37	-	-	>360	-
3750	-	-	-	88	-	-	-	-
2750	-	38	-	185	-	-	-	-
1750	-	-	-	>360	-	-	-	-

% Ethylene oxide

[a]Draves test, 3 g Hook, 0.1% solution, 25 C.

TABLE VII

Meroxapol Dynamic Foam Heights, 25 C[a]

Hydrophobe molecular weight	10	20	30	40	50	60	70	80
3100	15	40	-	215	-	-	-	-
2500	40	45	-	260	125	-	-	110
1700	115	195	-	300	-	-	-	145
1000	-	-	-	-	260	-	-	125

% Ethylene oxide

[a]For 0.1% solution at 400 ml/min flow rate.

Wetting

In each of the polymer series, the same wetting trend is observed in that wetting time, as measured by the Draves test for a 0.1% solution at 25 C, decreases as the percent hydrophile decreases. Also as the molecular weight of the hydrophobe increases, the wetting time decreases. However, above a certain limit, which varies with each series, there is no decrease in the wetting time as the hydrophobe molecular weight increases. This is exemplified in Table VI, by the poloxamine series, which shows that wetting time reaches a minimum as the hydrophobe molecular weight increases from 750 to 4750 but then rises slightly as the molecular weight increases further to 6750.

Foaming

Within each series, the foam property reaches a maximum at a different ethylene oxide/propylene oxide ratio. With the meroxapols, maximum foam height, at 25 C, is at a 40:60 ethylene oxide/propylene oxide ratio, but at 49 C, the maximum shifts to a 50:50 ratio. The poloxamers exhibit maximum foam at a slightly higher ethylene oxide/propylene oxide ratio, namely 60:40, at 49 C. From data on the limited number of polymers prepared in the poloxamine series, it appears that foam is maximized between the 40:60 and 70:30 ethylene oxide/propylene oxide ratios. Foam values in the PLURADOT series increase as the cloud point of the polymer increases. However, the limited number of polymers makes it impossible to draw any valid conclusions. Foam properties of each surfactant series increase and then decrease slightly, as the hydrophobe molecular weight increases. This is exemplified in Table VII where the numbers represent millimeters of foam generated at a 400 ml/min flow rate in the dynamic foam machine for the meroxapols.

However, the biggest difference in foam properties is found in a comparison of the foam properties of the two series which have terminal hydrophile groups, the poloxamers and the poloxamines, with the meroxapols, where the hydrophobe groups are on the outside. The latter series exhibits little or no foam, even by its most hydrophilic members. As an example, a 0.1% solution of poloxamer 188 has a foam value of 600 mm at 40 C at a 400 ml/min dynamic flow rate, while its meroxapol counterpart, 17R8, has a foam height of only 44 mm, under the same conditions. Poloxamer and poloxamine foam heights appear comparable for comparable polymers. Thus, for example, poloxamer 407 has a foam value of 160 mm at a 200 ml flow rate, while poloxamine 707 has a foam value of 180 mm, under identical test conditions.

For defoaming properties, all four series resemble each other in that the highest propylene oxide/ethylene oxide ratio surfactants are very effective defoamers and no trend lines can be drawn or large differences noted. If any generalization can be drawn, it might be that the meroxapols appear to be better defoamers than their corresponding poloxamers.

EMULSIFICATION

Attempts to correlate emulsification properties with ethylene oxide/propylene oxide ratios and hydrophobe molecular weights have not been very successful. Within any one series, the higher molecular weight hydrophobes are generally better emulsifiers than their lower molecular weight homologs. Some of the poloxamers appear to be better emulsifying agents for mineral oil or fluorocarbons in aqueous systems than the meroxapol or poloxamine polymers, while several of the latter appear superior for preparing stable emulsions of glyceryl trioleate in water. However, no trend lines can be presented.

Thickening

The thickening power of each series of surfactants in water increases as the hydrophobe molecule weight increases and as the ethylene oxide/propylene oxide ratio increases.

The available data, but not shown here, indicate that the meroxapol and PLURADOT series do not form gels at any concentrations in water, whereas only 20% of either poloxamer 407 or poloxamine 1508 is needed to form a

strong gel. In comparison, a 20% solution of poloxamer 403, poloxamer 188, poloxamine 1504, or poloxamine 908 is a fluid liquid at room temperature.

Cleansing

Because of the varying nature of substrates, soils, cleaning conditions, and types of equipment used, no one trend line can be drawn which would best describe the cleaning properties of the four series of block polymer surfactants.

Toxicity

Within any one series the toxicity of a block polymer surfactant decreases as the ethylene oxide/propylene oxide ratio increases and as the molecular weight of the hydrophobe increases. This has been shown by the acute oral LD_{50} values for the poloxamine and meraxopol series. Most values are very high, generally >5 g/kg, which is at the lower limit of the slightly toxic class in the classification scheme given in Clinical Toxicology of Commercial Products (12). It is not valid to compare the toxicity of any one series with another.

Critical Micelle Concentrations (CMC)

The early published reports (13-15) on the study of micelle formation of block copolymers of ethylene and propylene oxides claimed that these surfactants did not form micelles, in contrast to the oxyethylated fatty alcohols or alkylphenols. However, Becher (16) reported that the CMC for poloxamer 182 was 2.4 wt % while Ross and Olivier (17) reported the CMC for poloxamer 184 to be 0.026 wt %. Subsequently, Williams and Graham (private communication) determined critical micelle concentrations for several of the poloxamers, using surface tension depression methods. This controversy as to whether or not the poloxamers form micelles was examined once again when Schmolka and Raymond used a differential dye absorption technique (18) and verified the existence of micelles. The values they obtained, namely that the poloxamers had critical micelle concentrations in the range of 3.0 to 11.0 μmol per liter, agreed closely with the data previously found by Williams and Graham.

At about this time, Saski and Shah (19), using three different techniques, reported considerably higher critical micelle concentration values for the poloxamers. These were 2.4, 2.2, and 0.1 wt % respectively, for poloxamers 182, 184, and 188. On the other hand, Sheth (20) reported a critical micelle concentration value for poloxamer 188 of 0.2 wt %, by means of surface tension depression.

This confusion on CMC values has been compounded even further. Thus, Anderson (21) has reported, using the same surface tension depression method, that the critical micelle concentration values for poloxamers 181, 182, and 188 were significantly lower than those previously reported. Anderson also used the differential dye absorption technique with benzopurpurin 4B and iodine methods to study this problem, but claimed that, due to interaction of the iodine and dye with the polymers, resulting in increases in absorbance, these methods would not permit a satisfactory determination of the critical micelle concentration values of the block copolymer surfactants.

Nuclear magnetic resonance has been used (22) to study the interaction of poloxamer 188 and phenol. Starting with low phenol concentrations, up to 2%, in a 10% aqueous poloxamer 188 solution, the authors reported that the phenol was associated mainly with the poloxypropylene chain. However, as the ratio of phenol to poloxamer increased, it appeared that the polyoxypropylene chain became saturated with phenol and relatively more phenol entered the polyoxyethylene chain. The authors concluded that this indicated the presence of micelles in the poloxamer phenol water system. However, they suggested that

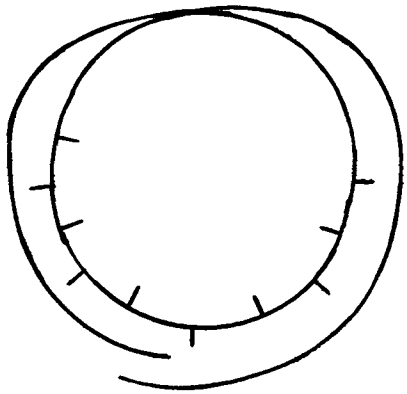

FIG. 6. Suggested poloxamer micelle configuration.

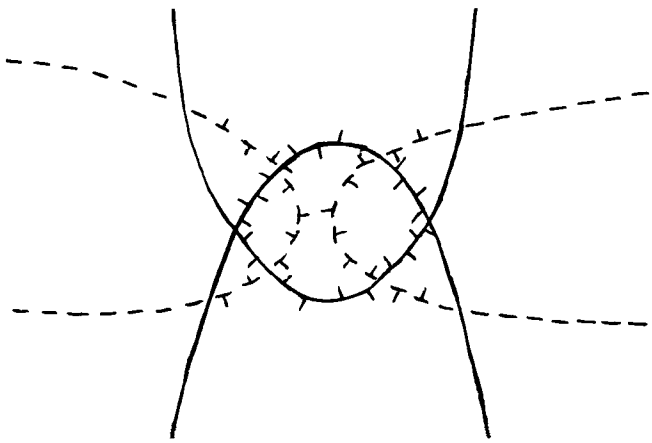

FIG. 7. Suggested poloxamer micelle configuration.

the micelle would not necessarily be aggregates of copolymer molecules as is found with other types of surfactants, but consisted of one molecule with the poloxyethylene chains rolled around the poloxypropylene region. This is illustrated in Figure 6.

The solution properties of several of the poloxamers were studied in water as well as in a nonaqueous solvent, such as benzene, dioxane, and butyl chloride. Considerable difference was found (23) between the weight and number-average molecular weight of the poloxamer micelles, as determined by light scattering and two methods of measuring vapor pressure lowering. The number of molecules per micelle found by light scattering varied, for example, for poloxamer 188, from 1.5 to 8 in the various solvents and less widely for poloxamers 108 and 338. The authors concluded that the poloxamers with a molecular weight below 2000, such as 101 and 105, failed to associate in benzene whereas higher molecular weight homologs, such as poloxamers 108 and 188, did.

In order to meet the requirements of 2-8 molecules per micelle, it is suggested that each surfactant molecule is shaped like a horseshoe, and that 2-8 interlocking horseshoe-shaped molecules form a micelle, as illustrated in Figure 7.

The solid lines represent the molecules which lie in the plane of the paper, while those represented by a dotted line are below and above the plane of the paper. On the other hand, the micellar molecular weight of poloxamer 188, as determined by light scattering, has been reported (24) to be 10^5.

Two of the poloxamines have been reported to exhibit micelles. Poloxamine 707 was found (18) to exhibit a critical micelle concentration of 0.005 wt % at 25 C, using the differential dye absorption technique. On the other

hand, the CMC value for poloxamine 908 was found to be 0.06 wt %, using both surface tension depression and solubility methods.

Previous measurements were carried out at 25 C. Most recently, the effects of temperature on the micellar properties of poloxamer 184 have been studied (25) over a range of temperatures by surface tension and light scattering techniques. The authors reported that at 25 C the micellar molecular weight is 2656, which is close to the molecular weight of 2900. However, at 30 C and 35 C, the authors reported aggregation numbers of 5.9 and 29.9, respectively. These results suggested to the authors that poloxamers behave differently from other nonionic surfactants. First, whereas other nonionic surfactant micellar sizes increase with temperature, with the poloxamers there may be temperature ranges within which no micelles form at all. Secondly, the authors believed that the growth of aggregates to a stable size takes place over much wider concentration ranges than for other nonionic surfactants, and lastly, the authors thought that the normal methods for determining CMC values of the poloxamers were inaccurate. Thus, one is led to conclude that the micellar nature of the block polymer surfactants and their critical micelle concentrations is a very complex and confused subject.

APPLICATION AREAS

Many new and interesting industrial applications for the block polymer nonionic surfactants have been developed, just in the past five or six years alone.

Most of these uses have been reported in publications such as magazine articles or patents and are not proprietary information. In reviewing these new applications, consideration will be given to the important physical property or properties which led to the selection of the block polymer. No attempt will be made to present a complete application picture, but rather only selected cases in just a few industries will be described.

The first application area to be reviewed will be cosmetics. Obviously, the primary reason for using block polymer surfactants here is their absence of toxicity, but in addition, other very specific physical properties are required.

A new dentifrice, designed for sensitive teeth, called PROTECT, uses poloxamer 407 because it is a gelling agent. The poloxamer/sodium citrate combination was reported (26) to have a highly significant desensitizing effect, in comparison with a control formulation of unknown composition. Another desirable property of the poloxamer in this application is its absence of any bitter taste. This is a new product currently being marketed in several locations in the United States.

An alcohol-based mouthwash was reported stabilized (27) by the addition of a poloxamer with an ethylene oxide content of >40%. The addition of the poloxamer prevents the formation of a cloudy appearance which would otherwise develop on standing. In this application, the lack of taste of the poloxamer, plus its ability to solubilize water insoluble aromatic flavors, are important considerations for its use.

In the field of aerosol antiperspirants, it has been reported (28) that the use of certain polyalkylene oxides, including certain poloxamers, would prevent the staining of clothing after repeated use of the antiperspirant formulation. The nonirritating properties, plus the solubilizing action, would be responsible for selecting the block polymer surfactants in this application. In the same type of aerosol product, the addition of a poloxamer to the formulation was reported (29) to prevent formation of lumps in storage. The dispersing properties of the poloxamer are believed to be the reasons for its selection in this application.

Many new applications in the medical field have been reported, and only a small number can be described here. The use of poloxamers with at least 50% ethylene oxide content has been reported (30) in a new process for the preparation of a stable and concentrated antiserum from human or animal plasma and serum, by fractional precipitation. At below room temperature conditions, the poloxamer selectively precipitates the protein fractions in various molecular weights. This precipitation is due to the ability of the two macromolecules, the polymeric poloxamer and the blood proteins, to form insoluble complexes at low temperatures. The complexes are then readily separated and purified.

Several poloxamines and their tetraesters have been found (31) to be useful as hypocholesterolaemic agents in animals and man. The starting poloxamines have a maximum ethylene oxide content of 30% and the hydrophobe molecular weight lies between 2250 and 3250. A dramatic reduction in blood serum cholesterol levels was reported when the polymers were regularly incorporated in the diet. It is suggested that the ability of the poloxamine or its esters to solubilize the sterol is the reason for this useful application.

The clinical use of poloxamer 188 as an emulsifying agent for a perfluorooctylbromide emulsion, useful as a radiopaque medium for contrast studies in medicine, is a relatively new development (32). The radiographs are equally as effective as, or more effective than, those obtained with organic iodide compounds and barium sulfate. The poloxamer was selected because of its ability to function as an emulsifying agent, and due to its lack of toxicity, including its nonthrombogenic properties.

In a similar application, poloxamer 188 has been the emulsifying agent of choice in the artificial blood program, for preparing stable emulsions of fluorocarbon in physiological saline (33).

An antiseptic skin cleaning formulation based upon chlorhexidine gluconate has been developed (34) containing 25% poloxamer 187. A problem is often encountered in hand wash formulations, namely that the cationic or antiseptic is inactivated in the micelles of the surfactant being used. This was eliminated by using a poloxamer as the wetting agent because, of all the nonionics tested, it exhibited the least inactivation of the chlorhexidine. The 187 grade was selected because it exhibited the highest foam. The 25% concentration was used in order to provide suitable foam viscosity and washing properties in the final product.

A method for enhancing drug or antibiotic levels in the blood has been reported (35) by oral administration of a capsule containing the drug and a poloxamer. Gastrointestinal hypomotility is induced and as a result of the delayed gastrointestinal transport, dwell time in the upper portion of the gastrointestinal tract is increased. This is desirable since drugs are preferentially absorbed in the upper G.I. tract. The properties associated with the selection of a poloxamer, which contains from 5-80% ethylene oxide, no doubt include absence of bitter taste, lack of toxicity, and its rate of solubility.

The effective control of bloat in beef cattle during feeding lot fattening, was reported (36) to be controlled when the cattle were fed a high concentration of a feed lot bloat inducing ration for an extended period of time and concurrently fed a bloat controlling compound, such as poloxamine 1501 or PLURADOT HA 520, together with a water soluble salt of a dimethyldialkyl quaternary ammonium compound.

Poloxamer 188 has been used (37) to study the development of tumor metastasis in rats. Treatment of rats, which had been intravenously administered tumor cells, with the poloxamer decreased the incidence of pulmonary metastasis

from 85.3% in the control to only 16.1%. The poloxamer property believed responsible for this application is its ability to prevent microvascular sludging of red cells, as well as its lack of toxicity. This is but one of a few hundred articles in various medical and pharmaceutical journals which describe the use of a poloxamer being studied in a research project.

In the paper industry, the preparation of a single transfer coating for paper utilized a poloxamer on a production scale (38). Poloxamer 182 was used as the wetting and dispersing agent to apply a coating on a backing surface of the paper sheet. After drying, the coating is tested for transfer properties by typing the front surface of the sheet with a second untreated sheet in facial contact with the coating. The second sheet was found to apply a transferred copy which had a sharp blue image and offered good smudge resistance.

It has been reported (39) that the moisture level in a sheet of cellulose, such as paper, can be stabilized by using a polyalkylene oxide as a stabilizing agent and a poloxamer to enhance the rate of absorption of the polyglycol by the sheet material. Using polyoxyethylene glycols of molecular weights varying from 400 to 4000, a dramatic decrease occurred in the time needed to saturate the sheet, from more than 2 min to less than 5 sec, upon addition of the block polymer. The wetting properties of the poloxamers proved useful in this application.

The textile industry has recognized the antistatic properties of the poloxamines and their derivatives. This is due to the following: (a) the presence of the two pairs of unshared electrons on the tertiary nitrogen atoms provides a slight cationic effect; (b) the poloxamine branched structure more readily lends itself to crosslinking and increased viscosity, and (c) the superior poloxamine thermal stability is believed to be due to the ability to form amine oxides upon oxidation. Hydrophobic fibers having antistatic properties were made (40) by incorporating an ester of a dibasic acid with a poloxamine having up to 30% propylene oxide at a mol wt of 200-10000 into the spin bath prior to spinning the nylon fiber.

A poloxamine having a mol wt between 4000-135,000 has been reported (41) to give excellent antistatic action in nylon 6 when used at 1-12%, based on the weight of the nylon. The fibers showed excellent antistatic activity through 25 washes.

An effective antistatic agent giving improved performance to nylon was obtained (42) by chain extending a poloxamine with a diepoxide or a diisocyanate. Even better antistatic effectiveness was reported achieved by further reaction with a sulfuric acid derivatives, such as sodium paratoluene sulfonate. This increased the viscosity of the polymer, thus making it more compatible with the high viscosity nylon melt prior to spinning.

A novel method for softening laundry was reported (43) by tumbling it in a damp state with coated polystyrene foam spheres. By dip-coating the spheres in a blend of a poloxamer 407, sodium tallow alcohol sulphate slurry, and ethyl alcohol, the softener was readily transferred to the laundry while tumbling in a dryer.

Improved lubricating oil compositions containing lubricating viscosity and conventional gear oil and hydraulic oil additives may be obtained (44) by incorporating relatively small amounts, as little as 0.01%, of a poloxamine with a molecular weight range of 1650-15000 and an ethylene oxide content of about 10-50%. The poloxamine addition serves to improve the oil compositions by giving improved rust protection, by a standardized test, by improving rate of demulsibility in a standard demulsification test, and by giving less emulsion sludge in a standard engine test. The surfactant properties reponsible for this improvement include its wetting, interfacial tension lowering, and dispersing abilities.

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