Nonionic Surfactants Derived From a New Hydrophobic Base[1]

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THE rapid increase in the production and use of nonionic surfactants in the United States is emphasized by reports of the Tariff Commission which show an increase from 30 million pounds in 1949 to 51 million pounds in 1950, continuing and increasing the growth trend noticeable in this field for the past several years. These products include among their many advantages the possibility of being tailored for specific applications through selection of the proper combination of hydrophobic and hydrophilic units to make up the nonionic molecule.

Among the most common hydrophilic units in general use are the polyhydroxy compounds, such as glycerol and the polyglycols obtained by the polymerization of ethylene oxide. These latter, because of the wide variation possible in their molecular weights and consequently their hydrophilic activity, can be used to provide the proper solubilizing effect for almost any hydrophobic unit. Although the patent literature indicates that propylene oxide can be substituted for ethylene oxide to provide the hydrophilic polyoxyalkylene glycol units for nonionic surfactants, propylene oxide does not appear to be used commercially except in the form of propylene and dipropylene glycols.

The hydrophobic units in common use are, for the most part, compounds having a substantial hydrocarbon residue such as fatty acids, amides and alcohols, alkyl phenols, and alkyl naphthols. The properties of the nonionic can be varied by choice of the class of compound used as the hydrophobic base and by the molecular weight of the compounds within the class. Thus a choice may be made in the alcohol class between lauryl or cetyl alcohols or in the alkyl phenol class between octyl or nonyl phenols, but variation is limited by number of suitable products available at a commercially practical price.

The ability to prepare hydrophobic base materials for nonionic surfactants by a condensation reaction in the manner in which the hydrophilic polyoxyethylene glycol unit is derived would appear to offer an attractive method for extending the range of hydrophobic units available. Ideally, such a method of synthesizing the base would permit almost unlimited variation in the molecular weight range and hydrophobic properties of the base and, when combined with the variations possible in the hydrophilic unit, should greatly extend the ability to tailor nonionic surfactants for specific applications. Up to the present such a method of synthesizing the hydrophobic units does not appear to have been reported. We have now found that highly effective hydrophobic bases for nonionic surfactants can be prepared by a procedure similar to that used for preparing the hydrophilic unit.

By reacting propylene oxide with water to form relatively water-insoluble polyoxypropylene glycols and then reacting these products with ethylene oxide, we have obtained a new class of nonionic surfactants.[2] The availability of propylene oxide at a relatively low price, coupled with its ease of reaction to form polyoxypropylene glycols opens the way to an almost unlimited number of relatively inexpensive base materials for the synthesis of nonionic surfactants.

TABLE I

Polyoxypropylene Glycols Tested as Hydrophobic Units in Nonionic Surfactants

Molecular Weights	Water Solubility at 25°C.
294	Infinite
763	23.0%
938	<0.10
1,270	<0.10
1,620	<0.10
2,320	<0.10

The combination of polyoxypropylene and polyoxyethylene glycols in one molecule makes possible wide variations of the molecular weight of the hydrophobic base and the ratio of the hydrophobic to hydrophilic units in the molecule to permit tailoring for specific applications.

Synthesis and Structure

The general procedure used for the preparation of this new class of nonionic surfactants may be divided into two phases. In the first phase a polyoxypropylene glycol which will serve as the hydrophobic unit is prepared by the addition of propylene oxide to water or propylene glycol in the presence of a catalytic amount of sodium hydroxide. The second phase consists of adding ethylene oxide to the polyoxypropylene glycol obtained in the first reaction. The structure of the new products is represented as:

$$\mathrm{HO{-}(C_2H_4O)_a\ (C_3H_6O)_b\ (C_2H_4O)_cH}$$

polyoxyethylene-polyoxypropylene-polyoxyethylene glycol

which places the hydrophobic unit in the middle of the molecule. This structure is based on the assumption that when ethylene oxide is reacted with the polyoxypropylene glycol, it will add to the free hydroxyls at each end of the polyoxypropylene glycol.

Low molecular weight polyoxypropylene glycols, because of their water solubility, are not effective as the hydrophobic unit of nonionic surfactants. To determine at what molecular weight these glycols become sufficiently water insoluble to function as the hydrophobic base in nonionic surfactants, the series of polyoxypropylene glycols of increasing molecular weights shown in Table I was prepared. The marked and abrupt decrease in water solubility of these polyglycols with increase in molecular weight as determined from hydroxyl number (1) is apparent from the data.

A series of experimental nonionic surfactants for evaluation was prepared from each of these polyoxypropylene glycols by reaction with sufficient ethyl-

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[1] Presented at 25th annual fall meeting, American Oil Chemists' Society, Chicago, Ill., Oct, 8-10, 1951.

[2] These products are manufactured by Wyandotte Chemicals Corporation under the trade name Pluronics.

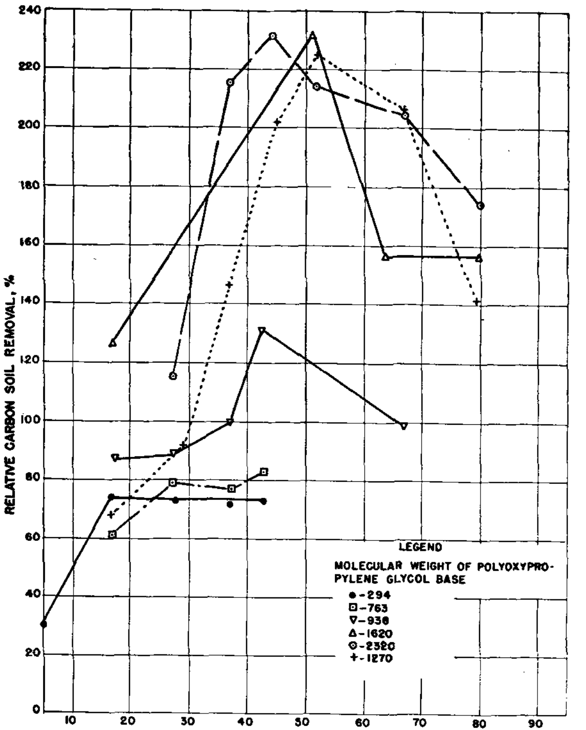

FIG. 1. Relative carbon soil removal properties of nonionics derived from polyoxypropylene glycols vs. oxyethylene content. 0.25% concentration, 140°C.

ene oxide to make the total weight of ethylene oxide added to the polyoxypropylene glycol equal to approximately 16 to 80% of the weight of the finished product.

Physical Properties

Of the polyoxypropylene glycols shown in Table I, those which are found suitable for use as hydrophobic base materials are essentially insoluble at room temperature. As ethylene oxide is added to the suitable base materials, the water solubility of the products increases until a stage is reached at which the products are miscible with water in all proportions at room temperature.

The quantity of ethylene oxide required to reach this stage varies with molecular weight of the base but is usually adequate when the oxyethylene units comprise 40% of the finished product. Solubility in organic solvents varies with the molecular weight of the polyoxypropylene glycol base and the weight ratio of the hydrophobic to the hydrophilic portions of the molecule in the expected manner.

By varying the quantity of ethylene oxide condensed with a polyoxypropylene glycol, it is possible to obtain products ranging in physical form from mobile liquids to solids sufficiently hard to be flaked, irrespective of the molecular weight of the starting polyoxypropylene glycol, but to obtain liquid, solid, or flake products showing high detergency it is necessary to start with an insoluble polyoxypropylene glycol base.

Products containing up to about 40% by weight of oxyethylene units are liquids whose viscosity varies with the percentage of oxyethylene units. Above 40% the products increase rapidly in viscosity and assume a pasty consistency which, above 50% oxyethylene content, changes to a soft wax-like character. Further additions of oxyethylene units result in products of gradually increasing hardness until in the range of 70% oxyethylene units and higher, the products became sufficiently hard to flake.

Surface Activity

Relative Carbon Soil Removal. As a rapid screening procedure for surfactant properties the products were tested for relative carbon soil removal activity in comparison with a commercial anionic detergent according to our previously published procedure (2). In this test 0.25% solutions of the test detergent and the standard detergent in distilled water are used to wash soiled cotton swatches at 140° F. in a Launderometer. The amount of soil removed by each detergent is measured and the effectiveness of the test detergent expressed as a percentage of the standard detergent.

Figure 1 illustrates the relative soil removal values of nonionic surfactants prepared from the various polyoxypropylene glycol bases as a function of the oxyethylene content of the molecule. This figure indicates that a minimum molecular weight of approximately 900 is required before the polyoxypropylene glycol will serve effectively as the hydrophobic base. Products based on higher molecular weight polyoxypropylene glycols show extreme effectiveness, reaching values for carbon soil removal which are in excess of 200% of the standard anionic detergent, a sodium alkylarylsulfonate type of product. It will be noted that maximum activity for carbon soil removal appears to be obtained with products having an oxyethylene content in the range of 40 to 55%.

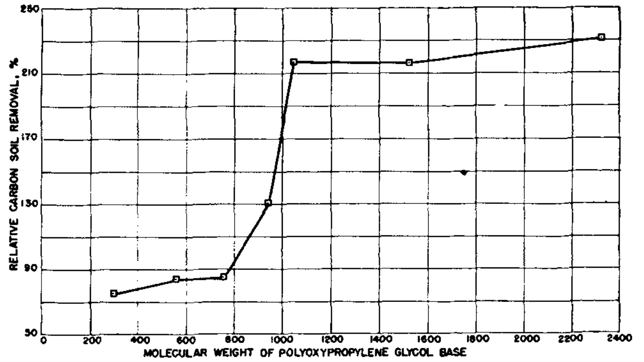

FIG. 2. Relative carbon soil removal properties of nonionics derived from polyoxypropylene glycols vs. molecular weight of the base. Oxyethylene content 44%. 0.25% concentration, 140°F.

In Figure 2 is shown the carbon soil removal activity for a series of nonionic surfactants obtained by the addition of sufficient ethylene oxide to the indicated polyoxypropylene glycol base to yield products containing 44% by weight of oxyethylene units. All of these products were prepared by the general procedure described in a previous section of this paper. This curve also emphasizes the necessity of a molecular weight of approximately 900 for the hydrophobic polyoxypropylene glycol unit to become effective, as measured by the carbon soil removal tests. The effectiveness of these new products for carbon soil removal can be appreciated more fully when it is realized that

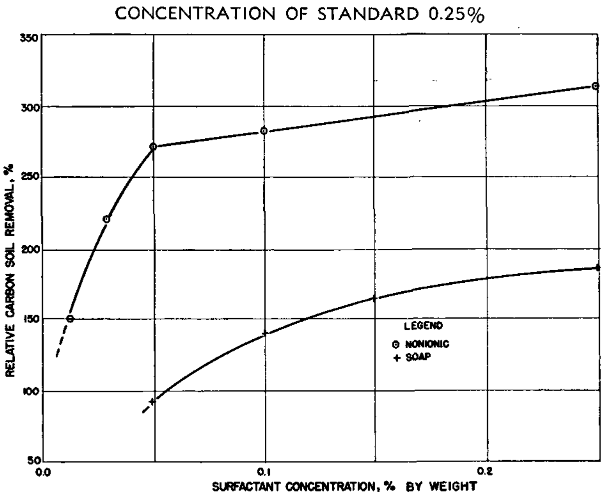

FIG. 3. Relative carbon soil removal properties of a nonionic derived from a polyoxypropylene glycol vs. concentration. Molecular weight of base 1050. Oxyethylene content 40%. Distilled water at 140°F.

on this scale a high titer soap has a relative carbon soil removal of 185%. It can be seen from these data that many of the new products are far superior to soap under the conditions of this test.

The effectiveness of the new products at low concentrations is shown by Figure 3, in which relative carbon soil removal activity at 140°F. is plotted against concentration of the surfactant. The concentration of the standard is maintained constant at 0.25%. The data shown are for a nonionic detergent which consists of approximately 40% oxyethylene units by weight and is derived from a polyoxypropylene glycol of 1,050 molecular weight as the hydrophobic base. This activity at low concentrations appears to be a common property of the new class of products. For comparison, results obtained with a high titer soap are also shown.

Relative Whiteness Retention. Carbon soil removal, which is a measure of the amount of soil removed from cotton cloth, is only one factor in detergency. A second important factor is the ability of the detergent to maintain the soil in suspension as measured by a whiteness retention test which has been described previously (2). In this test the ability of a 0.25% solution of the detergent in distilled water to prevent the deposition of a carbon soil on cotton cloth is measured in comparison with a commercial anionic detergent of the sodium alkylarylsulfonate type as standard and the efficiency of the detergent under test expressed as a percentage of the standard. By this test a high titer laundry soap has a value of 145% with the anionic detergent taken at 100. The new nonionics based on the polyoxypropylene glycol unit as the hydrophobic base all show values in the range of 250 to 300% and higher.

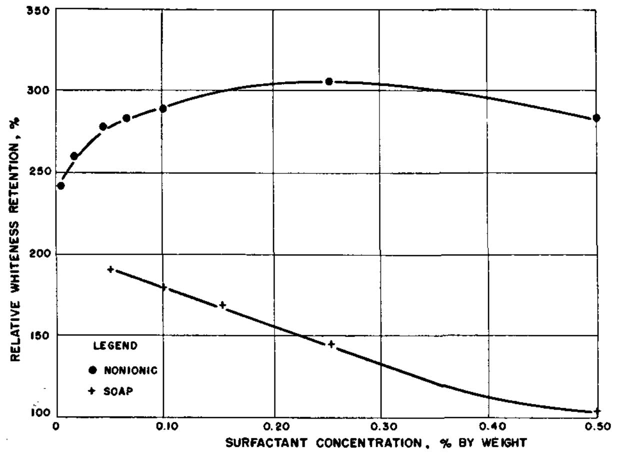

FIG. 4. Relative whiteness retention properties of a nonionic derived from polyoxypropylene glycol vs. concentration. Molecular weight of base 1050. Oxyethylene content 40%. Distilled water at 140°F.

The effect of concentration on the relative whiteness retention activity of the new products is shown by Figure 4 for a product in which the molecular weight of the polyoxypropylene glycol is approximately 1,050 and which contains 40% by weight of oxyethylene units. It can be seen from this curve, which is typical for the new class of products, that whiteness retention activity in distilled water is maintained even at extremely low concentrations of the nonionic surfactant.

Surface Tension. Data obtained on the ability of the new series of nonionics to lower the surface tension of distilled water are shown in Figure 5. It is apparent that in comparison with a value of 72 for distilled water all of the products exert a considerable lowering effect on the surface tension of water when added in concentrations of 1% or less. Within any series of products based on the same hydrophobic unit a slight decrease occurs in the effectiveness of the individual product as the weight percentage of oxyethylene units in the molecules increases, but as the molecular weight of the polyoxypropylene glycol base is increased, the surface tension lowering activity of the series appears to be increased. The effect of the increased molecular weight of the base on surface tension lowering at a constant oxyethylene content in the molecule is shown in Figure 6 for products containing 38% by weight of oxyethylene units.

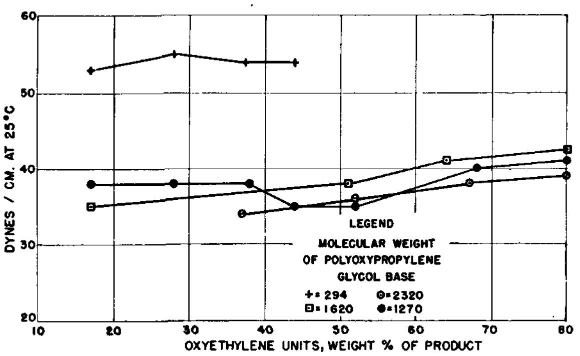

FIG. 5. Surface tensions of solutions of nonionics derived from polyoxypropylene glycols vs. oxyethylene content. 0.1% concentration at 25°C.

Wetting Action. The wetting action of the new group of surfactants was measured by the familiar canvas disc method (3) at 60°C. at 0.10% concentration in distilled water. With all products derived from a polyoxypropylene glycol having a molecular weight of 550 or less, the sink times exceeded 600

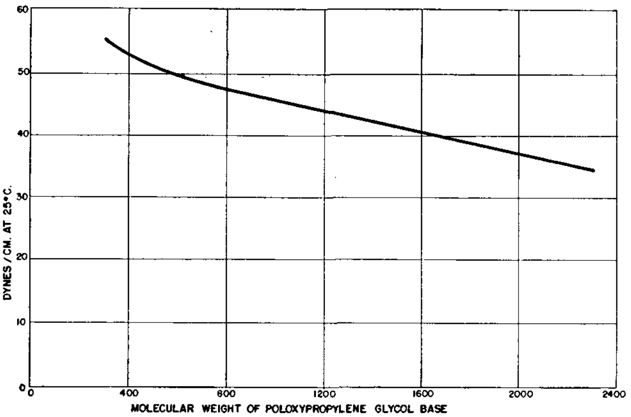

FIG. 6. Surface tensions of solutions of nonionics derived from polyoxypropylene glycols vs. molecular weight of the base. Oxyethylene content 38%. 0.1% concentration at 25°C.

seconds. As the molecular weight of the base was increased, the sink times decreased until at a molecular weight of approximately 1,600 for the polyoxypropylene glycol base, they reached 28 seconds. The products in this case contained between 40 and 50% by weight of oxyethylene units. Further increases in the molecular weight again resulted in an increase in the sink time. Figure 7 shows the variation in sink time for products derived from polyoxypropylene glycols having molecular weights of approximately 1,200, 1,600, and 2,300 as a function of the variation in oxyethylene content. It will be noted from these curves that the most effective products for wetting action, as measured by the canvas disc test, are those containing in the range of 40 to 50% by weight of oxyethylene units in the finished product.

Summary

A versatile new class of nonionic surfactants has been prepared essentially from ethylene and propylene oxides. The new products are based upon the discovery that a polyoxypropylene glycol having a molecular weight of approximately 900 or higher will function as the hydrophobic unit of a nonionic surfactant which may presumably be represented as $HO(C_2H_4O)_a\ (C_3H_6O)_b\ (CH_2O_4)_cH$. By selection of a polyoxypropylene glycol having a suitable molecular weight and by adjusting the weight ratio of oxypropylene to oxyethylene units in the product, nonionics have been prepared which range in physical form from liquids to solids which are sufficiently hard that they may be flaked.

The possibility of wide variation in the molecular weight of the hydrophobic unit and in the weight ratio of the hydrophobic to hydrophilic units in the molecules allows extensive tailoring of the products to give specific control of properties such as solubility in water, detergency, wetting action, and surface tension lowering.

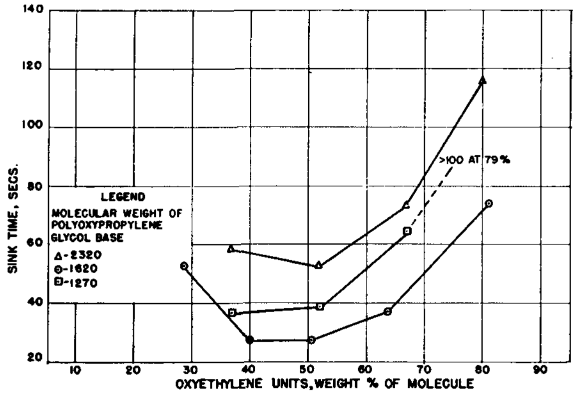

FIG. 7. Canvas disc wetting speeds of nonionics derived from polyoxyalkylene glycols vs. oxyethylene content. 0.1% concentration at 60°C.

REFERENCES

1. Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. Eng. Chem., Anal. Ed., *17*, 394 (1945).
2. Vaughn, T. H., and Suter, H. R., J. Am. Oil Chem. Soc., *27*, 249-257 (1950).
3. Seyferth and Morgan, Am. Dyestuff Reporter, *27*, 525 (1939).

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Report of the Referee Board

THIS report for the 1951-52 period is very routine as no new or major problems arose. The policies established by previous Boards have been closely followed. For the year ending May 31, 1952, thirty-four Referee Chemists were appointed. All except two were renewals. Twenty-four were given certificates on cottonseed, oil cake and meal, and fatty oils. Ten held restricted certificates either by choice of application or by the discretion of the Board.

The chemists are located in 12 states and 22 cities and represent 19 different laboratory organizations.

Many inquiries were received during the year relative to certification and handled as expeditiously as possible.

The Board again strongly urges any prospective applicants to participate in the Smalley Check Sample Program and to complete and report their results according to schedule. Performance on the check sample work has considerable bearing on our decisions.

Applications for certification for the 1952-53 period have already been given some consideration, and they were handled before May 31.

R. R. KING
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