# New Tertiary Amine-Based Surface Active Polymers[1]

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### Abstract

Surface active polymers with molecular weight ranging from 5600 up to 30,000 were synthesized by the oxyethylation of polyoxpropylene glycol adducts of ethylene diamine, which range in molecular weight from 4750 up to 6750. The toxicological properties of some of these new nonionics indicated that they would be nontoxic when used in contact with the skin and scalp. Their typical physical properties such as wetting, emulsifying, foaming and thickening are reported. A variety of cosmetic formulations has been prepared utilizing these new nonionic surface active polymers. This illustrates their versatility when used in products as diverse as a floating bath oil, an antiperspirant gel, a cold cream and a sun screen lotion.

### Introduction

OVER THE PAST FEW YEARS the cosmetic industry has exhibited a growing interest in nitrogen-containing surfactants. This has been exemplified by the increased use in consumer products of amine oxides, oxyethylated fatty amines, protein derivatives, etc. (1,2,3). The toilet goods industry has been showing great concern with measures proposed to maintain the safety of raw materials designed for use in consumer products (4). This prompted the Wyandotte Chemicals Corporation to examine various means for developing novel surfactant molecules for the cosmetic industry which would contain nitrogen and be nontoxic.

One well known commercially available series of nontoxic surface active agents, block copolymers of ethylene and propylene oxides based on a propylene glycol initiator, is the Pluronic polyols (Wyandotte Chemicals). In the past, these have tended to overshadow a lesser known series of surfactant polymers, based on ethylenediamine as the initiator, namely, the Tetronic polyols (Wyandotte Chemicals) (5). The commercially available Tetronic surfactants had been based on hydrophobes of low to moderate molecular weights, namely, 900 to 3750. Only very limited data covering physical properties, toxicology or applications were available (6).

### Experimental Procedures

A program was initiated to synthesize Tetronic surfactants having higher molecular weight hydrophobes, prepared by the oxypropylation of ethylenediamine. Figure 1 shows the structural formula of the tertiary diamines.

These hydrophobes were designed to have average molecular weights of 4750, 5750 and 6750. Allowing for the molecular weight of 60 for the ethylenediamine initiator, this corresponds to the addition of 81, 98 and 116 moles of propylene oxide, respectively, divided equally, it is believed, into four chains. Carefully controlled oxypropylation conditions (5), using an alkaline catalyst at elevated temperature and pressure, are followed. In the oxyethylation step, from about 20 moles to over 500 moles of ethylene oxide are added. The surfactant polyols thus synthesized and their nomenclature are shown in Fig. 2. The first two digits in the four digit number represent the average molecular weight of the hydrophobe. The last digit signifies approximately one tenth of the ethylene oxide content of the entire molecule. The surfactants based upon the 4750 molecular weight hydrophobe will be referred to as the 11 series, those based on the 5750 molecular weight hydrophobe as the 13 series, and those based on the 6750 molecular weight hydrophobe as the 15 series. It should be emphasized that in any vertical group shown in Fig. 2, e.g., polyols 1104, 1304 and 1504, the molecular weight of the hydrophile, as well as the hydrophobe, increases. The weight ratio of propylene oxide to ethylene oxide remains constant, but the mole ratio varies.

#### Toxicity

To obtain maximum data with a minimum number of samples, five surfactant polyols of widely different molecular weights and a wide range of ethylene oxide to propylene oxide ratios were selected for determination of the acute toxicological properties. To distinguish more readily among the new surfactant polyols, several polyols based upon lower molecular weight hydrophobes were included in these toxicity studies. The studies included the determination of the acute oral $LD_{50}$ on albino rats, and the acute dermal $LD_{50}$ on albino rabbits, using the techniques of Thompson and Weil (7,8,9). The eye irritation and skin irritation test procedures employed on albino rabbits were modeled after that of Draize et al. (10). The test results, summarized in Table I, are for the polyols at 100% concentration.

The data show that the molecular weight of the polyoxypropylene hydrophobe and the relative size of the polyoxyethylene hydrophile affect toxicological properties. As the molecular weight of the hydrophobe and the size of the hydrophile increase, the acute oral $LD_{50}$ increases and the eye and skin irritation decrease. This decrease in toxicity is shown by comparing the data for polyols 701 with 1101 and 701 with 707. These data indicate that the toxicological properties of the 11, 13 and 15 series polyols fall in the practically nontoxic class, according to the toxicity rating chart given in Gleason et al. (11). Because of the favorable toxicological data obtained, a study was made of the physical properties of these

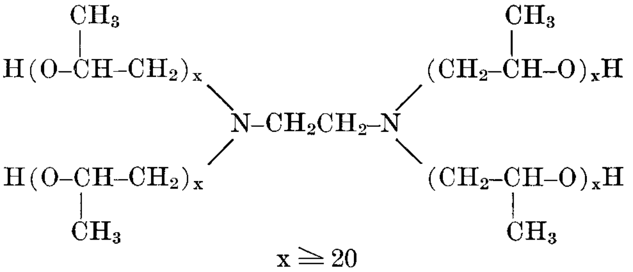

FIG. 1. Tertiary diamine hydrophobe.

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[1] Presented at the AOCS Meeting, Chicago, October 1967.

TABLE I

Acute Toxicity of Polyols

| Polyol | 701 | 707 | 908 | 1101 | 1304 |
|---|---|---|---|---|---|
| Hydrophobe molecular weight | 2750 | 2750 | 3750 | 4750 | 5750 |
| Polyol molecular weight | 3400 | 12,000 | 27,000 | 5600 | 10,500 |
| Acute oral $LD_{50}$, g/kg | 3.4 ± 0.3 | >23.1 | >23.1 | 18.8 ± 1.0 | >15.4 |
| Acute dermal toxicity $LD_{50}$, g/kg | >10.2 | >10.2 | >10.2 | >10.2 | >10.2 |
| Eye irritation | Moderate | Mild | Mild | Minimal | None |
| Skin irritation | Moderate | Mild | Mild | Mild | Slight |

new surfactant polyols and their potential applications for cosmetic products.

**Physical Properties**

Typical physical properties are listed in Table II. The physical forms vary from liquid to paste and solid. Product designations which have a last digit of 1 or 2 are indicative of liquid polyols, low in oxyethylene content. Product numbers with a last digit of 4 represent polyols in paste form while polyols which are high in oxyethylene content have a product number ending in 7 or 8 and are flakeable solids. The molecular weights of these polyols, determined by the ASTM method (12), range from a minimum of 5600 for 1101 to over 25,000 for 1508. All the liquid grades are slightly heavier than water and vary in viscosity from 700 to 1600 centipoises (Brookfield Synchro-lectric Viscometer, Model LVF) at 25 C. Melting points of the paste and solid members vary from 34 C to 60 C.

From the cloud point data in Table II, it can be seen that those polyols with the last digit ending in 1, namely those with only 10% of ethylene oxide in the molecule, are insoluble in water at 0.1%, and also at 0.01%, at 25 C. Polyol 1302 is different in that a 0.1% solution gives two cloud points, one at 20 C and the other at 60 C. A similar observation was made for the 10% cloud point of polyol 1502. It is suggested that the lower cloud points are due to the presence of lower oxyethylated homologs (13). The pH of all the polyols is 7.0 ± 1.0.

Some surface active properties of 0.1% solutions of these polyols are shown in Table III. All surfactants show good surface tension lowering with very little difference among the three series. The values for the low ethylene oxide-containing polyols are shown in parentheses because they are insoluble in water at 0.1% concentration. It is evident that the higher the ethylene oxide content is, the less is the surface activity. The Draves test (14), on the other hand, indicates a slight but not significant decrease in wetting properties, going from the 11 series to the 13 series and on to the 15 series. The dynamic foam height (15) data indicate maximum foam properties are exhibited by the 11 series, as shown by the 200 ml flow rate. However, there do not appear to be any large differences in the foam characteristics among the three series. For comparison, the corresponding foam data for a high foaming anionic, sodium lauryl sulfate, are also shown. The foam data indicate that these polyols are essentially low to moderate foamers. The addition of small amounts of a conventional foam stabilizer, such as an amine oxide or a fatty alkanolamide, was found to have little beneficial effect on the foaming properties of these polyols.

The next property studied was that of thickening aqueous solutions. Part of our objective was to develop a surfactant that would form a clear ringing gel with water at a polyol concentration of not more than 10 weight per cent. By a ringing gel is meant a rigid product which will vibrate when the container is tapped. This is thought to occur due to the formation of liquid crystals (16).

The thickening properties of the three series increase slowly, with an increase in molecular weight. The polyoxypropylene-rich molecules are not too amenable to gel formation because of their limited water solubility. Polyol 1101 was the only surfactant that did not form a gel, reaching a maximum viscosity of only 3600 cps at 80% concentration in water. Polyol 1102 formed a gel at 70% concentration, while polyol 1301 exhibited a gel at a concentration of both 70% and 80%. Polyol 1501 had a gel region from 40% through 80% concentration, while polyols 1104, 1302 and 1502 formed gels from 40% through 90% concentration. A broader gel region, from 30% through 90%, was shown by polyols 1107, 1304, 1307 and 1504. The broadest gel region, however, was exhibited by polyol 1508, which formed a gel at only 20% concentration and up through 90%. Two polyols of even higher molecular weight, namely a 1509 and a 1708, with molecular weights of 37,400 and 31,600, respectively, were then specially synthesized and tested for gel formation at 15% concentration. Neither formed the desired gel. Therefore, in formulating cosmetic products which are in gel form, the 1508 product was usually used for this type of application.

The procedure in preparing a gel is to add a weighed amount of polyol to cold water, with good mixing. Maintaining the solution temperature at 10 C or below, over a period of a few hours, gives a clear solution. As soon as the mixture is homogeneous,

TABLE II

Typical Physical Properties

| Tetronic polyol | Sp. gr. | Mp, C | Viscosity, cps, 25 C | Solution cloud point, C | | Mol. wt |
|---|---|---|---|---|---|---|
| | | | | 1% | 10% | |
| 1101 | 1.017 | .... | 700 | 17 | .... | 5,600 |
| 1102 | 1.027 | .... | 820 | 31 | 28 | 6,300 |
| 1104 | ........ | 34 | ...... | 72 | 69 | 8,300 |
| 1107 | ........ | 51 | ...... | 100 | 100 | 14,500 |
| 1301 | 1.017 | .... | 1000 | 16 | .... | 6,800 |
| 1302 | 1.030 | .... | 1300 | 20, 60 | 29 | 7,800 |
| 1304 | ........ | 36 | .... ... | 78 | 75 (gel) | 10,500 |
| 1307 | ........ | 54 | ........ | 100 | 100 | 18,600 |
| 1501 | 1.019 | .... | 1170 | 15 | .... | 7,900 |
| 1502 | 1.027 | .... | 1570 | 70 | 14, 30 | 9,000 |
| 1504 | ........ | 41 | ........ | 90 | 75 (gel) | 12,500 |
| 1508 | ........ | 60 | ........ | 100 | 100 | 26,600 |

TABLE III

Surface Active Properties

| Tetronic polyol | Surface tension, dynes/cm | Draves test, sec. | Dynamic foam height, mm (49 C) | |
|---|---|---|---|---|
| | | | 400 ml/min | 200 ml/min |
| 1101 | (34.0)[a] | (52)[a] | 10 | ...... |
| 1102 | 33.7 | 15 | 45 | ...... |
| 1104 | 36.3 | 37 | >600 | 160 |
| 1107 | 42.9 | >360 | >600 | 185 |
| 1301 | (33.4)[a] | (31)[a] | 5 | ...... |
| 1302 | 34.1 | 30 | 25 | ...... |
| 1304 | 35.5 | 48 | >600 | 155 |
| 1307 | 43.8 | >360 | >600 | 100 |
| 1501 | (33.9)[a] | (181)[a] | 5 | ...... |
| 1502 | 34.1 | 51 | 35 | ...... |
| 1504 | 37.3 | 84 | >600 | 75 |
| 1508 | 43.8 | >360 | >600 | 110 |
| SLS | ...... | ...... | >600 | >600 |

[a] Insoluble at 0.1% concentration.

the product is transferred to a container. When the polyol solution warms to ambient temperature, a clear ringing gel is formed. If the gel, containing only the 1508 polyol and water, is heated above room temperature it does not liquefy. However, some formulated products have been found to liquefy when heated above 45 C. The temperature at which gel formation occurs, namely the transition temperature between the cool mobile liquid and the ambient temperature rigid gel, varies with the other ingredients in the formulation and concentration of polyol used.

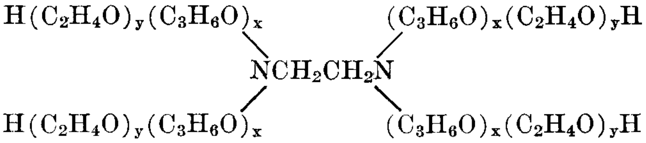
In preparing formulated products, the ingredients are added to a cold solution of the polyol in water. Water insoluble materials are sometimes solubilized in the 1508 polyol solution. An example is hexachlorophene. Where the ingredients are water insoluble but alcohol soluble and a clear gel is desired it has been found possible to dissolve the insolubles in isopropyl alcohol or acetone and add the organic solvent system to the cold aqueous polyol solution. However polyol 1508, since it is of such high molecular weight, has a slow rate of solution and time and agitation are required in order to prepare solutions. Many cosmetic products were prepared as clear ringing gels and some of these will be described later, together with the formulations used.

One of the more desirable properties of any group of surface active agents is the ability to function as emulsifiers. A series of tests was carried out in which aqueous solutions of each of the polyols prepared with mineral oil were evaluated for their ability to form a stable emulsion. Using mineral oil to water weight ratios of 2:98, 10:90, 25:75 and 50:50, 1, 5 and 10 g of each surfactant were first tested for their ability to form a stable emulsion at room temperature. Those emulsions that were stable for 24 hr at 25 C, were then subjected to freeze-thaw cycles, to a maximum of 6. Although many emulsions were stable at 25 C for 24 hr, only 10 systems survived one or more freeze-thaw cycles. These are shown in Table IV.

TABLE IV

Stable Mineral Oil Water Emulsions

| Tetronic polyol | Polyol, g | Mineral oil, g | Water, g | Freeze-thaw cycles survived |
|---|---|---|---|---|
| 1102 | 10 | 50 | 50 | 1 |
| 1104 | 1 | 25 | 75 | 1 |
| 1107 | 1 | 25 | 75 | 1 |
| 1107 | 5 | 50 | 50 | 3 |
| 1107 | 10 | 50 | 50 | 3 |
| 1304 | 10 | 50 | 50 | 1 |
| 1502 | 5 | 50 | 50 | 1 |
| 1502 | 10 | 50 | 50 | 5 |
| 1504 | 1 | 25 | 75 | 1 |
| 1504 | 10 | 50 | 50 | 6 |



$H(C_2H_4O)_y(C_3H_6O)_x$ $(C_3H_6O)_x(C_2H_4O)_yH$ $NCH_2CH_2N$ $H(C_2H_4O)_y(C_3H_6O)_x$ $(C_3H_6O)_x(C_2H_4O)_yH$

| Hydrophobe mol. wt | First digits | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 6501–7000 | 15 | 1501 | 1502 | | 1504 | | | | 1508 |
| 5501–6000 | 13 | 1301 | 1302 | | 1304 | | | 1307 | |
| 4501–5000 | 11 | 1101 | 1102 | | 1104 | | | 1107 | |
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |

% Polyoxyethylene (hydrophile) in total molecule

x = 20–29, y = 5–113

FIG. 2. Tetronic polyol grid.

The data indicate that the most stable emulsions have a relatively high mineral oil and surfactant content. However, by the judicious use of a balanced system of emulsifiers, usually including both a hydrophilic and a hydrophobic nonionic, several cosmetic products which contain only minor amounts of mineral oil were prepared. A few of these will be described later.

## Formulations

A wide variety of cosmetic products was prepared. The first series of formulated products to be described includes the ringing gels based upon polyol 1508. Table V shows two skin protection products, an insect repellent and a sun screen.

Each of these preparations is made by dissolving the organic additive in alcohol, and adding the alcoholic solution to a cool (5–10 C) aqueous solution of polyol 1508. The perfume and preservative are added and after a brief mixing period the product is transferred to suitable containers. Simple mixing equipment provided with an internal or external cooling device is satisfactory for preparing the 1508 solution. When the solution warms to room temperature, a clear ringing gel is formed. The polyol gels will tolerate minor amounts of alcohol, generally 5–10% without loss of gel structure. Excessive amounts of alcohol at a 20% level tend to prevent the gel from forming. These formulations are strong gels, despite the presence of 12% or 18% alcohol, due to the inclusion of an aromatic compound, some of which appear to increase the yield strength of the polyol gel structure. Although the polyols themselves are indefinitely stable when stored at room temperature, aqueous solutions of the polyols are subject to microbial decay. Therefore most cosmetic products are protected by the addition of small amounts of a preservative, such as Dioxin (Sindar Corporation) or Cinaryl 200 (Dow Chemical Corporation).

TABLE V

Skin Protection Gels

| A | B | Sun Screen<br>Insect Repellent |
|---|---|---|
| 20 | 14 | Polyol 1508 |
| 60.5 | 64 | Water |
| 18 | 12 | Isopropyl alcohol |
| 1.5 | .... | Amyl *p*-dimethylaminobenzoate[a] |
| ...... | 10 | m N,N-diethyltoluamide[b] |
| q.s. | q.s. | Perfume |
| q.s. | q.s. | Preservative |
| 100.0 | 100.0 | |

[a] Van Dyk & Co., Inc.

[b] Hercules, Inc. or Cowles Chemical Co.

TABLE VI

Cream Sachet

| | |
|---|---|
| 12 | Polyol 1504 |
| 6 | Propylene glycol |
| 2 | Lanolin |
| 5 | Polawax A31[a] |
| 10 | Glyceryl monostearate, s.e. |
| 4 | Perfume |
| 61 | Water |
| q.s. | Preservative |
| 100 | |

[a] Croda, Inc.

An anti-perspirant in gel form may be made quite readily from 20 parts polyol 1508, 38 parts aluminum chlorohydrate (50%), 1 part Plurafac RA 20 (Wyandotte Chemicals Corporation), 0.4 parts perfume and 40.6 parts of water. This system can be prepared by either one of two ways, the cold technique as previously described or what will be referred to as the hot technique. The latter method consists of heating all ingredients, except perfume and perfume solubilizer, to 60 C and stirring until a homogeneous liquid is formed. The product is cooled to 50 C and a mixture of perfume and perfume solubilizer is added. The inclusion of a small amount (0.1–0.5%) of hexachlorophene in this formulation increases the yield strength of the gel but results in an orange brown color.

In this product, the Plurafac RA-20 surfactant functions as the perfume solubilizer. This particular system liquefies above 45 C and below 20 C. In developing a new product for the first time the cold technique is used. Samples of the finished formulation are placed in one oven at 45 C and in another at 60 C. Most often the products fail to liquefy at either temperature. If the product does liquefy at 60 C, it means the product can be prepared by the hot technique. This technique does offer the formulator a time saving; however, the cold technique is preferred where heat sensitive materials, such as expensive perfumes, are utilized. All gel products were tested for stability by recycling between 0 C and 45 C for six cycles. Although the products liquefy in the refrigerator, they always return to their gel form upon rewarming.

Other cosmetic products prepared in gel form include a boric acid gel, an ammonium thioglycolate gel for use in hair products, a germicidal gel containing hexachlorophene, an antiseptic gel containing alkyl ($C_8$–$C_{18}$) dimethyl benzyl ammonium chloride, and a hair groom gel containing polypeptides.

Not all water soluble materials have been successfully formulated into gel products. Examples of this category are the attempted preparation of a cuticle remover based upon the use of lactic acid. Although a gel formed initially, it soon liquefied. A similar situation was encountered when an attempt was made to prepare hydrogen peroxide in gel form. Working at either 3% or 6% hydrogen peroxide concentration level, the gel that was formed initially soon liquefied. One possible cause of disappearance of the gel initially formed may be due to the gradual formation of a salt between the electrons of the sterically hindered tertiary diamine and the acid. It has been previously reported (17) that low molecular weight polyols of this structure readily react with chloramine to form the corresponding monoquaternary hydrazinium halide indicating that these nonionic polyols do exhibit cationic properties.

TABLE VII

Skin Care Creams

| A | | | Cold Cream |
|---|---|---|---|
| | B | | Moisturizing Cream |
| | | C | Hand Cream |
| .... | 10 | .... | Polyol 1302 |
| .... | 4 | .... | Polyol 1307 |
| 2 | .... | .... | Polyol 1502 |
| 4 | .... | .... | Polyol 1508 |
| .... | .... | 2 | Polyol 1501 |
| .... | .... | 3 | Polyol 1107 |
| 6 | 5 | .... | Propylene glycol |
| 35 | 9 | .... | Mineral oil |
| 2 | 2 | 1 | Lanolin |
| 12 | 10 | .... | Petrolatum |
| .... | 2 | 2 | Stearic Acid |
| .... | 4 | 3 | Glyceryl monostearate, s.e. |
| 4 | .... | 3 | Polawax A31[a] |
| 34.9 | 53.9 | 85.9 | Water |
| 0.1 | 0.1 | 0.1 | Perfume |
| q.s. | q.s. | q.s. | Preservative |
| 100.0 | 100.0 | 100.0 | |

[a] Croda, Inc.

TABLE VIII

Hair Groom Cream

| | | |
|---|---|---|
| I | 6 | Polyol 1302 |
| | 3 | Polyol 1508 |
| | 1 | Magnesium aluminum silicate[a] |
| | 57.5 | Water |
| II | 23 | OP-2000[b] |
| | 5 | Lanolin |
| | 2 | Polawax A31[c] |
| | 2 | Glyceryl monostearate, s.e. |
| III | 0.2 | Bactericide/fungicide[d] |
| | 0.1 | Citric acid, saturated soln. |
| | 0.2 | Perfume |
| | 100.0 | Total |

Add II to I, then add III.

[a] Veegum, R. T. Vanderbilt Co., Inc.
[b] Wyandotte Chemicals Corporation.
[c] Croda, Inc.
[d] Vancide 89RE, R. T. Vanderbilt Co., Inc.

It has been our experience that a higher concentration of polyol is needed to gel an aqueous solution of an acidic material than the corresponding amount of water in the absence of the acid. The boric acid gel is an example of this. Ringing gels of hydrogen peroxide or lactic acid have been prepared without difficulty using polyols which are high molecular weight block polymers of ethylene and propylene oxides derived from a propylene glycol initiator. However, it is not known just why salt formation should prevent the formation of a gel.

Table VI shows a formulation for a cream sachet based upon polyol 1504, although polyol 1304 may also be used. The 1504 serves partially as an emulsifying agent and partially as a thickening agent. This product is easily prepared by heating together all the ingredients except perfume and preservative, mixing until liquid and well homogenized with an Eppenbach Homo-mixer (Gifford-Wood Co.) or equivalent, adding the balance of the formulation and then transferring to containers. Upon cooling, it sets up into a rather viscous cream which dries readily, tack-free, upon the skin and leaves a very pleasant odor.

Both the emulsifying and thickening properties of the polyols are utilized in the products shown in Table VII. Each of these formulations, a cold cream, a moisturizing cream and a hand cream is made by heating all ingredients together until liquid, homogenizing with an Eppenbach Homo-mixer and transferring to the final container while molten. The products thicken upon cooling. The formulations were tested for stability by subjecting to six freeze-thaw cycles, recycling between a 5 C refrigerator and a 45 C oven. The products survived six complete cycles without exhibiting any phase separation.

A stable opaque hair groom cream, shown in Table VIII, is made in a slightly more complicated fashion. The water, polyols 1302 and 1508, and the magnesium aluminum silicate are heated to 60 C and mixed until homogeneous. The fatty ingredients (II) are heated in a separate vessel to 60 C, mixed and added while hot, with gentle mixing, to the hot aqueous system (I). The mixture is cooled slightly to 45 C, and the balance of the ingredients are then mixed into the product. This formulation utilizes an oxypropylated oleic acid, the OP-2000, to provide a nice film on the hair, and the two polyols provide emulsification and viscosity control. A similar product has also been prepared in which mineral oil replaced the OP-2000.

A different type of cosmetic product, a floating bath oil, is prepared by blending together 1% polyol 1301, 22% isopropyl myristate, 13% isopropyl palmitate, 60% mineral oil, 4% perfume and a trace of color. The polyol 1301 is used as the surface active agent to prepare a product that spreads rapidly on the surface of the bath water leaving a very thin layer of oil. The fatty esters serve to couple the polyol and mineral oil to give a sparkling clear product. Simple mixing at room temperature is used for this preparation.

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