

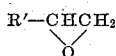
3

n-tetradecyl, n-pentadecyl, tert-octadecyl, 2,6,8-trimethyl-nonyl, and 7-ethyl-2-methyl-4-undecyl alcohols.

An especially valuable class of alcohols which are useful for the preparation of the presently provided new compounds of my invention include the branched-chain alcohols wherein the alkyl radical is derived from an al-
fin monomer, dimer, trimer, tetramer, pentamer, or the like, carbon monoxide, and hydrogen according to the "Oxo" process. Such alcohols include the branched-chain tridecyl alcohol derived from propylene tetramer or but-
ylene trimer, carbon monoxide and hydrogen; branched-chain decyl alcohol prepared from propylene trimer, car-
bon monoxide and hydrogen; branched-chain hexadecyl alcohol prepared from propylene pentamer, carbon mon-
oxide and hydrogen; and branched-chain nonyl alcohol prepared from diisobutylene, carbon monoxide and hy-
drogen.

Illustrative examples of some alkylphenols which can be employed as reactants in this invention include tert-
octylphenol, nonylphenol, (2-ethylheptyl)phenol, decyl-
phenol, 4-tert-dodecylphenol, 2-tridecylphenol, 3-tert-
octadecylphenol, 2-nonyl-1-naphthol, 1-(2-butyloctyl)-2-
naphthol, 2,4-dimethylphenol, 3-butylphenol, and 2,4-
dinonylphenol.

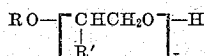
The epoxyalkane reactant used in the reaction of this invention can be any epoxyalkane having a terminal
group; i.e., an epoxyalkane having the structure



wherein R' is selected from the group consisting of hy-
drogen and lower alkyl radicals. Preferably, the alkyl
radical contains less than 6 carbon atoms and may have
either straight chain or branched-chain configuration.
Such alkyl radicals include methyl, ethyl, propyl, iso-
propyl, butyl, isobutyl, pentyl, hexyl, isohexyl, tert-butyl,
2-methylbutyl, 2,2-dimethylpropyl, and 2-methylpentyl.

Illustrative examples of some epoxyalkanes which can be used in the process of this invention include ethylene
oxide, 1,2-epoxypropane (propylene oxide), 1,2-epoxy-
butane, 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxy
heptane, 1,2-epoxyoctane, 3-methyl-1,2-epoxybutane, 4-
methyl-1,2-epoxypentane, and 4,4-dimethyl-1,2-epoxy-
pentane.

The product of the first alkenoxylation step is an
alkoxyalkenoxyalkanol or an alkaroxyalkenoxyalkanol,
including an alkoxypolyalkenoxyalkanol or an alkaroxy-
polyalkenoxyalkanol, having from 1 to as many as 10
alkenoxy groups in the molecule depending upon the num-
ber of moles of the epoxyalkane reactant used. Thus,
using 1 mole of the epoxyalkane reactant and an alcohol,
the product is an alkoxymonoalkenoxyalkanol whereas
using 2 moles of the epoxyalkane and 1 mole of the alkyl
alcohol gives a product of alkoxydi(alkenoxy)alkanol.
Ordinarily, the major product of the alkenoxylation step
has the structure shown in Equation 1 with the alkyl
group identified by R' attached to the carbon atom ad-
jacent the oxygen atom of the alkenoxy group. However,
this reaction usually results in the formation of some
alkoxyalkenoxyalkanol or some alkaroxyalkenoxyalkanol
products of the structure



wherein the alkyl group identified by R' is attached to the
carbon atom separated from the oxygen atom of the
alkenoxy group by a methylene group. Although the
predominant product is one in which the alkyl radical
is attached to the carbon atom in the 1 position, as shown
in Equation 1, it is also intended to include products
wherein the alkyl group is attached to the carbon atom
in the 2 position and it is intended that the alkenoxy
group cover both isomers.

The first alkenoxylation step is preferably conducted
in the presence of a catalyst which can be either an alka-
line type catalyst or an acid type catalyst. Suitable

4

alkaline type catalysts include the alkali metal oxides,
hydroxides, carbonates, borates, and the like which are
alkaline reacting. Such catalysts include sodium oxide,
potassium oxide, lithium oxide, sodium hydroxide, potas-
sium hydroxide, lithium hydroxide, sodium carbonate,
potassium carbonate, lithium carbonate, sodium bicar-
bonate, sodium borate, potassium borate, and the like.
Suitable acid type catalysts include sulfuric acid, alkane-
sulfonic acids, arylsulfonic acids, and Lewis acids. The
Lewis type acids include aluminum chloride, boron tri-
fluoride, stannic chloride, ferric chloride, and the like.
Boron trifluoride etherate is a preferred catalyst of this
type. Although either the alkaline or the acid type cat-
alyst can be used in the first alkenoxylation step, it is
usually preferred to use the alkaline type catalyst.

The amount of the catalyst present in the first alken-
oxylation step can be varied over wide limits as deter-
mined by the particular epoxyalkane reactant used, by the
temperature desired, and by the reaction time selected.
Ordinarily, the amount of catalyst will be between about
0.1% and 5.0% by weight of the amount of the alcohol
reactant present.

Ordinarily, the first alkenoxylation reaction is carried
out at a temperature in the range of from 50° C. to 160°
C.; however, the temperature selected depends to a con-
siderable extent upon the nature of the catalyst employed.
Thus, it is usually sufficient to use a temperature in the
range of from 50° C. to 100° C. when using an acid-type
catalyst whereas a temperature in the range of from 100°
C. to 160° C. will usually be employed with an alkaline
type catalyst. Alkenoxylation of the alcohol with the
lower molecular weight epoxyalkanes usually requires
the use of the alkaline-type catalyst and, therefore, a
temperature in the range of 100-160° C. In compari-
son, alkenoxylation of the alcohol with the higher molec-
ular weight epoxyalkanes may require the use of an acid-
type catalyst, and therefore a temperature below 100° C.
Alkenoxylation using the lower molecular epoxyalkanes
can also be conducted using the acid-type catalyst; how-
ever, a temperature in the lower portion of the range must
be used in order to minimize the formation of by-
products.

The first alkenoxylation reaction may be carried out
at substantially atmospheric pressure although elevated
pressures can also be used advantageously.

The reaction of the alcohol with the epoxyalkane is
primarily an addition-type reaction resulting in the forma-
tion of a single product. But some reaction conditions
may result in the formation of by-products, necessitating
a separation step. Thus, some ketone by-products may
be formed in the reaction requiring removal by distilla-
tion. The presence of water in the alkenoxylation step
results in the formation of glycol but the formation of
this by-product can be reduced by dehydrating the alcohol
reactant before conducting the reaction. If an alkaline-
type catalyst is used in the first alkenoxylation step, this
catalyst must be removed before conducting the second
alkenoxylation step using epichlorohydrin. This alkaline
catalyst is best removed from the alkoxyalkenoxyalkanol
product by washing with water. It is not necessary to
remove an acid-type catalyst used in the first step of the
alkenoxylation reaction since this same catalyst can be
used in the second alkenoxylation step with epichloro-
hydrin.

The second alkenoxylation reaction step using epi-
chlorohydrin is conducted using substantially only 1 mole
of epichlorohydrin per mole of the alcohol reactant used
in the first alkenoxylation step. The use of more than
1 mole of epichlorohydrin results in the formation of a
polyglyceryl ether substituted with a number of chloro-
methyl groups which would then be converted into poly-
sulfonate groups in the subsequent sulfonation. This
second alkenoxylation step differs from the first alken-
oxylation step in that the alkenoxylating reactant is a
chloro-substituted epoxyalkane instead of an alkyl-sub-

5

stituted epoxyalkane as in the first step and substantially only 1 mole of the epoxyalkane per mole of alcohol is used in the second step whereas more than 1 mole of the epoxyalkane can be used in the first step. As used in this specification, substantially 1 mole is defined as being one or slightly more than 1 mole and always less than 2 moles; that is, substantially 1 mole can be as much as 1.25 or 1.3 moles. In conducting the second alkenoxylation reaction, it is preferred to use at least 1 mole of the epichlorohydrin per mole of the alcohol reactant, and very often as much as 1.2 moles, in order to insure complete chloroalkenoxylation of the alkoxyalkenoxalkanol product produced in the first alkenoxylation step. The presence of unreacted alkoxyalkenoxalkanol in the final product is not desirable since it is detrimental to surfactancy and not readily separated from the desired product.

The second alkenoxylation step using epichlorohydrin is conducted in the presence of a catalyst. This catalyst can be any of the acid-type catalysts used in the first alkenoxylation step but the alkaline-type catalyst can not be used. A preferred catalyst is boron trifluoride. As in the first alkenoxylation step, the amount of catalyst used will usually amount to 0.1% to 5% by weight of the amount of alcohol reactant used. As noted previously, if an acid catalyst is used in the first alkenoxylation step, additional catalyst will not be necessary in the second alkenoxylation step except to replace any catalyst which may have been lost.

The second alkenoxylation step can be carried out at room temperature; however, usually elevated temperatures are employed in order to shorten reaction times. Ordinarily, the temperature will be maintained at less than 140° C. A preferred temperature range is from 60° to 120° C. The temperature is dependent so some extent upon the nature of the catalyst used; less active catalysts requiring higher temperatures. Thus, boron trifluoride acts as a very reactive catalyst in this step so that usually the temperature is maintained below 100° C.

As in the first alkenoxylation step, the pressure is ordinarily maintained at substantially atmospheric pressure in the second step although elevated pressures can be employed.

The product from the second alkenoxylation step is primarily a polyether-substituted chlorohydrin, more specifically a 1-alkoxyalkenoxy-3-chloro-2-propanol, 1-alkoxyalkenoxy-3-chloro-2-propanol, 1-alkoxypolyalkenoxy-3-chloro-2-propanol, or 1-alkoxypolyalkenoxy-3-chloro-2-propanol, as shown in reaction 2.

The second alkenoxylation reaction is primarily one of addition so that usually there are very few other products to be found in the reaction product.

Formation of the glycidyl ethers as shown in equation 3 above, takes place readily by contacting the polyether-substituted chlorohydrin produced in the second alkenoxylation step with an aqueous alkaline solution. This reaction involves dehydrochlorination of the chlorohydrin to form the epoxy group. The alkaline solution may be an aqueous solution of an alkali metal hydroxide or a basically reacting salt thereof, e.g., sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, sodium acetate and the like. Ammonium hydroxide or ammonium salts can not be used. Advantageously, the dehydrochlorination reaction is carried out in a solvent media in order to obtain suitable reaction times and complete dehydrochlorination. The solvent should be one which is soluble in water and suitable solvents may include aliphatic and aromatic hydrocarbons such as toluene or hexane, ethers such as isopropyl ether or dioxane and the dialkyl sulfoxides. The dialkyl sulfoxides are preferred solvents and those in which there are present from 1 to 5 carbon atoms in each alkyl radical e.g., dimethyl sulfoxide, diethyl sulfoxide, dipropyl sulfoxide, di-n-butyl sulfoxide, di-tert-amyl sulfoxide, ethylmethyl sulfoxide, n-amyl-n-propyl sulfoxide, and the like. The quantity of diluent employed

6

depends somewhat upon the nature of the individual chlorohydrin and upon the amount of the alkali hydroxide present. With respect to the quantity of sulfoxide, there should be present a quantity of sulfoxide which is at least 10% by weight of the amount of the chlorohydrin and preferably from 25 to 100% by weight of the amount of the chlorohydrin. Advantageously, substantially equal amounts of the sulfoxide and the chlorohydrin are employed. A molecular equivalent of the alkali metal hydroxide with respect to the chlorohydrin should be present and the best results are obtained by employing a slight excess of the hydroxide.

The dehydrochlorination step takes place by contacting the chlorohydrin with the aqueous alkali hydroxide in the presence of the diluent at ordinary or moderately increased temperatures, e.g., at temperatures of from room-temperature to 120° C. External heating need not generally be employed, although under certain conditions, e.g., when the reaction is effected in the presence of a dilute aqueous alkali metal hydroxide, external heating may be used.

When the dehydrochlorination reaction has been completed, which can be noted by cessation in changes of refractive index, the glycidyl ether is separated from the reaction mixture by customary isolation procedures. By-product salt may be removed by filtration. Preferably, the ether product is recovered by solvent extraction, whereby the upper layer is separated, water washed to remove any residual salt and diluent, and finally distilled. The lower layer, which comprises most of the sulfoxide and excess alkali can be recycled in a continuous process. Generally good results are obtained by simply filtering the crude reaction mixture to remove the salt and allowing the filtrate to stratify, whereby the ether product is recovered as the upper layer. Water washing of the upper layer generally gives a satisfactory ether product without further purification.

The product of the dehydrochlorination step is a glycidyl ether, more specifically, 3-alkoxyalkenoxy-1,2-epoxypropane, 3-alkoxyalkenoxy-1,2-epoxypropane, 3-alkoxypolyalkenoxy-1,2-epoxypropane, or 3-alkoxypolyalkenoxy-1,2-epoxypropane. There can be several lower alkyl radicals identified by R' in the formulas when x is greater than 1; such as, when x is 2, there are two R' groups in the formula. These lower alkyl groups can be the same or different, including hydrogen. For example, when x is 2, one R' can be methyl and the other ethyl, or one can be methyl and the other hydrogen or both can be methyl. These products are generally mobile to viscous liquids which vary in color from water-white to amber. Illustrative examples of some of these glycidyl ethers are as follows:

- 3-(2-tert-octadecyloxyethoxy)-1,2-epoxypropane
- 3-(2-nonylphenoxyethoxy)-1,2-epoxypropane
- 3-[1-(2-propylheptyloxy)-2-propoxy]-1,2-epoxypropane
- 3-[1-(n-hexadecyloxy)-2-propoxy]-1,2-epoxypropane
- 3-[1-(2,4-dinonylphenoxy)-2-butoxy]-1,2-epoxypropane
- 3-[1-(n-hexadecyloxy)-2-butoxy]-1,2-epoxypropane
- 3-[1-(n-octadecyloxy)-2-butoxy]-1,2-epoxypropane
- 3{2-[2-butyl-octyloxyethoxy]ethoxy}-1,2-epoxypropane
- 3-{2-[2-(decylphenoxy)ethoxy]ethoxy}-1,2-epoxypropane
- 3-{1-[1-(tridecyloxy)-2-propoxy]-2-propoxy}-1,2-epoxypropane
- 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-1,2-epoxypropane
- 3-{1-[1-(2-ethylheptyl)phenoxy]-2-hexoxy}-2-hexoxy}-1,2-epoxypropane
- 3-{1-[1-(lauryloxy)-2-butoxy]-2-butoxy}-1,2-epoxypropane
- 3-{2-[2-(2-ethylhexyloxy)ethoxy]ethoxy}ethoxy}-1,2-epoxypropane
- 3-{2-[2-[2-(4-tert-dodecylphenoxy)]ethoxy]ethoxy}-1,2-epoxypropane
- 3-(1-tert-dodecyloxytri-2-propenoxy)-1,2-epoxypropane
- 3-(1-tert-dodecyloxytri-2-butenoxy)-1,2-epoxypropane

- 3-(1-isononyloxyhexa-2-ethenoxy)-1,2-epoxypropane
 3-[1-(2-tridecylphenoxy)hexa-2-ethenoxy]-1,2-epoxypropane
 3-(1-n-pentadecyloxyhexa-2-pentenoxy)-1,2-epoxypropane
 3-[1-(3-butylphenoxy)hexa-2-propenoxy]-1,2-epoxypropane
 3-(1-isodecyloxyhexa-2-propenoxy)-1,2-epoxypropane
 3-{1-[1-(nonyloxy)-2-propoxy]-2-butoxy}-1,2-epoxypropane
 3-{1-[1-tert-octadecyloxy]-2-propoxy]-2-ethoxy}-1,2-epoxypropane

As disclosed hereinafter, these glycidyl ethers are readily converted upon reaction with an alkali metal sulfite into exceptionally valuable surfactants having good "lime soap" dispersion properties.

As shown in Equation 4, the glycidyl ether can be reacted with an alkali metal sulfite or bisulfite to form an alkali metal salt of the polyether-substituted 2-hydroxy-1-propanesulfonate and, an alkali metal hydroxide as a by-product. The alkali metal can be selected from the group consisting of sodium, potassium, and lithium. If desired, an alkaline earth metal sulfite or bisulfite can be used in place of the alkali metal sulfite and when using this reactant, the alkaline earth metal can be selected from the group consisting of calcium, strontium, barium and magnesium. The reaction of the glycidyl ether with the alkali metal or alkaline earth metal sulfite or bisulfite is advantageously effected while substantially neutralizing the alkali metal or alkaline earth metal hydroxide as it is formed in the reaction. Thus, to get good yields of the propanesulfonate it is preferred to neutralize the hydroxide as it is formed by the continuous addition of an acid, such as hydrochloric or sulfuric acid, at a rate so as to maintain the pH of the reaction mixture at from approximately pH 6-8 and definitely below 10 when using preferred solvents. It is also advantageous to conduct this reaction step in the presence of a diluent or solvent, e.g., water, ethanol, isopropanol, hexane, or the like. Although water can be used without admixture with one of the other solvents, it is usually preferred to admix the water with ethanol in approximately equal amounts for use as a solvent. The use of water as a solvent without admixture with ethanol requires more elevated temperatures in order to effect the reaction. Furthermore, the use of water without admixture with ethanol generally requires the use of elevated pressures.

The sulfonation reaction can be carried out at temperatures within the range of from 50° C.-120° C. using a water-ethanol solvent. The reaction can also be carried out at a temperature within the same range using water as a single solvent but a reaction time of from 2 to 3 days will be required unless a temperature of 190° C. is used when the reaction time will be 1 to 2 hours.

The sulfonation reaction can be carried out at atmospheric pressure or substantially atmospheric pressure when using a water-ethanol solvent. However, if water is used as a single solvent superatmospheric pressure will be required in order to effect the reaction in reasonable periods.

When the addition reaction has been completed, the sulfonate product is readily recovered by customarily employed isolating procedures. A product of good purity is obtained by removing the water in the reaction mixture by azeotropic distillation using a suitable azeotrope-former such as isopropanol. The inorganic salts present in the reaction mixture are insoluble in hot isopropanol and, since the sulfonate is substantially soluble therein, the salts may be removed by filtration. It is usually desirable to have a small amount of water present in the mixture to be filtered, particularly with the higher molecular weight sulfonate products, in order to prevent any of the sulfonate product from precipitating out of solution. The sulfonate product is then recovered from the isopropanol solution by volatilization of the solvent.

An alternative method for forming the polyether-substituted 2-hydroxy-1-propanesulfonate product of this invention involves treatment of the polyether-substituted chlorohydrin obtained from the second alkenoxylation step with epichlorohydrin directly with the alkali metal sulfite or bisulfite. This method requires the use of elevated pressures and temperatures, usually in the range of 150-210° C., and somewhat longer reaction times in order to effect conversion to the alkali metal sulfonate. This method is less preferred than the method involving formation of the glycidyl ether.

The sulfonate product of this invention, as shown in Equation 4, is an 3-(alkoxyalkenoxy)-2-hydroxy-1-propanesulfonate salt or an 3-(alkaroxyalkenoxy)-2-hydroxy-1-propanesulfonate salt and, where an excess of the epoxyalkane was employed in the first alkenoxylation step, the product is an 3-(alkoxyalkenoxy)-2-hydroxy-1-propanesulfonate salt or a 3-(alkaroxypolyalkenoxy)-2-hydroxy-1-propanesulfonate salt. Illustrative examples of some of the sulfonate products of this invention are as follows:

- Sodium, potassium or lithium 3-(2-tert-octadecyloxyethoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(2-nonylphenoxyethoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(2-propylheptyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(2,4-dinonylphenoxy)-2-butoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium, or lithium 3-[1-(n-hexadecyloxy)-2-butoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(n-octadecyloxy)-2-butoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[2-[2-(2-butyloctyloxy)ethoxy]ethoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[2-[2-(decylphenoxy)ethoxy]ethoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-{1-[1-(tridecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-[1-(2-ethylheptyl)phenoxy]-2-hexoxy]-2-hexoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-[1-(lauryloxy)-2-butoxy]-2-butoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[2-[2-[2-(2-ethylhexyloxy)-ethoxy]ethoxy]ethoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[2-[2-[2-(4-tert-dodecylphenoxy)]ethoxy]ethoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-[1-(nonyloxy)-2-propoxy]-2-butoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(1-tert-dodecyloxytri-2-propenoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(1-tert-dodecyloxytri-2-butenoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(1-isononyloxyhexa-2-ethenoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(2-tridecylphenoxy)hexa-2-ethenoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(1-n-pentadecyloxyhexa-2-pentenoxy)-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-[1-(3-butylphenoxy)hexa-2-propenoxy]-2-hydroxy-1-propanesulfonate
 Sodium, potassium or lithium 3-(1-isodecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate
- The sulfonate products of this invention are stable, usually water soluble, friable solids or viscous gums. They are valuable articles of commercial interest and have many varied uses, particularly as surface active agents. They can be used as wetting, frothing or wash-

ing agents in the treatment and processing of textiles, for dyeing, for pasting of dyestuffs, fulling, sizing, impregnating and bleaching, and the like. In addition, these compounds are useful for preparing foam in fire extinguishers, for use as froth flotation agents, as air entraining agents for concrete or cement, and as aids in the preparation of other articles of commerce. These sulfonate compounds are particularly useful in soap and synthetic detergent compositions as lime soap dispersants.

The advantages, the desirability and usefulness of the present invention will be illustrated by the following examples.

Example 1

In this example, 3-[1-(n-hexadecyloxy)-2-propoxy]-1,2-epoxypropane, and sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxypropanesulfonate were prepared from substantially 1 mole of propylene oxide and 1.2 moles of epichlorohydrin. Cetyl alcohol was dried by heating and stirring in a suitable vessel 242 g. (1.0 mole) of cetyl alcohol for a period of 2 hours at a temperature of approximately 60° C. in a nitrogen stream. Then 2.3 g. of potassium metal was added. After dissolution of the potassium in the cetyl alcohol, 87 g. (1.5 moles) of propylene oxide was added dropwise during a period of two hours, during which time the temperature was increased from 90° C. to 150° C. After completion of the reaction, the reaction mixture was cooled to approximately 100° C. and the catalyst neutralized using Dry Ice and water. Thereafter, the reaction product was dried over anhydrous sodium sulfate. After standing overnight, the drying agent was filtered off and the filter cake washed with hexane. The filtrate was distilled to obtain a 114.9 g. fraction boiling at 0.3 mm. between 144° C. and 161° C. This product is mainly 1-n-hexadecyloxy-2-propanol and was found to have a carbon and hydrogen analysis of 75.70 wt. percent carbon and 13.39 wt. percent hydrogen as compared with calculated values of 76.0 wt. percent carbon and 13.4 wt. percent hydrogen.

The second alkenoxylation step was carried out by heating 113 g. (0.376 mole) of the 1-n-hexadecyloxy-2-propanol with 41.6 g. (0.45 mole) of epichlorohydrin using 1.01 ml. boron trifluoride-diethyl ether complex (47% BF₃) as a catalyst. The reaction temperature was maintained at 85–90° C. by regulating the rate of addition of the epichlorohydrin. After the addition of epichlorohydrin was completed, the reaction mixture was heated for an additional one hour while maintaining the temperature at 90° C. The product of this reaction, 1-(1-n-hexadecyloxy-2-propoxy)-3-chloro-2-propanol, was not separated from the reaction mixture but was dehydrochlorinated in the next step to form the glycidyl ether.

In the dehydrochlorinating step, 50 g. (0.50 mole) of 40% sodium hydroxide and 50 ml. of water were added to the above reaction mixture to which was also added 100 ml. of dimethyl sulfoxide. This mixture was then heated at a temperature of 90° C. for a period of 1.5 hours. The hot reaction mixture was then filtered to remove the sodium chloride formed in the reaction and the oily layer was washed twice with hot saturated aqueous sodium chloride solution in the presence of hexane. The oil was dried over sodium sulfate and the hexane was removed by evaporation under reduced pressure to obtain a faintly yellow oil which is the glycidyl ether, 3-[1-(n-hexadecyloxy)-2-propoxy]-1,2-epoxypropane.

The sodium hydroxy sulfonate product was formed by heating 53.5 g. (0.15 mole) of the glycidyl ether obtained in the above dehydrochlorination step with 25.2 g. (0.20 mole) of sodium sulfite in 100 ml. of ethanol mixed with 100 ml. of water. The pH of the solution was maintained at pH 7–9 by the periodic addition of 6 N hydrochloric acid. The heating was continued for a period of 10.5 hours while maintaining the temper-

ature at 80° C. At the end of this time, the reaction mixture was dried by stripping off the water under reduced pressure while replacing it with isopropanol. The hot isopropanol solution was then filtered to remove insoluble material and the hot filtrate cooled to crystallize out the sulfonate product which was recovered by filtration. The recovered product was dried in an oven at a temperature of 45° C. to obtain 39 g. of the desired sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate which is substantially white in color.

Example 2

In Example 1 a fraction boiling from 166° C. to 205° C. at 0.3 mm. (mainly from 182 to 197° C.) is the product resulting from the reaction of 1 mole of the cetyl alcohol with 2 moles of propylene oxide, identified as 1-(1-n-hexadecyloxy-2-propoxy)-2-propanol. It contained 73.67% C and 13.10% H; the calculated values are 73.7 and 12.9, respectively. Then, in the second alkenoxylation step, 95.5 g. (0.266 mole) of the above reaction product was heated with 29.6 g. (0.319 mole) of epichlorohydrin using 1.0 ml. of boron trifluoride-diethyl ether complex as a catalyst. The epichlorohydrin was added over a period of 30 minutes at a rate to maintain the temperature at approximately 85° C. After the addition of all the epichlorohydrin, the heating was continued for a period of 1 hour at 85–90° C. The reaction product, 1-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-3-chloro-2-propanol, was not separated but was treated directly in the next dehydrochlorination step.

In the dehydrochlorination step, 40 g. of 40% sodium hydroxide solution, 40 ml. of water, and 80 ml. of dimethyl sulfoxide were added to the above reaction mixture which was then heated for a period of 2 hours while maintaining the temperature at 80–85° C. The reaction mixture was cooled overnight and the sodium chloride formed in the reaction was then removed by filtration. Hexane was used to wash the residue on the filter paper and the filtrate was separated; the oily layer was washed with saturated sodium chloride solution and dried over sodium sulfate-magnesium sulfate and distilled to remove the hexane and to obtain as residue 106.3 g. of the glycidyl ether, 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-1,2-epoxypropane, which is a light yellow oil.

The sulfonate was formed by heating 62.2 g. (0.150 mole) of the glycidyl ether obtained above with 25.2 g. (0.20 mole) of sodium sulfite in a mixture of 80 ml. each of water and ethanol. The mixture was heated at a temperature of 82° C. for a period of 19 hours while maintaining the pH of the solution at 7–9 by the dropwise addition of 6 N hydrochloric acid as required. At the end of this time, the solution was dried by stripping off water at reduced pressure while replacing it with isopropanol. The hot isopropanol solution was then filtered to remove the insoluble salts and the filtrate then cooled to permit crystallization of the sulfonate product. The sulfonate product was separated by filtration and washed 3 times with isopropanol before being dried in a vacuum oven at a temperature of 50° C. to obtain 55.2 g. of the sodium 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate which is a white solid.

Example 3

In this example, 1-(1-isodecyloxy-penta-2-propenoxy)-2-propanol was prepared as in Example 1 from decyl alcohol and approximately 6 moles of propylene oxide. This material was then alkenoxylated in a second alkenoxylation step using 101.4 g. (0.20 mole) of the 1-(1-isodecyloxy-penta-2-propenoxy)-2-propanol and 1 ml. of boron trifluoride-diethyl ether as a catalyst. The epichlorohydrin in an amount of 22.2 g. (0.24 mole) was added to the mixture at a rate so as to maintain the temperature at 85–95° C. After addition of the epichlorohydrin during a period of 30 minutes, the reaction mix-

ture was heated for an additional 90 minutes while maintaining the temperature at 80–85° C. The product, 1-(1-isodecyloxyhexa-2-propenoxy)-3-chloro-2-propanol, was not separated from the reaction mixture but was treated in the dehydrochlorination to form the glycidyl ether.

In the dehydrochlorination step, 40 g. (0.4 mole) of 40% sodium hydroxide solution, 30 ml. of water and 60 ml. of dimethyl sulfoxide were added to the reaction mixture obtained above and the mixture was heated for a period of 1 hour while maintaining the temperature at 85–90° C. At the end of this time, the sodium chloride formed in the reaction was separated by filtration of the hot reaction mixture using hexane to improve the separation. The oily layer was washed with saturated sodium chloride solution and then dried over magnesium sulfate. The dried filtrate was distilled to remove the hexane and to obtain 105.5 g. of the glycidyl ether, 3-(1-isodecyloxyhexa-2-propenoxy)-1,2-epoxypropane, which is a light yellow oil.

The sulfonate was then prepared by heating 58.1 g. of the glycidyl ether (0.1 mole) with 18.9 g. of sodium sulfite (0.15 mole) using 100 ml. each of water and ethanol. The heating of the reaction mixture was continued for a period of 4.75 hours while maintaining the temperature at 82° C. and using 6 N hydrochloric acid to maintain the pH in the range of 7–9. The sulfonate product was dried by stripping off the water at reduced pressure while replacing it with isopropanol. The sulfonate product was permitted to crystallize from the isopropanol solution by cooling overnight and was recovered by filtration using a filter aid. The filtrate was concentrated to dryness under reduced pressure to obtain a light yellow oil in an amount of 52.0 g. which is the desired sodium 3-(1-isodecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate.

Example 4

In this example, a mixture of saturated fatty alcohols having an average molecular weight of about 258, corresponding to a mixture of C₁₆ and C₁₈ saturated fatty alcohols, marketed by Archer-Daniels-Midland Company as Adol 65, was used to prepare a glycidyl ether and sulfonate product thereof using approximately 1 mole each of butylene oxide and epichlorohydrin.

In the first alkenoxylation step, 258 g. (approximately 1.0 mole) of Adol 65 was dried and then heated with 108 g. (1.5 moles) of butylene oxide using 3 ml. of boron trifluoride-diethyl ether as a catalyst. The addition of the butylene oxide was done at a temperature of 90° C. and the exothermic heat of reaction caused the temperature to rise to 110° C. After completing the addition of the butylene oxide, the reaction mixture was heated for an additional 2 hours while maintaining the temperature at 90° C. At the end of this time, the reaction mixture obtained was filtered at 80° C. using SuperFiltrol and Hyflo Supercel to improve the filtration. The filter cake was washed with hexane and the filtrate was aspirated at 150° C. to obtain 343 g. of the alkenoxylated product.

The second alkenoxylation step was performed by adding 111 g. (1.20 moles) of epichlorohydrin slowly over a period of 40 minutes to the product obtained in the first alkenoxylation step using 2.0 ml. of boron trifluoride-diethyl ether as a catalyst. During the epichlorohydrin addition, the temperature was maintained in the range of 80–90° C. by external cooling and after the addition of the epichlorohydrin, the reaction mixture was heated for an additional 2 hours while maintaining the temperature at 85–90° C.

The reaction product from the second alkenoxylation step was dehydrochlorinated directly using 150 g. (1.5 moles) of 40% sodium hydroxide solution, 150 ml. of water, and 100 ml. of dimethyl sulfoxide. This mixture was heated in a period of 1 hour while maintaining the temperature at 100–105° C. At the end of this time, the sodium chloride formed in the reaction was removed by filtration, using hexane to promote separation. The oily layer was washed with saturated sodium chloride solu-

tion and dried over magnesium sulfate then distilled to remove the hexane. The glycidyl ether product was obtained as an amber material in an amount of 346.2 g.

The sulfonate product was formed by heating 62.6 g. of the glycidyl ether with 26.2 g. (0.20 mole) of sodium sulfite using 100 ml. each of ethanol and water. The reaction mixture was heated for a period of 9.25 hours while maintaining the temperature at 82° C. and the pH at 7–9 by the periodic addition of 6 N hydrochloric acid. The reaction mixture was then dried by stripping off the water at reduced pressure while replacing it with isopropanol. The hot isopropanol solution was then filtered to remove salts and the filtrate permitted to cool. The sulfonate product was recovered by evaporating the solution to dryness at 100° C./13 mm. to obtain 70.2 g. of the sulfonate which is a light amber colored gum.

Example 5

In this example, a mixture of saturated fatty alcohols 90% of which boiled at 264–322° C. at 760 mm. corresponding to 61.0% lauryl alcohol, 23.0% myristyl alcohol and 11.2% cetyl alcohol, marketed by E. I. du Pont and Company as Lorol No. 5, was used to prepare corresponding glycidyl ethers and sulfonates thereof.

In the first alkenoxylation step, 186.3 g. (approximately 1.0 mole) Lorol No. 5 was treated with 216 g. (3.0 moles) of butylene oxide using 1.0 ml. of boron trifluoride as a catalyst. The butylene oxide was added dropwise to the Lorol No. 5 with cooling to maintain a temperature of 85–90° C. After heating the mixture for a period of 1.5 hours, the temperature was raised to 133° C. to distill over 81 g. of volatile materials, principally methyl ethyl ketone. The product from the distillation is an ether alcohol derived from 2 moles of the butylene oxide per mole of the original alcohol.

The product from the first alkenoxylation step was alkenoxylated in a second step using 111 g. (1.2 moles) of epichlorohydrin and 1.0 ml. of boron trifluoride-diethyl ether as a catalyst. After addition of the epichlorohydrin the reaction mixture was heated for a period of 2 hours while maintaining the temperature at 85–90° C. The product of this reaction was the chlorohydrin substituted with an alkoxydialkenoxy group.

The chlorohydrin obtained in the above step was then dehydrochlorinated directly by the addition thereto of 150 g. (1.5 moles) of 40% sodium hydroxide, 100 ml. of water and 200 ml. of dimethyl sulfoxide. This mixture was heated at a temperature of 105–110° C. for a period of 2 hours. After this time the sodium chloride formed was separated by filtration at an elevated temperature and the oily layer washed with saturated sodium chloride solution, using hexane to effect the separation. The wet oil was dried over magnesium sulfate-sodium sulfate and then distilled to remove the hexane, leaving 359 g. of the glycidyl ether, which is a very faint yellow colored oil.

The sulfonate product was made by heating 81.0 g. (0.20 mole) of the glycidyl ether with 37.8 g. (0.30 mole) of sodium sulfite in 100 ml. each of water and ethanol. The mixture was heated for a period of 6.5 hours while maintaining the temperature at 82–83° C. and using 6 N hydrochloric acid, as needed, to maintain the pH at approximately 9. At the end of this time, the salts present in the reaction mixture were removed by filtration and the filtrate was dried by stripping off the water at reduced pressure while replacing it with isopropanol. The isopropanol was removed from the sulfonate solution thereof by evaporation at 130° C./13 mm. leaving 104.5 g. of the sodium sulfonate. This sulfonate is a translucent gum having a very light yellow color and is very viscous when cool.

Example 6

In this example, the sulfonate of the glycidyl ether, 3-[1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy]-1,2-

epoxypropane, was prepared by heating 48.1 g. (0.10 mole) of the glycidyl ether with 18.9 g. (0.15 mole) of sodium sulfite using 100 ml. each of water and ethanol. The reaction mixture was heated for a period of 25 hours while maintaining the temperature at 82° C. and using 6 N hydrochloric acid to maintain the pH in the range of 8-9. At the end of this time, the sulfonate product was dried by stripping off the water at reduced pressure while replacing it with isopropanol. The isopropanol solution was filtered hot to remove inorganic salts. The filtrate was then concentrated to dryness under reduced pressure at a temperature of 90° C.-100° C. to leave 53.5 g. of the sodium 3-{1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy}-2-hydroxy-1-propanesulfonate which is a light yellow gum.

Example 7

In this example, the sulfonate of the glycidyl ether, 3-{1-[1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy]-2-propoxy}-1,2-epoxypropane, was prepared from 57.7 g. (0.10 mole) of the glycidyl ether, 11.4 g. of sodium metabisulfite, 30 ml. water, and 3 g. (0.03 mole) of 40% sodium hydroxide. The above reactants were placed in a 300 ml. pressure bomb which was pressure sealed and heated for approximately 2 hours at a temperature in the range of 175° C. to 195° C. At the end of this time, the reaction mixture was washed out of the bomb using 100 ml. of ethanol. The insoluble inorganic salts were removed by filtration. The filtrate was then dried by stripping off the water at reduced pressure while replacing it with isopropanol. The isopropanol solution was again filtered to remove insoluble salts. The filtrate was then concentrated to dryness under reduced pressure at a temperature of 100° C. to leave 61.6 g. of the sodium 3-{1-[1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate which is a hard, amber colored gum.

Example 8

In this example, the sulfonate of the glycidyl ether, 3-(1-tridecyloxyhexa-2-propenoxy)-1,2-epoxypropane, was prepared from 62.3 g. (0.10 mole) of the glycidyl ether, 3.0 g. of 40% sodium hydroxide, 11.4 g. sodium metabisulfite, and 30 ml. water. The above reactants were placed in a 300 ml. pressure bomb which was pressure sealed and heated for approximately 2 hours at a temperature in the range of 175° C. to 195° C. At the end of this time, the reaction products were removed from the bomb using 100 ml. of ethanol. The ethanol solution was dried by stripping off the water at reduced pressure while replacing it with isopropanol. The insoluble salts were removed from the isopropanol solution by filtration. The filtrate was then concentrated to dryness under reduced pressure at elevated temperature to leave 60.4 g. of sodium 3-(1-tridecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate which is a light amber colored oil.

Example 9

In this example, the sulfonate of the glycidyl ether, 3-(1-tridecyloxytetra-2-propenoxy)-1,2-epoxypropane, was prepared from 51.1 g. (0.10 mole) of the glycidyl ether, 11.4 g. of sodium metabisulfite, 3 g. of 40% sodium hydroxide, and 30 ml. of water. The above reactants were placed in a 300 ml. pressure bomb which was pressure sealed and heated for approximately 1.75 hours at a temperature in the range of 175° C. to 195° C. At the end of this time, the reaction mixture was taken out of the bomb with 100 ml. of ethanol. The ethanol solution was dried by stripping off the water at reduced pressure while replacing it with isopropanol. The insoluble salts were then removed from the isopropanol solution by filtration. The filtrate was concentrated to dryness under reduced pressure at elevated temperature to leave 57.1 g. of the sodium 3-(1-tridecyloxytetra-2-propenoxy)-2-

hydroxy-1-propanesulfonate which is an amber colored viscous gum.

Example 10

The wetting efficiencies of the sodium 3-(1-isodecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate of example 3 and the sodium sulfonate product of example 5 were determined by the Draves Wetting Test of the American Association of Textile Chemists. The following wetting times were measured at the concentration shown:

Compound	Time in Seconds				
	0.5%	0.25%	0.125%	0.0625%	0.03125%
Product of Example 3.....	¹ Inst.	3.4	8.2	27.5	+180
Product of Example 5.....	18.7	27.8	46.5	110.5	+180

¹ Inst. = instantaneous.

Example 11

In this example the lime soap dispersion efficiencies of a number of the new sodium sulfonates of this invention were determined using the procedure described by J. C. Harris in ASTM Bulletin 140, pp. 1-13, May 1946. These results are reported in the table below wherein the dispersion number is equal to ten times the milliliters of the test compound required to disperse 45.5 mg. of calcium oleate formed.

Compound:	Dispersion number
Sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate	20
Sodium 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate ..	20
The sodium sulfonate product of Example 5 ..	20
3-{1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy}-2-hydroxy-1-propanesulfonate	>80
3-{1-[1-[1-(dodecylphenoxy)-2-butoxy]-2-butoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate	10
3-(1-tridecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate	80
3-(1-tridecyloxytetra-2-propenoxy)-2-hydroxy-1-propanesulfonate	80

Example 12

The detergency properties of three of the sodium sulfonate products of this invention were measured by employing the method described by J. C. Harris and E. L. Brown in the Journal of the American Oil Chemists Society, 27, 135-143 (1950). In this method, the detergency of the candidate compound is compared with the detergency of Gardinol WA, a commercial detergent produced by sulfating the mixture of alcohols, principally C₁₂ obtained by hydrogenating coconut oil fatty acids. The following detergency efficiencies were measured:

Product	50 p.p.m. water hardness	300 p.p.m. water hardness
Sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate	101	104
Sodium 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate	80	109
Sodium 3-(1-isodecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate	133	113

Using the detergency evaluation procedure noted above, the detergency of "built" materials using sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate and sodium 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate were determined. The products were formulated by using 15% of the "active" surfactant with the balance of the formulation being composed of sodium tripolyphosphate, sodium tetrapyro-

phosphate, sodium silicate and soda ash. The following results were obtained:

Product	50 p.p.m. water hardness	300 p.p.m. water hardness
Sodium 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate	100	120
Sodium 3-[1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy]-2-hydroxy-1-propanesulfonate	98	110

As surface active compositions, the alkali metal polyether-substituted 2-hydroxy-1-propanesulfonates of this invention comprise either the pure compounds or an admixture of the pure compounds with an adjuvant material or a diluent. Ordinarily, the compounds of this invention are employed in surface active applications in a diluted form where the compound is dissolved or suspended in some liquid medium such as water. The compounds of this invention can also be admixed with adjuvant materials, particularly when used in soap or synthetic detergent compositions, such as common inorganic builders of the type of carbonates, phosphates, silicates, and fillers such as starch.

The new alkali metal sulfonates of this invention are particularly useful in soap and synthetic detergent compositions because these compounds possess unusually high "lime soap" dispersion properties. The relative proportions of the alkali metal sulfonate of this invention and the soap and/or synthetic detergent in the new compositions may vary greatly, depending upon the use intended for the composition. Although useful detergent compositions can be formed by mixing small proportions of soap with large proportions of the alkali metal sulfonates of this invention, usually the greatest value of soap compositions of the present invention lie in compositions having less than 75% by weight of the alkali metal sulfonate. In general, it is preferred to incorporate in the soap composition about 5-50% by weight of the soap and the alkali metal sulfonate. Of course, other materials such as perfumes, fillers, and inorganic builders of the type such as carbonates, phosphates and silicates, can also be present in the compositions.

The soaps which are useful in the novel compositions of this invention are the so-called water soluble soaps of the soap-making art and include sodium, potassium ammonium and amine salts of the higher fatty acids, that is, those having about 8 to 20 carbon atoms per molecule.

These soaps are normally prepared from such naturally-occurring esters as coconut oil, palm oil, olive oil, cottonseed oil, tung oil, corn oil, castor oil, soybean oil, wood fat, tallow, whale oil, menhaden oil, and the like, as well as mixtures of these.

Reasonable variation and modification of the invention as described are possible, the essence of which is that there have been provided (1) methods for preparing alkali metal sulfonates of polyether derivatives of glycidyl ethers, (2) said alkali metal sulfonates of said polyether derivatives of glycidyl ethers as new compounds, (3) said alkali metal sulfonate polyether derivatives of glycidyl ethers as new surface active compositions, (4) detergent compositions comprising a sodium, potassium, or ammonium long chain fatty acid soap and said alkali metal sulfonate polyether derivatives of glycidyl ethers, and (5) methods for increasing the lime soap dispersion efficiency of soap-containing detergent compositions by incorporating an alkali metal sulfonate of a polyether derivative of glycidyl ether therein.

I claim:

1. The sodium salt of 3-[1-(n-hexadecyloxy)-2-propoxy]-2-hydroxy-1-propanesulfonate.

2. The sodium salt of 3-{1-[1-(n-hexadecyloxy)-2-propoxy]-2-propoxy}-2-hydroxy-1-propanesulfonate.

3. The sodium salt of 3-(1-isodecyloxyhexa-2-propenoxy)-2-hydroxy-1-propanesulfonate.

4. The sodium salt of 3-{1-[1-dodecylphenoxy)-2-butoxy]-2-butoxy}-2-propoxy}-2-hydroxy-1-propanesulfonate.

References Cited by the Examiner

UNITED STATES PATENTS

2,094,489	9/1937	Hueter et al.	260—513
2,115,192	4/1938	Bruson	260—512
2,535,678	12/1950	Hollander et al.	260—512
2,677,700	5/1954	Jackson et al.	260—513
2,991,253	7/1961	Sheely et al.	252—121
3,030,310	4/1962	Turck	252—121
3,036,130	5/1962	Jackson et al.	260—513

FOREIGN PATENTS

486,909 6/1938 Great Britain.

LORRAINE A. WEINBERGER, *Primary Examiner*.

JULIUS GREENWALD, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,228,979

January 11, 1966

Van R. Gaertner

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, lines 6 and 7, "alefin" should read -- olefin --; line 27, "epoxyalkyane" should read -- epoxyalkane --. Column 5, line 34, "so" should read -- to --; line 46, "1-alkoxypolyal-" should read -- 1-alkoxypolyal- --. Column 9, line 43, "1.01 ml." should read -- 1.0 ml. --. Column 12, line 39, "he" should read -- the --.

Signed and sealed this 23rd day of September 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents