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# UNITED STATES PATENT OFFICE

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## AMINO ALKYLENEOXIDE POLYMERIZATION PRODUCT

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5 Claims. (Cl. 260—584)

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This invention relates to the use of certain copolymers as superior synthetic lubricants, and is particularly concerned with the use of copolymers, such as the copolymers of alkylene oxides or glycols with epichlorohydrin, as extreme pressure lubricants and extreme pressure additives for certain other synthetic lubricants.

The use of mineral oil fractions for lubricating is suitable for many purposes, but it is well-known that such lubricants possess certain inherent limitations, such as tendency to oxidize, thickening at low temperatures, etc. A large number of additives have been employed with mineral oils in order to improve these shortcomings. To a certain degree, the resulting compositions may be used successfully for most lubricating purposes.

Various synthetic lubricants have been proposed from time to time. These include polymers of cracked wax olefines, alkylated aromatics such as alkylated napthylenes, and so on. Some of these are useful for special purposes, but especially if the previously known synthetic lubricants were derived from olefinic sources, they usually possessed corrosion and oxidation characteristics limiting their utility to a substantial degree.

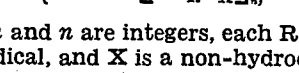
Another type of synthetic lubricant which has been investigated is the alkylene oxide polymer type, such as polymerized propylene oxide. Such polymers are useful under mild operating conditions, but form volatile decomposition products which result in substantial lubricant consumption.

The preparation of adducts of certain unsaturated compounds with hydrogen sulfide or mercaptans has been proposed. However, a complicated mixture of derivatives is present in the adduct product. The mixture prepared by previously proposed methods contains relatively large proportions of volatile constituents, with a correspondingly lower fraction having lubricating properties.

It is an object of this invention to provide a novel method of lubrication. It is another object of this invention to provide novel lubricating compositions. It is a further object of this invention to provide novel extreme pressure compositions. It is still another object of this invention to provide novel non-mineral oil lubricants of improved oxidation stability. Other objects will become evident from the following disclosure.

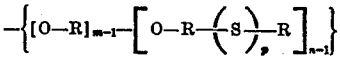
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Now, in accordance with this invention, it has been found that superior non-mineral oil lubricants comprise copolymers having structural units of the general configuration



wherein $m$ and $n$ are integers, each R is a hydrocarbon radical, and X is a non-hydrocarbon substituent such as an ether group, hydroxyl group, amino group or halogen atom. Preferably each R is a saturated aliphatic hydrocarbon radical.

Still in accordance with this invention it has been found that such copolymers may be used to modify other synthetic lubricants, particularly those having units of the general configuration

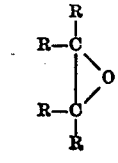


wherein $m$, $n$ and $p$ are integers, and each R is an organic radical, preferably a hydrocarbon radical.

Again in accordance with this invention it has been found that the copolymers initially defined act as extreme pressure lubricants or as extreme pressure additives for the other synthetic lubricants defined above, especially if the group represented by X is a chlorine atom.

The first-defined copolymer may be obtained by copolymerizing alkylene oxides or alkylene glycols with derivatives thereof, said derivatives having one hydrogen replaced with the group —R—X, said group being directly attached to a carbon atom. In the group —R—X, R is a hydrocarbon radical and X is a substituent such as an ether radical, hydroxyl group, amino group or halogen atom.

Alkylene oxides which may be used in the preparation of the present copolymeric lubricants have the general configuration



wherein each R is a hydrogen atom or an organic radical, preferably a hydrocarbon radical. When R is a substitutent other than hydrogen, it may be a hydrocarbon group such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-amyl, hexyl, heptyl, phenyl, etc. radicals. Thus, the epoxy group may be at one end of a carbon chain or at any other position on the chain. Such alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, dimethylethylene oxide, diethylethylene oxide, α,α'-dimethylethylene oxide, α,α'-diethylethylene oxide, α-methyl-α'-ethylethylene oxide, α-methyl-α'-isopropylethylene oxide, as well as polymerizable derivatives, homologs and analogs of the same.

Glycols from which the copolymers of the present invention may be made include derivatives of ethylene glycols and of higher alkylene glycols such as trimethylene glycol. The ethylene glycol derivatives are exemplified by ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol.

Trimethylene glycol derivatives which may be used in the manufacture of the copolymeric lubricants of the present invention include trimethylene glycol itself as well as alkyl-substituted trimethylene glycols.

Typical of the trimethylene alkyl substituted glycols are the methylated trimethylene glycols, including 1-methyl - 1,3 - propanediol; 2-methyl-1,3-propanediol; 1,1-dimethyl -1,3- propanediol; 1,2-dimethyl-1,3-propanediol; 1,3 - dimethyl-1,3-propanediol; 2,2-dimethyl-1,3-propanediol; 1,1,2-trimethyl - 1,3 - propanediol; 1,1,3-trimethyl-1,3-propanediol; 1,2,2 - trimethyl - 1,3 - propanediol; 1,2,3 - trimethyl-1,3-propanediol; 1,1,2,2 - tetramethyl-1,3-propanediol; 1,1,3,3-tetramethyl-1,3-propanediol; 1,2,3,3-tetramethyl-1,3-propanediol; 1,1,2,2,3 -pentamethyl-1,3-propanediol; 1,1,2,3,3-pentamethyl-1,3-propanediol; and hexamethyl-1,3-propanediol.

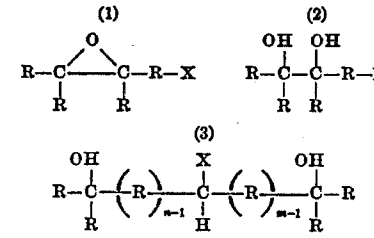
In place of the methyl groups other alkyl groups may be utilized, such as ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl, etc. Other substituted trimethylene glycols which may be utilized in carrying out the present invention include 1-methyl-2-ethyl-1,3-propanediol; 2-methyl-2-ethyl-1,3-propanediol; 1 - methyl - 2 - ethyl-1,3 - propanediol; 2-methyl-2-butyl-1,3-propanediol; 2 - methyl - 3 - butyl-1,3-propanediol; and homologs, analogs and derivatives of the same.

Another group of glycols which are suitable are those in which the glycollic hydroxyls are separated by more than 5 carbon atoms, such as hexamethylene glycol, heptamethylene glycol, octamethylene glycol, nonamethylene glycol, decamethylene glycol, dodecamethylene glycol, etc. as well as alkyl-substituted derivatives of the same.

Glycols which fall within the above classification include 1,6-heptanediol; 1,6-octanediol; 1,6-nonanediol; 1,7-dodecanediol; 1,8-nonanediol; 1,8-decanediol; 1,8-dodecanediol; 1,9-decanediol; 1,9-dodecanediol; 1,10 - dodecanediol; 2,7-octanediol; 2,7-nonanediol; 2,7-decanediol; 2,7-dodecanediol; 2,8-nonanediol; 2,8-decanediol; 2,8-dodecanediol; 2,9-decanediol; 2,9-dodecanediol; 2,3-dimethyl-1,6 - hexanediol; 2,4 - dimethyl-1,6-hexanediol; 2,5-dimethyl-1,6-hexanediol; 2,2-dimethyl-1,6-hexanediol; 3,3-dimethyl-1,6-hexanediol; 4,4-dimethyl-1,6-hexanediol; 5,5-dimethyl-1,6-hexanediol; 2 - methyl-3-ethyl-1,7-heptanediol; 2 - ethyl-3-methyl-1,7-heptanediol; 3,3-diethyl-1,7-heptanediol; 3,4-diisopropyl-1,8-octanediol; etc. and their polymerizable homologs, analogs and derivatives.



The above types of epoxides and glycols may be copolymerized with the following types of epoxides and glycols in order to prepare the copolymeric lubricants which are the subject of this invention:




wherein $m$ and $n$ are integers, each R is a hydrocarbon radical (preferably a saturated hydrocarbon radical), and X is a substituent selected from the group consisting of ether radicals, hydroxyl groups, halogen atoms or amino groups.

Group 1 includes, as the important class, the glycidyl ethers, including glycidyl methyl ether, glycidyl ethyl ether, glycidyl propyl ether, glycidyl isopropyl ether, glycidyl n-butyl ether, glycidyl sec-butyl ether, glycidyl tert-butyl ether, glycidyl amyl ethers, glycidyl hexyl ethers, glycidyl heptyl ethers, glycidyl octyl ethers, glycidyl nonyl ethers, glycidyl decyl ethers, glycidyl dodecyl ethers, and their homologs and analogs.

Substituted glycidyl ethers also may be copolymerized with the defined epoxides and glycols. Typical members of this group are 2,3-epoxy-4-methoxybutane, 2,3-epoxy-4-ethoxybutane, 2,3-epoxy-4-isopropoxybutane, 1,2 - epoxy-3-methyl-3 - methoxypropane, 1,2 - epoxy-3-methyl-3-butoxypropane, 1,2 - epoxy - 3,3-dimethyl-3-isopropoxypropane, 1,2-epoxy - 3 - isopropyl - 3-isopropoxypropane, 1,2-epoxy-2-methyl-3-isopropoxypropane, 1,2-epoxy - 2 - n-amyl-3-isopropoxypropane, 4,5-epoxy-6-methyl-6 - isopropoxyhexane, and their polymerizable homologs and analogs.

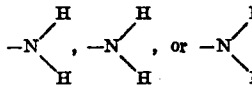
Other suitable epoxides containing ether groups have more than 1 carbon atom separating the ether group from the epoxide group. Among the ethers having the preferred configurations are 1,2-epoxy-4-methoxybutane, 1,2-epoxy-4-isopropoxybutane, 1,2-epoxy - 5 - ethoxypentane, 1,2-epoxy-4-methyl-5-tert-butylpentane, 2,3-epoxy-5-isopropoxypentane as well as their copolymerizable homologs and analogs.

In each of the above cases, X (in the general Formula 1 given hereinbefore), is an ether group. Said group may be replaced with a halogen to give another class of compounds, of which the following members are typical: epichlorohydrin, 2,3-epoxy-4-chlorobutane, 1,2-epoxy-3-methyl-3-chloropropane, 1,2-epoxy-3,3-dimethyl-3-chloropropane, 1,2 - epoxy - 3 - isopropyl -3 -chloropropane, 1,2-epoxy-2-methyl-3-chloropropane, 2,3-epoxy-4-methyl - 1 - chlorohexane, 1,2-epoxy-4-chlorobutane, 1,2 - epoxy-5-chloropentane, 1,2-epoxy-4-methyl-5-chloropentane, etc.

As stated above, the substituent X of Formula 1 given above may be a hydroxyl group. This class of copolymerizable monomers are represented by 1,2-epoxy-4-hydroxybutane, 1,2-epoxy-5-hydroxypentane, 1,2-epoxy-4-methyl-5-hydroxypentane, 2,3-epoxy-5-hydroxypentane, 1,2-epoxy-3-hydroxypropane, 2,3 - epoxy - 4 - hydroxybutane, 1,2 - epoxy - 3 - methyl - 3 - hydroxypropane, 1,2-epoxy - 3,3 - dimethyl - 3 - hydroxypropane, 1,2-epoxy-3-isopropyl-3-hydroxypropane, etc.

Still another group of epoxide compounds with

which the alkylene oxides and alkylene glycols may be copolymerized are those having the general Formula 1 given hereinbefore, wherein X is an amino group. The amino group may have the general formulas



wherein R is an organic radical, especially a saturated aliphatic hydrocarbon radical or a hydroxyalkyl radical. Typical members of this class are 1,2-epoxy-3-aminopropane, 1,2-epoxy-3-methylaminopropane, 1,2-epoxy-3,3-dimethylaminopropane, 2,3-epoxy-4-ethylaminobutane, 1,2-epoxy-5,5-diisopropylaminopentane, and their homologs and analogs.

Glycols having the general configuration according to Formula 2 given hereinbefore may be copolymerized with alkylene oxides and glycols to obtain synthetic lubricants. Suitable glycols having this configuration include 1,2-dihydroxy-3-methoxypropane, 2,3-dihydroxy-4-aminobutane, 1,2-dihydroxy-3-diethylaminopropane, 1,2-dihydroxy-5-chloropentane, 2,3-dihydroxy-3-methyl-4-fluorobutane, and 1,2-dihydroxy-3-isopropyl-3-bromobutane, etc.

The glycols represented by Formula 3 given hereinbefore include 1,3-dihydroxy-2-methoxypropane, 2,4-dihydroxy-3-chlorobutane, 1,5-dihydroxy-4-aminopentane, and their homologs and analogs.

The copolymeric lubricants of the present invention may be prepared by heating the monomeric alkylene oxide or glycol with one or more of the substituted epoxides or glycols as defined hereinbefore in the presence of a catalyst.

When copolymerizing epoxide derivatives the preferred catalyst is boron trifluoride, usually employed, as shown in the examples given hereinafter, as a complex with ether, which is gradually added to the copolymerization mixture. Another preferred catalyst is aluminum chloride. The above catalysts are preferred because of their relatively great activity and the consequent low temperatures at which they may be used.

Other catalysts which may be used in the preparation of the subject copolymeric lubricants include mineral acids, such as concentrated sulfuric acid, halogen acids, especially hydrogen iodide (especially for copolymerizing glycols), heavy metal salts such as stannic chloride, sulfonic acids such as para-toluenesulfonic acid, and basic substances such as sodium and potassium hydroxides.

The catalysts may be employed in solid, liquid or gaseous form, or may be present as an aqueous or organic solution. Hydrogen iodide, for example, is conveniently utilized in the present process as a concentrated aqueous solution, initially containing about 50% water. Others, such as the sulfonic acids, may be added as solids, liquids, or in either organic or aqueous solutions.

Dependent upon the nature of the monomer, the identity of the catalyst, the temperature of the polymerization reaction and the polymerization rate desired, the catalyst may be used in ratios with the monomers varying from about 1:500 to 1:10. Preferably, however, the ratio of catalyst is confined to the range from about 1:200 to 1:25, but a ratio of 1:100 gives satisfactory results in most circumstances.

The polymerization reaction may take place in either liquid, solution, emulsion or gaseous phases. Hence, the use of either liquid or gaseous diluents



is contemplated. Liquid diluents may perform several functions by their presence, acting as solvents for the monomer and/or the polymer, as solvents for the catalyst, as azeotropic constituents for carrying off water formed during the polymerization, as diluents for the control of polymerization rate, or, by their boiling points, as controls for the temperature of the reaction, as one phase of an emulsified reaction mixture, etc. Gaseous diluents are used primarily when the polymerization is carried out in gaseous phase, but also may be injected to carry off the water formed during polymerization, or as coolants, etc.

Both gaseous and liquid diluents are preferably substantially inert toward the other components of the reaction mixture in the temperature range encountered prior to, during and after reaction. The most satisfactory diluents are hydrocarbons of either aromatic or aliphatic character, but preferably are saturated aliphatic hydrocarbons. When the diluent is to be used in an aqueous phase polymerization, it is preferably chosen from the group of hydrocarbons boiling between about 125° C. to about 300° C., especially if it is expected to participate in azeotropic distillation of water during polymerization. Hydrocarbons which serve as suitable diluents include the dihydronaphthalenes; cycloheptane, the decanes, including 2-methyl nonane and 2,6-dimethyloctane, the octanes, including 2,2,3-trimethylpentane and 2-methyl-3-ethylpentane; the nonanes, such as 2-methyloctane, 2,4-dimethylheptane, 4-ethylheptane, the dodecanes such as dihexyl or 2,4,5,7-tetramethyloctane, etc.

When the polymerization is carried out in gaseous phase, the diluent may be a lower hydrocarbon such as methane, ethane, propane, butane, etc. which acts as a regulator or diluent for the reaction, but which can be stripped from the product with facility, subsequent to the polymerization.

The proportion of diluent is not a critical factor in carrying out the process of the present invention. However, it is a preferred practice to keep the reaction mixture as concentrated as possible, consistent with maintaining homogeneity, rate of polymerization, etc. Ordinarily, when a diluent is used for a liquid phase polymerization the initial proportion of diluent to monomer is from about 1:1 to about 20:1, but preferably is initially from about 2:1 to about 5:1. When the temperature of the reaction is substantially below the boiling point of the diluent, this ratio will remain unchanged throughout the reaction. If, however, the conditions are such that water formed during polymerization distills azeotropically with part of the diluent passing over in the azeotrope the diluent may be replaced in or near the polymerization zone, so as to maintain a substantially constant diluent:glycol ratio.

Other ingredients may be included in the polymerization mixture, or may be added from time to time during the polymerization. For example, the polymerization may be carried out in a closed system, such as an autoclave. In such a case, the water formed during the polymerization may be effectively removed by the presence of dehydrating agents which will combine with or absorb the water as it is formed. Inert gases such as nitrogen may be added to protect the hot polymerization mass from oxidation. Reactants, such as alcohols, may be present for the purpose of converting the hydroxyls normally present on both ends of the polymer chains to other functional groups, as more particularly set forth hereinafter.

The temperature when copolymerizing glycol derivatives may vary considerably, but unless the reaction mixture is substantially above about 150° C. only a negligible amount of polymerization occurs, at least within a reasonable reaction period. If the reaction temperature is substantially above about 300° C., decomposition of the monomeric glycols and the polymers takes place to such an extent that undue losses occur and the product requires extensive purification. The preferred polymerization temperature range is from about 170 to 225° C., with the optimum range being from about 175 to about 200° C. Therefore, it is a preferred practice to conduct the polymerization at temperatures somewhat below the point at which the glycols, thioethers, or polysulfides will commence distilling, but, if higher temperatures are employed, the apparatus may be arranged so as to return the distilled glycols to or near the polymerization zone.

The copolymerization of alkylene oxide derivatives may take place at temperatures from about 25° C. to about 175° C. but preferably is conducted within the range 35° C. to 150° C. When using active catalysts such as boron trifluoride or aluminum chloride, relatively low temperatures are preferable so that the reaction rate may be conveniently controlled and copolymers of any desired molecular weight may be obtained.

When the polymerization is carried out by assembling all of the reactants in a vessel and heating with continuous or intermittent distillation of water, the reaction time required to obtain products having molecular weights of about 200 or more is at least about 2 hours, and usually is about 20 hours or even longer. Under a given set of conditions the molecular weight of the polymer varies directly with the amount of water formed. Consequently, the average molecular weight of the polymeric product can be readily calculated by the amount of water which has distilled out of the polymerization zone.

Following the polymerization period, the product is purified. The first step in purification is removal of catalyst. If this is a solid, suspended in the liquid polymer or a solution of the polymer, a simple filtration is all that is required. When the catalyst is in solution other means must be employed. For example, when sulfonic acids are the catalyst used, a preferred means for their removal from the polymer comprises dissolving or thinning the polymer with an organic solvent such as benzene, washing with concentrated caustic to convert the acid to the sodium salt, and subsequently extracting with water to remove the sodium salts of the acids and any remaining traces of caustic.

After removal of the catalyst, the product is dehydrated in order to remove the last traces of water formed during polymerization and any water remaining from catalyst extraction operations. Water may be removed by the use of dehydrating agents, or by distillation, preferably under diminished pressure. If this latter method is employed, any solvents present and any monomers may be removed at the same time. Consequently, at the end of these operations there remains the copolymers free from solvents, water and catalyst.

The product may be decolorized if desired by treatment with bleaching agents, percolation through activated clays such as fuller's earth, hydrogenation, etc. The preferred treatment is a combination of percolation through fuller's earth followed by hydrogenation.



Percolation through fuller's earth is preferably carried out in an inert solvent, suitably a hydrocarbon such as benzene, toluene, xylene, hexane, etc.

The percolation is preferably carried out at room temperature or below, but may be conducted at elevated temperatures, as long as the temperature and pressure adjustments are such as to prevent boiling of the solvent and consequent deposition of the copolymer in the percolation tower. This percolation treatment results in the production of copolymers having improved colors satisfactory for many purposes, in which case all that remains to be done is to flash off the solvent in order to recover the colpolymer.

On the other hand copolymers having the least color can be obtained only by following the percolation with hydrogenation. Neither percolation alone, nor hydrogenation alone, nor any of the ordinary decolorizing or bleaching procedures results in the formation of light colored copolymers such as those obtained by treatment with fuller's earth followed by hydrogenation.

In carrying out the percolation through fuller's earth, oxygen-containing solvents such as acetone, methyl alcohol and dioxane are relatively ineffective for aiding in the removal of color from the subject copolymers. The color removal appears to be specific in that hydrocarbon solvents, and especially aromatic hydrocarbon solvents are required, benzene and toluene giving the best results.

The hydrogenation step is essential for the reduction of color-sensitive functional groups, supposedly carbonylic in character. Raney, nickel, nickel sulfide, copper, palladium, platinum and other catalysts suitable for the reduction of carbonyls may be used, although Raney nickel is preferred. Temperatures employed vary from about 125 to about 250° C., and hydrogen pressures from about 500 to about 3000 lbs. per square inch are utilized. Subsequent to hydrogenation, the catalysts may be removed from the product by super-centrifuging or filtration, and any solvents present are flashed off to yield the light yellow copolymer.

The copolymers formed as described hereinbefore have hydroxyl groups on one or both ends of each copolymer chain. These hydroxyls may be acted upon with such materials as etherifying or esterifying agents in order to obtain products having altered properties, such as solubility or improved action as lubricants, plasticizers, etc.

Various etherifying agents may be used for etherifying terminal hydroxyls. These include alkyl halides, such as methyl iodide, methyl bromide, ethyl chloride, propyl iodide; aralkyl halides such as benzyl chloride and methylbenzyl chloride; alkoxyalkyl chlorides such as methoxyethyl chloride; carboxyalkylating agents such as sodium monochloracetate; and alkylene halides such as allyl chloride. Ordinarily, the etherification is carried out in strongly basic environments; sodium hydroxide, liquid ammonia and quaternary ammonium bases and salts being the usual basic substances present.

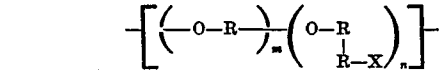
Esterification of the terminal hydroxyls may be accomplished with various inorganic groups such as nitrates, phosphates or sulfates. However, preferred esterifying agents are the organic acid anhydrides or acid chlorides, and especially fatty acid anhydrides and their chlorides, including for example formic, acetic, propionic, butyric, hexoic, 2-ethylhexoic, and higher fatty acids such as lauric, stearic, myristic, palmitic

and capric acids. Usually, the esters are formed by treatment of the hydroxylated copolymer with the anhydride of the acid in the presence of a catalyst such as sulfuric or phosphoric acid. The saturated fatty acids form the most stable esters with the copolymers.

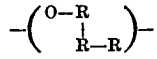
At times it is preferable to allow only partial etherification or esterification thus forming half-ethers of half-esters instead of the di-ethers or di-esters theoretically possible. For other purposes the end-group hydroxyls may not only be partially or completely esterified or etherified, but also may be treated so as to result in the formation of mixed ethers, mixed esters or ether-esters.

Etherification or esterification of the end-groups may take place simultaneously with or subsequent to copolymerization, and may be effected prior to or subsequent to the decolorizing and purifying processes described hereinbefore. Preferably, the end-group modification is carried out immediately after copolymerization and before purification or decolorizing, but a secondary preferred time for modification is during the copolymerization step itself.

As stated hereinbefore, the copolymeric lubricants prepared as described have units of the general formula



wherein $m$ and $n$ are integers, each R is hydrocarbon radical and X is a substituent such as an ether radical, amino radical, hydroxyl group or halogen atom. The copolymer chains terminate with hydroxyl groups, ester groups, ether groups, amino groups, etc., dependent upon the treatment to which the copolymer has been subjected. When the ratio of —(O—R)— groups to



groups is between 10 to 1 and 1 to 10, the properties of the copolymer are substantially different from those of a homopolymer of either monomer.

The preferred group of copolymers having the above general configuration are those in which X is a halogen atom, especially a chlorine atom, since such copolymers have excellent extreme pressure characteristics.

The present copolymers vary from thin liquids to viscous oils and, if the molecular weight is great enough, products which are gels or solids at room temperature are formed which are useful as lubricant additives. The copolymeric lubricants may have molecular weights from about 100 to about 10,000 but the most useful lubricants are those having average molecular weights from about 200 to about 1500.

One feature of the present copolymers which makes them useful as low-temperature lubricants is their low pour points. For example a 1:1 copolymer of glycidyl isopropyl ether and propylene oxide having an average molecular weight of 665 has a pour point of —45° F. Likewise, a copolymer of propylene oxide and glycidyl methylisobutylcarbinyl ether has a pour point of —45° F.

The copolymeric lubricants of the present invention have excellent viscosity indices, thus enabling their use as lubricants where a wide range of operating temperatures is encountered, such as in aircraft lubrication. Ordinarily, the viscosity index of one of the subject copolymers is at least 105, and may be 140 or even higher. This property is useful, furthermore, in improving lubricants having relatively poor viscosity indices, by blending the subject copolymeric lubricants therewith.

As noted hereinabove, those copolymeric lubricants wherein X is a halogen atom, especially a chlorine atom, possess extreme pressure lubricant characteristics, both when used as the major lubricant of a composition or when present as an extreme pressure agent together with other lubricants in lubricating compositions. Such copolymers are particularly effective as extreme pressure agents in synthetic lubricants which have units of the general configuration

$$-\{[O-R]_{m-1}-[O-R-(S)_p-R]_{n-1}\}-$$

wherein $m$, $n$ and $p$ are integers and each R is an organic radical, preferably a hydrocarbon radical. Such lubricants include polymers of alkylene oxides and alkylene glycols, bis (hydroxyalkyl) sulfides, polymers of the latter, polymeric adducts of hydrogen sulfide or mercaptans with unsaturated ethers such as diallyl ether, and copolymers of the same, such as the copolymers of alkylene glycols and bis (hydroxyalkyl) sulfides or polysulfides.

The subject copolymeric lubricants may be used in combination with modifying substances such as anti-oxidants, anti-corrosion agents, gelling agents for the preparation of synthetic greases, etc. When X in the general formulas discussed is a halogen, the copolymeric lubricant may be treated with an alkali prior to use in order to remove the more labile halogen atoms, and the lubricating compositions containing such copolymers also may contain a basic substance such as an amine in order to prevent corrosion which might be caused by lubricant decomposition.

The following examples illustrate the preparation, properties and use of the subject copolymeric lubricants:

*Example 1*

Four parts N,N-diethyl epihydrin amine and 400 parts propylene oxide were dissolved in 1000 parts isopentane. Twenty parts boron trifluoride-ether complex were slowly dropped into the mixture. After distilling of the volatile fractions, there remained 293 parts of a light yellow oil having the following properties:

| | |
|---|---|
| Molecular weight | 511 |
| Viscosity, centistokes at 100° F | 45.3 |
| Viscosity, centistokes at 210° F | 7.34 |
| Viscosity index | 128 |
| SAE grade | 10 |

*Example 2*

Fifteen parts N,N-diethyl epihydrin amine, and 300 parts propylene oxide were dissolved in 750 parts isopentane. Forty parts boron trifluoride-ether complex were slowly dropped into the solution, after which the solvent and volatile fractions were removed by distillation, leaving 137 parts of a deep yellow oil having the following properties:

| | |
|---|---|
| Molecular weight | 422 |
| Viscosity, centistokes at 100° F | 25.42 |
| Viscosity, centistokes at 210° F | 4.63 |
| Viscosity index | 109 |
| SAE grade | less than 10 |

*Example 3*

Twelve and one-half parts N,N-diethyl epihydrin amine, 250 parts propylene oxide, 2.3 parts water and 11.7 parts sodium methylate

were heated at 100° C. for 40 hours. The product was water-washed and then dehydrated by heating at 100° C. under sub-atmospheric pressure to yield 162 parts of a viscous brown oil having the following properties:

| | |
|---|---|
| Molecular weight | 565 |
| Viscosity, centistokes at 100° F | 37.69 |
| Viscosity, centistokes at 210° F | 6.67 |
| Viscosity index | 136 |
| SAE grade | 10 |

*Example 4*

One hundred twenty-four parts epichlorohydrin and 1245 parts propylene oxide were dissolved in 1750 parts isopentane. Forty parts boron trifluoride-ether complex were slowly dropped into the mixture, after which the solvent and volatile fraction of the product were removed by distillation, leaving 1163 parts of a yellow oil having the following properties:

| | |
|---|---|
| Molecular weight | 875 |
| Viscosity, centistokes at 100° F | 117.8 |
| Viscosity, centistokes at 210° F | 15.0 |
| Viscosity index | 126 |
| SAE grade | 40 |

*Example 5*

Five hundred eighty parts glycidyl isopropyl ether, 290 parts propylene oxide, 30 parts methyl alcohol and 30 parts potassium hydroxide were heated at 100° C. for 16 hours. The product was washed with water and dehydrated by heating at 100° C. under sub-atmospheric pressure in order to obtain 858 parts of a viscous oil having the following properties:

| | |
|---|---|
| Specific gravity | 0.9950 |
| Refractive index 20/D | 1.4458 |
| Flash point, °F | 370 |
| Fire point, °F | 550 |
| Pour point, °F | —45 |
| Molecular weight | 665 |
| Viscosity, centistokes at 100° F | 42.8 |
| Viscosity, centistokes at 210° F | 6.35 |
| Viscosity index | 106 |
| SAE grade | 10 |

*Example 6*

Six hundred parts glycidyl methylisobutylcarbinyl ether and 600 parts propylene oxide were dissolved in 2000 parts isopentane. Thirty parts boron trifluoride-ether complex were slowly dropped into the solution, after which the solvent and volatile fractions of the product were removed by distillation, leaving 1137 parts of a pale yellow oil soluble in mineral oils and having the following properties:

| | |
|---|---|
| Specific gravity | 0.9842 |
| Refractive index 20/D | 1.4486 |
| Flash point, °F | 280 |
| Fire point, °F | 300 |
| Pour point, °F | —45 |
| Molecular weight | 554 |
| Viscosity, centistokes at 100° F | 40.84 |
| Viscosity, centistokes at 210° F | 6.34 |
| Viscosity index | 114 |
| SAE grade | 10 |

*Example 7*

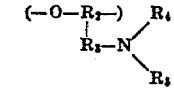
The copolymeric lubricant prepared as described in Example 4 was used as an engine lubricant in a Lauson engine, the test being conducted for 40 hours, with a jacket temperature of 100° F. Lacquer formation was very low, there was little evidence of corrosion, oil consumption was at a minimum, the viscosity of the lubricant remained substantially constant throughout the test, and there were very small deposits on the piston crowns, on the piston ring belts and in the sump.

*Example 8*

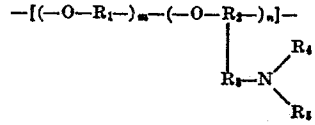
The copolymeric lubricant prepared as described in Example 6 was used as an engine lubricant in a 40 hour Lauson engine test, 100° F. jacket temperature being employed. There was practically no evidence of corrosion, little lacquer formation, moderate oil consumption, a moderate increase in lubricant viscosity, and minimum formation deposits on pistons and in the sump.

We claim as our invention:

1. A composition of matter comprising a normally liquid mixture of linear copolymers having 1,2-oxyalkylene —(O—$R_1$—) units of from 2 to 6 carbon atoms and amino-substituted oxyalkylene

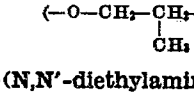


units of from 3 to 12 carbon atoms joined in the copolymer molecules thereof in units of the general formula

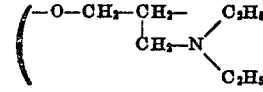


wherein $R_1$ is a hydrocarbon 1,2-alkylene radical of from 2 to 6 carbon atoms, $R_2$ is a hydrocarbon 1,2-alkylene radical of from 2 to 3 carbon atoms, $R_3$ is a hydrocarbon alkylene radical of from 1 to 3 carbon atoms and is attached by a carbon atom thereof to a carbon atom of the $R_2$ radical one carbon atom removed from the oxygen atom of said amino-substituted oxyalkylene unit, $R_5$ and $R_4$ are selected from the group consisting of hydrogen and saturated hydrocarbon radicals of 1 to 3 carbon atoms, and $m$ and $n$ are integers, said mixture being oxidation stable, having an average molecular weight between 200 and 1500 and the ratio of said oxyalkylene units and said amino-substituted oxyalkylene units in the mixture of copolymers being between 10 to 1 and 1 to 10.

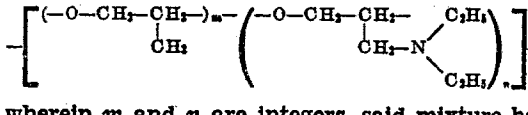
2. A composition of matter comprising a normally liquid mixture of linear copolymers having 1,2-oxypropylene



units and 3-(N,N'-diethylamino)-1,2-oxypropylene



units joined in the copolymer molecules thereof in units of the general formula

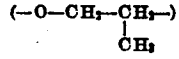


wherein $m$ and $n$ are integers, said mixture being oxidation stable, having an average molecular weight between 200 and 1500 and the ratio of said 1,2-oxypropylene units and 3-(N,N'-diethylamino)-1,2-oxypropylene units in the mixture of copolymers being between 10 to 1 and 1 to 10.

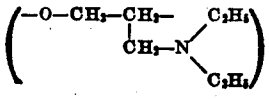
3. A composition in accordance with claim 2 wherein the mixture of copolymers has an average weight of from about 422 to about 565 and is produced by catalytic copolymerization of N,N'-diethylepihydrinamine and propylene oxide in respective proportions of from about 1:100 to about 5:100, at a temperature from about 35° C. to about 150° C. while admixed with an inert diluent.

4. A composition in accordance with claim 2 wherein the mixture of copolymers has an average molecular weight of from about 422 to about 511 and is produced by catalytic copolymerization with boron trifluoride-ether complex catalyst of N,N-diethyl epihydrin amine and propylene oxide, in respective proportion of from 1:100 to 5:100, while admixed with a liquid hydrocarbon inert diluent.

5. A composition of matter consisting essentially of a normally liquid linear copolymer having 1,2-oxypropylene

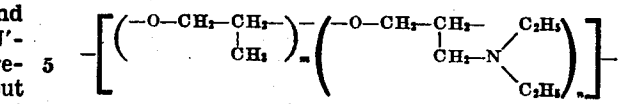


units and 3-(N,N-diethylamino)-1,2-oxypropylene





units joined in the copolymer molecule as units of the general formula



wherein $m$ and $n$ are integers, said copolymer being oxidation resistant, having a molecular weight of from about 200 to about 1500 and the ratio of said 1,2-oxypropylene units and 3-(N,N-diethylamino)-1,2-oxypropylene units in the copolymer molecule being between 10 to 1 and 1 to 10.

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JOHN L. VAN WINKLE.


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