

UNITED STATES PATENT OFFICE

2,484,370

LIQUID SULFOALKYLENE-OXYALKYLENE
COPOLYMERS

Seaver A. Ballard, Orinda, Rupert C. Morris, Berkeley, and John L. Van Winkle, San Lorenzo, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application October 8, 1946,
Serial No. 702,054

7 Claims. (Cl. 260—609)

1 This invention relates to superior lubricating materials, and more particularly it relates to improved non-hydrocarbon lubricants.

Mineral oil lubricants such as those made from paraffin base or naphthenic base petroleum are useful for most lubricating purposes when the conditions to which said lubricants are subjected are relatively mild. However, lubricants of petroleum origin are limited in their utility by certain inherent characteristics. For example, especially when employed for aviation purposes, a lubricant is often subjected to wide temperature variations, such as hot ground temperatures and the extremely cold temperatures encountered in the atmosphere, say, about 10–20,000 feet altitude. In these circumstances the ordinary mineral oil base lubricants fail to function properly, either being too fluid when warm, or hardening to a solid or semi-solid state when cooled.

The tendency of mineral oils to oxidize rapidly, especially in the presence of certain metallic substances such as copper, iron oxide, etc., is well-known. While the addition of anti-oxidants corrects this adverse feature to a limited extent, in many instances mineral oil lubricants are unsatisfactory, due to sludge and gum formation, both results of oxidation reactions.

Certain non-hydrocarbon substances of synthetic origin have been used for specialized lubrication purposes. For example, polymeric alkylene oxides, such as polymerized propylene oxide, have been used for lubricating purposes. Other similar polymers have found restricted use as substitutes for mineral oil lubricants.

Synthetic lubricants such as these contain ether oxygen linkages which appear to be especially sensitive to oxidation. Various means of reducing this sensitivity have been investigated, such as the addition of certain oxidation inhibitors. However, the sensitivity of such polymers, which consist of chains of units each having the general configuration



wherein R is a hydrocarbon radical or substituted hydrocarbon radical, seems to be inherent in polymeric lubricants of the above configuration.

It is an object of this invention to provide improved non-mineral oil lubricants. It is another object of this invention to provide a non-petroleum base lubricant having improved resistance to oxidation. It is a third object of this invention to provide a process for preparing non-hydrocarbon lubricants having substantially no

2 ability to absorb water. It is still another object of this invention to provide new lubricants which are thermally stable. Other objects will appear hereinafter.

Now in accordance with this invention it has been found that copolymeric lubricants having units of the general configuration



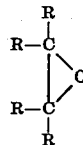
wherein m, n, and r are integers and each R is an organic radical (preferably a hydrocarbon radical) have substantially greater oxidation stability than simple polymers having repeating units of the general configuration



referred to hereinbefore.

Still in accordance with the present invention it has been found that copolymeric lubricants such as those above may be prepared by copolymerizing an alkylene (including substituted alkylene) oxide or glycol with an alkylene (including substituted alkylene) sulfide or thioglycol. Again in accordance with the present invention it has been discovered that the resulting copolymers are not only highly resistant to oxidation but act as excellent extreme pressure lubricants or lubricant additives as well.

Alkylene oxides 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 substituent 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, symmetrical dimethylethylene oxide, symmetrical diethylethylene oxide, 2,2-dimethylethylene oxide, 2,2-diethylethylene oxide, 2-methyl-2'-ethylethylene oxide, 2-methyl-2'-isopropylethylene oxide, as well as polymerizable derivatives, homologs and analogs of the same.

3

Another class of oxides from which the copolymeric lubricants may be prepared are the glycidyl ethers containing one or more ether groups. These include glycidyl methyl ether, glycidyl ethyl ether, glycidyl - beta - methoxyethyl ether, and glycidyl - n - decyl ether.

A third class of oxides forming copolymers of the structure described hereinbefore are the glycidyl esters, such as glycidyl formate, glycidyl acetate, glycidyl propionate, glycidyl butyrate, etc.

The glycidyl amines also may be copolymerized with alkylene sulfides according to the process of the present invention. Typical amines of this class are glycidylamine, methyl glycidylamine, ethyl glycidylamine, propyl glycidylamine, isopropyl glycidylamine, butyl glycidylamine, dimethyl glycidylamine, diethyl glycidylamine, methylethyl glycidylamine, etc.

Still another class of suitable oxides are the epihalohydrins, such as epichlorohydrin, epibromohydrin and epiodohydrin.

Glycols from which the copolymeric lubricants 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 may be used in the manufacture of the copolymeric lubricants of the present invention, such as 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 groups, 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-3-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 for the present purpose 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-do-

4

decanediol; 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.

Any of the above oxides and glycols may contain elements other than carbon, hydrogen, oxygen, or groups other than hydrocarbon, ether or ester groups, such as the elements selenium, tellurium, phosphorus and nitrogen, as well as groups such as carbonyl groups, etc.

As stated hereinbefore, alkylene oxides or glycols are copolymerized, according to the process of the present invention, with alkylene sulfides or thioglycols in order to obtain copolymeric lubricants having extreme pressure properties and enhanced oxidation stability.

Alkylene sulfides which may be copolymerized, as described hereinafter, include ethylene sulfide, propylene sulfide, butylene sulfide, isobutylene sulfide, amylene sulfide, etc.

Mercaptoalcohols may be copolymerized with alkylene glycols to form the copolymeric lubricants of the present invention. Typical of this class of alcohols are 2-mercaptoethyl alcohol, 2-mercaptopropyl alcohol, 3-mercaptopropyl alcohol, 4-mercaptopbutyl alcohol, etc.

A third class of sulfur compounds which may be used in the preparation of the copolymeric lubricants of the present invention are the dimercaptans, such as ethylene dimercaptan, propylene dimercaptan, butylene dimercaptan, trimethylene dimercaptan, hexamethylene dimercaptan.

The copolymerization reaction is conducted by heating the alkylene oxide or glycol with the alkylene sulfide or thioglycol in the presence of a copolymerization catalyst. When copolymerizing an alkylene oxide with an alkylene sulfide, it is preferred practice to heat the two components at temperatures from about 25° C. to about 175° C. for periods from about 1 hour to about 40 hours. Lower temperatures may be used if active catalysts, such as boron trifluoride, are present, but somewhat higher temperatures are preferred in order to promote more rapid reaction. Likewise, temperatures higher than about 175° C. may be employed, particularly if the reactants are passing at a relatively rapid rate through a reaction zone. Care must be taken, when utilizing higher temperatures, that decomposition of the monomers and the copolymer derived therefrom is minimized and that side-reactions are prevented.

The time and temperature of copolymerization will be governed to some extent by the nature of the catalysts employed. The preferred catalysts include active types such as aluminum chloride and boron trifluoride, and other catalysts of a milder type, including alkali metal hydroxides such as potassium hydroxide and sodium hydroxide, as well as metallic salts such as stannic chloride, ferric chloride, etc.

When copolymerizing alkylene glycols with alkylene thioglycols (including mercapto alcohols and dimercaptans), other conditions and catalysts may be employed. Catalysts which are suitable for this type of copolymerization are those promoting dehydration, such as sulfuric acid, phosphoric acid, sulfonic acids such as para-tolu-

ene sulfonic acid, as well as iodine, hydrogen iodide, etc. Preferably, the copolymerization is carried out in a system whereby water and hydrogen sulfide, formed during the reaction, may be continuously removed from the reaction zone. The copolymerization of alkylene glycols with alkylene thioglycols preferably is conducted at temperatures from about 150° C. to about 300° C. with optimum reaction within the range from about 175° C. to about 225° C. If the reaction is above about 300° C. there is a certain amount of decomposition of the monomers and the copolymer formed therefrom, so that undue losses occur and the product requires extensive purification.

When the copolymerization 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 6 hours, and usually is about 24 hours or even longer. When alkylene glycols comprise one of the monomers under a given set of conditions the molecular weight of the copolymer varies directly with the amount of water formed, since a molecule of water is formed for every additional link added to the copolymer chain. Consequently, the average molecular weight of the copolymeric product can be readily calculated by the amount of water and hydrogen sulfide which has distilled out of the copolymerization zone.

The copolymerization 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 monomers and/or the polymer, as solvents for the catalyst, as azeotropic constituents for carrying off water formed during the copolymerization, as diluents for the control of copolymerization 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 copolymerization is carried out in gaseous phase, but also may be injected to carry off the water formed during polymerization, 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 copolymerization, it is preferably chosen from the group of hydrocarbons boiling between about 125° C. to about 300° C., especially if it expected to participate in azeotropic distillation of water during copolymerization. Hydrocarbons having boiling points within this range 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 copolymerization is carried out in gaseous phase, the diluent may be a lower hydrocarbon such as methane, ethane, propane, butane, etc., which act as regulators or diluents for the reaction, but which can be stripped from

the product with facility, subsequent to the copolymerization.

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 copolymerization the initial proportion of diluent to glycol 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 by dehydration during copolymerization distills azeotropically with part of the diluent, it is a preferred practice to arrange a return inlet so that the diluent passing over in the azeotrope may be replaced in or near the copolymerization zone, so as to maintain a constant diluent:glycol ratio.

Other ingredients may be included in the copolymerization mixture, or may be added from time to time during the polymerization. For example, the copolymerization may be carried out in a closed system, such as an autoclave. In such a case, the water formed in the copolymerization 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 copolymerization 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.

Following the copolymerization 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 catalysts 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 copolymerization 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 and relatively volatile copolymer fractions may be removed at the same time. Consequently, at the end of these operations there remains the copolymer free of solvents, water, catalyst and low-boiling fractions.

For some purposes it may be necessary to decolorize the copolymers formed as described above. Various bleaching and decolorizing processes may be used, but the most effective means of color removal are percolation through or treatment with an activated clay, such as fuller's earth, and hydrogenation, or a combination of the two treatments.

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 copolymer.

On the other hand, copolymers having the least color can be obtained only by following the percolation by 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. Any catalyst which is not poisoned by sulfur or sulfur compounds is suitable for the reduction of carbonyls although nickel sulfide is preferred. Temperatures employed vary from about 125 to about 250° C., and hydrogen pressures from about 500 to about 3000 lb. per square inch are utilized. Subsequent to hydrogenation, the catalyst 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 of the present invention may have one or more hydroxyl end-groups, and also may have sulfhydryl end-groups.

These hydroxyl groups and/or sulfhydryl groups may be acted upon by the usual methods 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 hydroxyl groups and/or sulfhydryl groups. These include alkyl halides, such as methyl iodide, methyl bromide, ethyl chloride, propyl iodide; aralkyl halides such as benzyl chloride and methylbenzyl chloride; hydroxyalkyl chlorides such as hydroxyethyl 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 groups may be accomplished with various inorganic groups such as nitrates, phosphates or sulfates. However, preferred esterifying agents are the organic acids anhydrides or acid chlorides, and especially fatty acids, acid anhydrides and their chlorides, including for example those of formic, acetic, propionic, butyric, hexoic, 2-ethylhexoic acids, and

higher fatty acids such as lauric, stearic, myristic, palmitic and capric acids. Usually, the esters are formed by treatment of the copolymer with the anhydride of the acid in the presence of a catalyst such as sulfuric or phosphoric acid or a sulfonic acid such as para-toluene sulfonic acid. The saturated fatty acids form the most stable esters with the subject copolymers.

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

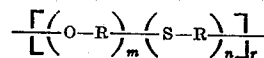
Etherification or esterification of the end-groups may take place simultaneously with or subsequent to copolymerization, and may be effected prior to or subsequent to the decolorizing and purifying processes described hereinbefore. Preferably, the end-group modification is carried out immediately after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

In carrying out this latter, the exact mechanism by which substitution of the end-groups occurs is obscure. However, it has been discovered, in accordance with this invention, that by using an active modifying agent, such as an alcohol, as the diluent during the copolymerization, reaction occurs to give copolymers having at least one substituted end-group, such as an ether group or ester group. For example, if alcohols such as n-octyl alcohol, n-decyl alcohol, n-dodecyl alcohol, etc., or their isomers, are used as diluents during the copolymerization, the corresponding ethers of the copolymers are formed. This provides a convenient method for modifying the properties of the copolymer. The reactive diluent may be the only diluent present, or may be mixed with one or more inert diluents.

Other preferred means of modifying the end-groups of the copolymers of the present invention comprise treatment thereof with amines, or water, either during the copolymerization step or at any time subsequent thereto.

When amino end-groups are desired it is preferred practice to treat the copolymer with a primary or secondary amine or with ammonia subsequent to copolymerization, using a dehydration catalyst to promote the reaction. By introducing as little as 2% amino end-groups into the copolymer, the stability of the latter to oxidation is considerably enhanced.

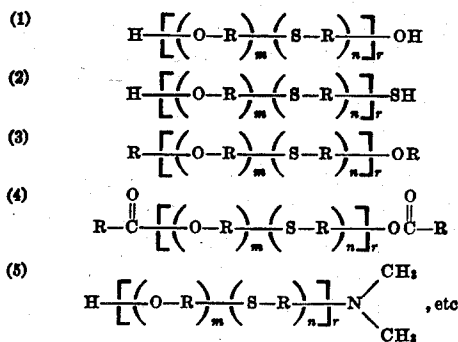
The copolymeric lubricants of the present invention have units of the general configuration



wherein m , n and r are integers and each R is an organic radical, preferably a hydrocarbon radical. The ratio of —O—R-groups to —S—R-groups may vary widely, dependent primarily upon the purpose for which the copolymer is intended. By copolymerizing as little as one mol per cent of the above described sulfur compounds with alkylene oxides or glycols a product is obtained which has considerably improved oxidation stability over that obtained when the sulfur units are not present in the polymer. Furthermore, by copolymerizing an alkylene oxide or glycol with at least 10 mol per cent of the hereinafter defined sulfur compounds a copolymer is obtained having ex-

extreme pressure characteristics, either when used alone, or when employed as an extreme pressure additive for mineral oils or synthetic lubricants. Thus, copolymers having only a very minor amount of —S—R-groups, or containing any amount up to a predominating proportion of —S—R-groups may be prepared.

Dependent in part upon the monomers employed and the modification of the end-groups effected during or subsequent to copolymerization, the copolymers have various configurations, of which the following are typical:



wherein m , n and r are integers, and each R is an organic radical, preferably a hydrocarbon radical, and especially a saturated aliphatic hydrocarbon radical.

The copolymeric lubricants described above vary from thin liquids to viscous oils and, if the molecular weight is great enough, products which are gels or solids useful as lubricant additives are formed. Polymers having molecular weights from about 100 to about 4,000 are readily prepared, but those having molecular weights from about 200 to about 1500 are preferred, since they have properties of viscosity and solubility which give them extensive utility as lubricants and in lubricating compositions.

When the molecular weight is less than about 1500, the copolymers have pour points varying from about -20°F. to less than -40°F. The viscosity of the copolymers is generally higher than that of a polymeric alkylene oxide or glycol of corresponding molecular weight. A copolymer of propylene oxide with only 2% propylene sulfide and having a molecular weight of about 1000 had a viscosity of 192 centistokes at 100°F. , while a propylene oxide polymer of similar molecular weight had a viscosity of 95 centistokes at 100°F.

Another characteristic of the copolymers of the present invention, which makes them particularly useful as lubricants or as lubricant additives, is their excellent viscosity index. Dependent upon the four variables of molecular weight, monomer identity, ratio of the several monomers and end-group modification, the viscosity indices of the present copolymers vary from about 100 to about 165. For example, the copolymer referred to in the preceding paragraph had a viscosity index of 137.

The resistance of the copolymers described hereinbefore to oxidation is outstanding, especially in comparison with the stability of the homopolymers of alkylene oxides or alkylene glycols. The reason for this exceptional difference, which is apparent even when the copolymer contains as little as 1 mol per cent of groups derived from a sulfur-containing monomer, has not been ascertained. For example, the copolymer referred to in the preceding two paragraphs required a substantially greater period to absorb a given

quantity of oxygen than did a propylene oxide polymer prepared under similar conditions.

While the subject copolymers are stable enough for many purposes for use without further modification, their stability is enhanced by the addition of 1,2-dihydroxybenzene or of certain types of amines, such as polycyclic aromatic diamines, monocyclic amino phenols and certain monocyclic amines. Minor amounts, between 0.05% and 5% by weight of the copolymer, substantially increase the resistance of the latter to oxidation.

When about 10 mol per cent of the units of the copolymer are derived from alkylene sulfides or thioglycols the copolymer exhibits superior extreme pressure characteristics, either when used as the only lubricant in a composition, or in combination with other natural or synthetic lubricants. Many of the more difficultly soluble copolymers are rendered more soluble by the introduction of alkyl substituents, particularly those having more than four carbon atoms. The isomyl, octyl, lauryl, and octadecyl radicals and radicals from paraffin wax greatly increase the solubility of the copolymers in mineral oils.

Other lubricants with which the subject copolymers may be combined include synthetic oils such as polymers of alkylene oxides and alkylene glycols, high molecular weight esters such as bis (2-ethylhexyl) sebacate, etc.

The copolymers may contain other additives, such as anti-corrosion agents, especially organic acids capable of forming water-insoluble metallic soaps. They may be combined with gelling agents such as metallic soaps, graphite, etc., to form synthetic greases, or may contain water or emulsifying agents for use in cutting oil compositions.

The following examples are presented to illustrate the preparation and stability of typical copolymers:

I. Four parts propylene sulfide, 196 parts propylene oxide and 6.9 parts potassium hydroxide were heated in an autoclave for 24 hours at $100-115^\circ \text{C.}$ The copolymer so formed (92% of the reactants) was washed with water and dehydrated by heating at 100°C. under reduced pressure. The product had the following properties:

Viscosity at 100°F. , centistokes.....	192.00
Viscosity at 210°F. , centistokes.....	28.04
Viscosity index.....	137
SAE number.....	70
Per cent sulfur.....	0.816
Molecular weight.....	995

Seventy-five grams of the copolymer were combined with 1.5% phenyl-alpha-naphthylamine and heated at 140°C. in the presence of 1 sq. cm. copper per gram oil with continuous introduction of oxygen. It required 32.5 hours for the copolymer to absorb 1800 cc. oxygen. A homopolymer of propylene oxide of similar molecular weight and prepared under the same conditions when combined with 1.5% phenyl-alpha-naphthylamine required only 9.3 hours to absorb the same quantity of oxygen.

The copolymer so formed was employed as an engine lubricant in a 40 hour Lauson engine test, using a jacket temperature of 100°F. There was moderate lacquer formation and corrosion, minimum oil consumption, and normal deposits on pistons and in the sump.

II. One hundred parts propylene oxide, 100 parts propylene sulfide and 500 parts isopentane were treated at the reflux temperature with an excess of boron trifluoride, added dropwise. The

11

polymer so formed was washed with water, dilute sodium hydroxide, again with water, and then was dried at 100° C. under reduced pressure.

The polymer was tested for extreme pressure properties in the four-ball machine described by Boelage in "Engineering," June 14, 1933. Table I present the data obtained:

Table I

Load, Kg.	Scar Diameter, mm.
100	0.78
140	0.85
200	1.02
300	1.85
400	2.71
500	2.76
600	2.62
700	3.08

We claim as our invention:

1. A method of preparing a liquid mixture of linear copolymers having improved oxidation stability which comprises heating an alkylene sulfide and an alkylene oxide with an alkali metal hydroxide catalyst in an autoclave at a temperature from 25° to 175° C. for a period of 1 to 40 hours, the molar ratio of sulfide to oxide being from 1:100 to 1:1, the time and temperature being so regulated as to produce a mixture of copolymers having an average molecular weight from 200 to 1500.

2. A method of preparing a liquid mixture of linear copolymers having improved oxidation stability which comprises heating propylene sulfide and propylene oxide with sodium hydroxide in an autoclave at a temperature from 25° C. to 175° C. for a period of 1 to 40 hours, the molar ratio of propylene sulfide to propylene oxide being from 1:100 to 1:1, the time and temperature being so regulated as to produce a mixture of copolymers having an average molecular weight between 200 and 1500.

3. A mixture of liquid linear sulfoalkylene-oxyalkylene copolymers, having randomly distributed sulfoalkylene and oxyalkylene groups, the molar proportion of sulfoalkylene to oxyalkylene groups being from 1:100 to 1:1, said mixture having an average molecular weight between 200 and 1500 and each copolymer having, in addition to the sulfoalkylene and oxyalkylene groups, terminal radicals of the group consisting of hydroxy, alkoxy and acyloxy radicals.

4. A mixture of liquid linear oxypropylene-sulfopropylene copolymers, having randomly distributed oxypropylene and sulfopropylene groups in a molar ratio of oxypropylene to sulfopropylene of about 1:1, said mixture having an average molecular weight between 200 and 1500

12

and each copolymer having, in addition to oxypropylene and sulfopropylene groups, terminal hydroxy radicals.

5. A mixture of liquid linear oxypropylene-sulfopropylene copolymers having randomly distributed oxypropylene and sulfopropylene groups in a molar ratio of sulfopropylene to oxypropylene groups of about 2:98, said mixture having an average molecular weight between 200 and 1500 and each copolymer having, in addition to oxypropylene and sulfopropylene groups, terminal hydroxy radicals.

6. A mixture of liquid linear oxypropylene-sulfopropylene copolymers having randomly distributed oxypropylene and sulfopropylene groups combined in a sulfopropylene to oxypropylene molar ratio from 1:100 to 1:1, said mixture having an average molecular weight between 200 and 1500 and each copolymer having, in addition to oxypropylene and sulfopropylene groups, terminal hydroxy groups.

7. A mixture of liquid linear oxyalkylene-sulfoalkylene copolymers having randomly distributed oxyalkylene and sulfoalkylene groups combined in a sulfoalkylene to oxyalkylene molar ratio from 1:100 to 1:1 and each copolymer having, in addition to oxyalkylene and sulfoalkylene groups, terminal alkoxy groups, said mixture having an average molecular weight between 200 and 1500.

SEAVER A. BALLARD.

RUPERT C. MORRIS.

JOHN L. VAN WINKLE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,107,366	Bruson	Feb. 8, 1938
2,129,709	Schuetz	Sept. 13, 1938
2,136,928	Schlack	Nov. 15, 1938
2,149,498	Bludworth	Mar. 7, 1939
2,293,868	Toussaint	Aug. 25, 1942
2,326,483	Moran	Aug. 10, 1943
2,383,915	Morgan	Aug. 28, 1945
2,425,755	Roberts	Aug. 19, 1947
2,425,845	Toussaint	Aug. 19, 1947
2,434,978	Zisman	Jan. 27, 1948

FOREIGN PATENTS

Number	Country	Date
769,216	France	June 5, 1934

OTHER REFERENCES

Patrick, "Transactions of the Faraday Society," vol. 35 (1936), pages 347-358.