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SULFURIZED PRODUCT AND PREPARATION THEREOF

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This invention relates to novel products and to their preparation and use. More particularly it pertains to the use of certain sulfur containing linear polymers especially useful as synthetic lubricants or as lubricant additives.

Mineral oil fractions are suitable for many lubricating purposes, but it is well known that such lubricants possess certain inherent limitations such as tendency to oxidize, thickening at low temperatures and poor inherent lubricating characteristics under conditions of relatively extreme pressure such as in hypoid gear lubrication. A large number of additives have been employed with mineral oils in order to improve these shortcomings with a certain degree of success.

Various synthetic materials have been proposed for use as synthetic lubricants. These include polymers of cracked wax olefins and alkylated aromatics such as alkylated naphthalenes. Some of these are useful for special purposes but, especially if the synthetic lubricants are derived from olefinic sources, they usually possess corrosion and oxidation characteristics limiting their utilization to a substantial degree. Another type of synthetic lubricant which has been investigated is the alkylene oxide polymer type such as polymerized propylene oxide. This latter type of synthetic lubricant is suitable for use only under mild operating conditions. If even moderate extreme pressure conditions are encountered this type of polymeric lubricant fails to function satisfactorily and results in rapid wear of the machinery or engine being lubricated.

It is an object of this invention to provide novel sulfur containing products. It is another object of this invention to provide a process for the production of such materials. It is a further object of this invention to provide novel synthetic lubricants. A further object of this invention is to provide novel additives for lubricating compositions, said additives providing such compositions with extreme pressure properties. Other objects will become apparent during the following discussion.

Now in accordance with this invention, it has been found that polymers containing units having the general configuration



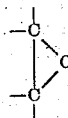
wherein R is an organic radical (especially a hydrocarbon radical) may be converted to more useful products by reaction with sulfur, with compounds containing sulfur to halide linkages or with compounds containing sulfur to phos-

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phorus linkages. Still in accordance with this invention it has been found that such products may be prepared by heating the two ingredients together, either alone or in the presence of a solvent for one or more of the ingredients of the reaction mixture or of a solvent for the products prepared. Again in accordance with this invention, it has been found that these sulfurized polymers have excellent lubricating characteristics and inherently possess extreme pressure properties. Still in accordance with this invention, it has been found that the subject sulfurized polymers may be used in combination with lubricating materials in order to enhance the extreme pressure properties and other characteristics thereof.

Polymers which may be sulfurized for the purpose of the present invention include especially those prepared from alkylene oxides and alkylene glycols.

Alkylene oxides, and particularly the alkylene oxides having the oxygen bound to adjacent carbon atoms, form polymers of the above configuration. These monomeric oxides have the general configuration



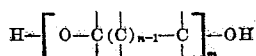
wherein the free valences are satisfied with hydrogens or organic radicals.

Alkylene oxides which form such polymers include ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, isobutylene oxide, tetramethylethylene oxide, methylphenylethylene oxide, cyclohexene oxide, methylcyclohexene oxide, 1,2-cetene oxide; and other substances containing the epoxide linkages such as epichlorohydrin, epibromohydrin, and glycidides such as glycidol and 1,2-epoxy-2-butanol, as well as derivatives and polymerizable homologs and analogs of the aforementioned substances.

Copolymers of the alkylene oxides useful in compositions of the present invention include for example, the copolymers of ethylene oxide and propylene oxide; and copolymers of ethylene oxide and isobutylene oxide; the copolymers of propylene oxide and epichlorohydrin; the copolymers of propylene oxide and 1,2-butylene oxide; the copolymers of propylene oxide and glycidol; and the copolymers of propylene oxide and isobutylene oxide.

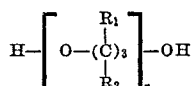
Polymers similar to those above are formed from the alkylene glycols, including the poly-

methylene glycols and the ethylene glycols. The monomeric and lower polymeric glycols have the general configuration



wherein m and n are integers and the free valences are satisfied with hydrogen atoms or organic radicals. When n is 1, the general formula is that of an ethylene glycol, wherein the glycollic hydroxyls are on adjacent carbon atoms.

Glycols having three carbon atoms separating the glycollic hydroxyls are derived from 1,3-propanediol (trimethylene glycol) and have the general formula

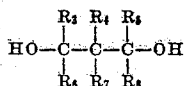


wherein n is an integer and R_1 and R_2 are hydrogens or organic radicals.

If R_1 and/or R_2 are not hydrogen atoms, they may be organic radicals such as alkyl, aralkyl, aryl, etc. Preferably, if they are not hydrogens, they are aliphatic radicals, especially saturated lower aliphatic radicals, but may also be groups which contain olefinic or acetylenic links. 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; 1,2,3,3-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, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, etc., as well as their isomers. Preferably, when alkyl groups are the substituents R_1 and R_2 , they have from 1 to 10 carbon atoms, and still more preferably from 1 to 5.

It will be understood that R_1 and R_2 may be similar or dissimilar groups. Thus, when expanding the general formula given hereinbefore to its indicated number of carbon atoms, it then becomes



wherein R_3 through R_8 are either hydrogen atoms or similar or dissimilar organic radicals. Those derivatives of trimethylene glycol, other than trimethylene glycol itself, which gives the most satisfactory polymers for general use have either one or two of the R 's as lower alkyl groups. Thus, 2-methyl-1,3-propanediol and 2,2-dimethyl-1,3-propanediol form excellent polymers when treated according to the method of the present invention.

Other lower alkyl substituted trimethylene glycols which polymerize readily are 1-methyl-2-ethyl-1,3-propanediol; 2-methyl-2-ethyl-1,3-propanediol; 1-methyl-3-ethyl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; 1-methyl-2-isopropyl-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.

Cycloaliphatic radicals may be one or more of the substituents represented by R_3 to R_8 in the above general formula. Thus R_3 through R_8 may be such radicals as cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, etc. However, open chain alkyl substituents form polymers having preferred properties.

The polymers have modified properties if the trimethylene glycol derivative contains other active groups, such as additional hydroxyls, carboxyls, carbonyls, halogens, sulfur, phosphorus, nitrogen, etc.

Polymethylene glycols having 6 or more carbon atoms separating the glycollic hydroxyls also form polymers and copolymers which are readily improved by the present process.

The polymethylene glycols from which such polymers are prepared have the general formula



wherein z is an integer, y is an integer greater than 5 and the R 's are substituents attached to each carbon atom, such as hydrogen atoms or organic radicals, especially hydrocarbon radicals. Preferably z is an integer less than 10, and more preferably is an integer from 1 to 4. Actually, when z is more than 1, the glycol is a dimer, trimer, etc., of the corresponding monomeric glycol. The polymethylene glycols polymerizing most readily are those in which y is an integer from 6 to 20.

Monomeric, unsubstituted polymethylene glycols falling within the above formula include 1,6-hexanediol; 1,7-heptanediol; 1,8-octanediol; 1,9-nonanediol; 1,10-decanediol; 1,12-dodecanediol; and polymerizable homologs, analogs and derivatives of the same.

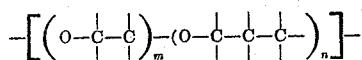
The above glycols are those in which all of the R substituents attached to the carbon atoms are hydrogen atoms. When one or more of the R 's are substituents other than hydrogen atoms they may be hydrocarbon radicals, such as aliphatic, aromatic, or alicyclic hydrocarbon radicals, or radicals containing non-hydrocarbon members, such as hydroxyl, carboxyl, or carbonyl groups, or sulfur, selenium, tellurium, phosphorus or nitrogen atoms. Preferably, however, any organic radicals attached to the polymethylene glycol are hydrocarbon radicals. Of these, the aliphatic hydrocarbons are preferred, and the saturated lower aliphatic radicals give the most stable polymers and have the widest utility. Hence, the preferred R 's, other than hydrogen, are the lower alkyls, such as methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, tert-butyl, amyl, iso-amyl, hexyl, etc. groups. Again, even when R 's other than hydrogen are present, it is preferred that the monomeric glycol contain a preponderance of hydrogen substituent R 's. The most reactive glycols are those in which less than 4 R 's are other than hydrogen, and the greatest reactivity is possessed by those having 2 or less R 's which are organic radicals.

Glycols which fall within the above classification include 1,6-heptanediol; 1,6-octanediol; 1,6-nonanediol; 1,6-dodecanediol; 1,6-decanediol; 1,7-octanediol; 1,7-nonanediol; 1,7-decanediol; 1,7-dodecanediol; 1,8-nonanediol; 1,8-decanediol; 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-dec-

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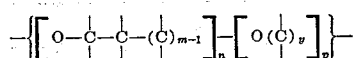
anediol; 2,8-dodecanediol; 2,9-decanediol; 2,9-dodecanediol; 2,3-dimethyl-1,6-hexanediol; 2,4-dimethyl-1,6-hexanediol; 2,5-dimethyl-1,6-hexanediol; 4,4-dimethyl-1,6-hexanediol; 5,5-dimethyl-1,6-hexanediol; 2-methyl-3-ethyl-1,7-heptanediol; 2-ethyl-3-methyl-1,7-heptanediol; 3,3-diethyl-1,7-heptanediol; 3,4-diisopropyl-1,8-octanediol; etc. and their polymerizable homologs, analogs and derivatives.

The polymers described hereinbefore may be homopolymers or may be copolymers. For example, an ethylene glycol may be copolymerized with a trimethylene glycol to give copolymers having units of the general configuration



wherein m and n are integers and the free valences within the brackets are satisfied with hydrogen atoms or organic radicals. These include copolymers of ethylene glycol and trimethylene glycol; ethylene glycol and 1-methyl-1, 3-propanediol; ethylene glycol and 2-methyl-1,3-propanediol; ethylene glycol and 2,2-dimethyl-1,3-propanediol; ethylene glycol and 1,3-diethyl-1,3-propanediol; 1,2-dimethylethylene glycol and trimethylene glycol; 1,2-dimethylethylene glycol and 1,3-dibutyl-1,3-propanediol, etc.

Other copolymers falling within the general formula of substances stabilized according to the present invention include the copolymers of an ethylene glycol or a trimethylene glycol with a polymethylene glycol having more than 5 carbon atoms separating the glycolic hydroxyls. These copolymers have units of the general configuration



wherein m , n , p and y are integers, and the free valences are satisfied with hydrogen atoms or organic radicals. These include for example, copolymers of ethylene glycol and hexamethylene glycol; trimethylene glycol and hexamethylene glycol, etc.

The alkylene oxides usually are polymerized at temperatures from about -60°C. to about 100°C. in the presence of alkalis, acids, amines or salts. The glycols are polymerized at higher temperatures ($150-300^\circ \text{C.}$) in the presence of dehydration catalysts, such as iodine, mineral acids, such as nitric acid or sulfuric acid, hydrogen halides such as hydrogen iodide or hydrogen chloride; or organic sulfonic acids such as paratoluene sulfonic acid.

In producing the sulfurized polymers according to the process of the present invention, it is preferred practice to heat one or more of the polymers at a temperature from about 50°C. to about 200°C. for a period of about 3 to 5 hours with an agent or agents from the group consisting of sulfur, sulfur compounds containing sulfur to halide linkages, and sulfur compounds containing sulfur to phosphorus linkages. Typical members of this group include sulfur monochloride, sulfur dichloride and phosphorus pentasulfide as well as their homologs. The two ingredients of the reaction mixture, namely the polymer and the sulfur or sulfur compound, may be heated in the absence of other materials or in the presence of solvents for one or more of the ingredients or products. Suitable solvents include chlorinated hydrocarbons, unsaturated aliphatic compounds such as hydrocarbons or alcohols, etc.

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The proportion of sulfur or sulfur compound to the polymer may vary within relatively wide limits depending upon the purpose for which the product is intended. If the product is to be used as a synthetic lubricant it is preferred that the proportion of sulfur to polymer be within the range from about 1% to about 20% by weight of the polymer. However, higher or lower percentages of the sulfur or sulfur compound may be employed. In order to obtain a synthetic lubricating material having satisfactory extreme pressure properties at high loads it is usually preferred that the percentage of sulfur be from about 3% to about 10%, based on the weight of the polymer. For exceptional cases sulfur containing up to about 30% or more may be obtained.

Under normal operating conditions it is advisable to employ an amount of sulfur in excess of that amount with which it is desired to modify the polymer. By the use of such an excess the rate of reaction is increased to a satisfactory degree. If an excess is used it becomes necessary at the end of the heating period to separate the unreacted sulfur or sulfur compound from the modified polymeric material. Ordinarily the excess agent will remain in suspension and may be separated by a filtration or centrifuging operation. Under some conditions however, the excess agent dissolves in the polymer and, if it is necessary to separate therefrom, it must be removed by such means as solvent extraction. For many lubricating purposes an excess of sulfur is not objectionable if it is dissolved in the body of the lubricant.

The sulfurizing operation normally may be effected without undue discolorization or other adverse effects on the subject polymers. However, it may be desirable to colorize or decolorize the product by subjecting it to an operation such as filtration through activated carbon, treatment with an absorbent clay or by chemical means of decolorization.

The products obtained by the sulfurization of polymers such as those described above, are solids or liquids useful for a number of purposes. The solids are particularly effective as extreme pressure additives in lubricants, while the liquid members of the sulfurized series are effective not only as extreme pressure additives but as lubricants themselves. The oily products have satisfactory lubricating characteristics, having high viscosity indices and low pour points.

Lubricants which may be modified by the addition of a solid or liquid sulfurized polymer as described hereinbefore include oleaginous materials such as mineral oils, fatty oils, vegetable oils such as corn oil, cottonseed oil and castor oil; animal oil such as neat's-foot oil; and fish oils such as sperm oil. Oleaginous materials when modified by such means as halogenation, hydrogenation, alkylation and other means may be modified by the sulfurized polymers of the present invention. Depending upon the application intended, oleaginous materials of extreme low or extreme high viscosities may be used successfully. Lubricating oils of a viscosity from about 30 seconds at 100°F. to about 250 seconds at 210°F. and higher may be used if desired. Furthermore, paraffinic, naphthenic, asphaltic base oils or carbons or mixtures may be used in combination with the sulfurized polymers.

A special type of lubricant which is particularly suited to modification with the subject sulfurized polymers includes lubricants comprising or de-

derived from the alkylene oxide or alkylene glycol polymers listed above. These polymers may be the same as the polymers from which the sulfurized materials are derived or they may be different members of the same class. A particularly desirable means of preparing lubricating compositions of this variety comprises treating such polymers with a minor amount of sulfur or sulfur compounds as listed hereinbefore so as to produce in situ a polymeric lubricant, a minor amount of which is in a sulfurized condition. It will be considered within the scope of this invention that the sulfurization may be complete or at any stage short of completion so that a greater or less amount of the main body of the polymeric lubricant is in a sulfurized state.

The lubricating compositions of this invention may contain other modifying ingredients such as gelling agents, stabilizers, anti-corrosion agents, viscosity index improvers, thickener, and the like. Particularly suitable gelling agents for polymeric alkylene oxides or glycols which contain or comprise sulfurized polymers are lithium soaps of the higher fatty acids such as lithium stearate.

The use of these sulfurized polymers either in or as lubricants is particularly suitable where extreme pressure or heavy duty conditions prevail. It has been discovered that by the sulfurization as described hereinabove pressure characteristics are imparted to the alkylene oxide and glycol polymers. The examples which follow describe the preparation and use of this invention. It is not intended that the invention be limited specifically to these examples but that they be treated as specific illustrations thereof.

Example I

100 parts of a polymerized propylene oxide were heated with 5 parts by weight of flowers of sulfur at a temperature of 170° C. for 3 hours. The product was a cloudy oil which was clarified by filtration. It had the following characteristics:

Sulfur, per cent by weight	1.20
Free sulfur, per cent by weight	0.22
Viscosity index	143
Pour point, °F	-25

Example II

100 parts of a copolymer of trimethylene glycol and diethylene glycol was heated with 5 parts by weight of flowers of sulfur at a temperature of 190° C. for 5 hours. The product was filtered to give a clear light yellow oil having the following properties:

Sulfur, per cent by weight	2.02
Mercaptan sulfur, per cent by weight	0.6
Viscosity index	125
Pour point, °F	-35

Example III

100 parts of a polymerized propylene oxide was heated with 5 parts by weight of sulfur monochloride at 175° C. for a period of 4 hours. The product was filtered to yield a light brown oil. The oil was sparged with nitrogen at room temperature to remove the odor of chlorine compounds. The product so derived was odorless and had the following characteristics:

Sulfur, per cent by weight	0.90
Chlorine, per cent by weight	0.56
Viscosity index	145
Pour point, °F	-20

Example IV

100 parts by weight of a polymer of propylene oxide was heated with 5 parts by weight of sulfur dichloride at a temperature of 185° C. for a period of 3 hours. The product was filtered to yield an odorless yellow oil having the following properties:

Sulfur, per cent by weight	0.64
Chlorine, per cent by weight	0.58
Viscosity index	145
Pour point, °F	-30

Example V

100 parts by weight of a polymer of propylene oxide was heated with 5 parts by weight of phosphorus pentasulfide at a temperature of 190° C. for 5 hours. The product was filtered and then consisted of a light yellow oil having the following properties:

Sulfur, per cent by weight	3.45
Viscosity index	135
Pour point, °F	-10

Example VI

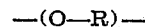
The non-sulfurized and sulfurized polymers described in Examples 1 through 5 were treated for extreme pressure properties, using the 4 ball machine described by Boelage in "Engineering" (July 14, 1933). The following table represents the data obtained:

Lubricant	Wear in mm. at Various Loads (kgs.)									
	60	80	100	140	200	300	400	500	600	700
Polymerized:										
Propylene oxide	0.57	1.63	2.50	W						
Propylene oxide + Sulfur			0.61	1.26	1.215	1.61	1.63	1.69	1.86	1.88
Propylene oxide + SCl ₂				1.04	1.56	1.84	1.94	2.06	2.16	W
Propylene oxide + S ₂ Cl ₂				0.98	1.21	1.78	1.87	1.88	2.01	W
Propylene oxide + P ₂ S ₅					0.86		2.45	5.09		
Copolymer of trimethylene glycol and ethylene glycol	0.40	0.45	1.91	2.13	W					
Ethylene glycol + S					1.39	1.92	1.66		1.91	2.11

W indicates welding.

We claim as our invention:

1. The process which consists essentially of heating a polymer having recurring units of the general configuration



wherein R is an alkylene hydrocarbon radical, with an agent selected from the group consisting of sulfur, compounds containing sulfur to chlorine linkages and compounds containing sulfur to phosphorus linkages for a period of 3 to 5 hours at a temperature between 50° and 200° C., the amount of said agent being sufficient to impart a sulfur content of 1 to 30% by weight of said polymer to the reaction product.

2. The reaction products prepared according to the process of claim 1.

3. The process which consists essentially of heating 100 parts by weight of a copolymer of trimethylene glycol and diethylene glycol with 5 parts by weight of sulfur at a temperature of 190° C. for 5 hours.

4. The process which consists essentially of heating 100 parts by weight of a propylene oxide polymer with 5 parts by weight of sulfur at a temperature of 170° C. for 3 hours.

5. The process which consists essentially of heating 100 parts by weight of a propylene oxide polymer with 5 parts by weight of phosphorus pentasulfide at 190° C. for 5 hours.

6. A lubricating composition comprising a major proportion of an alkylene glycol polymer and a minor amount, sufficient to impart extreme pressure properties to said composition, of a polymeric alkylene glycol reaction product with sulfur, said reaction product being prepared by the process of claim 1.

7. A lubricating composition comprising a major proportion of an alkylene oxide polymer and a minor amount, sufficient to impart extreme pressure properties to said composition, of a polymeric alkylene oxide reaction product with sulfur, said reaction product being prepared by the process of claim 1.

8. A lubricating composition comprising a major proportion of a mineral oil lubricant and a minor amount, sufficient to impart extreme pressure properties to said composition, of a polymeric alkylene oxide reaction product with phosphorus pentasulfide, said reaction product being prepared by the process of claim 1.

9. A lubricating composition suitable for use as an extreme pressure lubricant comprising a major proportion of an oleaginous lubricant and a minor amount, sufficient to impart extreme pressure properties to said composition, of the

reaction product of an oxyalkylene polymer with an agent of the group consisting of sulfur, compounds containing sulfur directly attached to a halogen atom and compounds containing sulfur directly attached to a phosphorus atom, said reaction product containing 1 to 30% by weight of sulfur based on the weight of the polymer, said product having been prepared according to the process of claim 1.

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