Patented Feb. 17, 1953 2,628,939

UNITED STATES PATENT OFFICE

2,628,939

MINERAL OIL COMPOSITION

Edward S. Blake, Medford, Mass., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application November 21, 1947, Serial No. 787,485

4 Claims. (Cl. 252—46.6)

1

This invention relates to lubricating compositions and to methods of preparing the same and more particularly to lubricating compositions adapted for use under extreme pressure conditions.

Various types of modern machinery such as the hypoid gears in motor vehicles develop enormous pressures between engaged surfaces. The ordinary type of hydrocarbon lubricant composed only of a petroleum fraction is incapable of satisfying the severe requirements demanded in the proper lubricant of hypoid gears, bearing surfaces, metal cutting tools, and the like subjected to unusually heavy loads per unit area of surface. This invention has to do with ingredients which may be added to a suitable carrying agent such as mineral oil and are capable of maintaining between the engaged surfaces a lubricating film under high pressures.

A primary object of this invention is to provide a new and novel sulfur bearing material capable of imparting desirable properties to a lubricating oil composition otherwise unsatisfactory under the conditions encountered. A further object is to provide a mineral oil adjuvant which is not corrosive and does not decrease the oxidation stability of the oil. A still further object is to provide a class of lubricants capable of maintaining a lubricating film between surfaces engaged under high pressures. A still further object is to provide a class of lubricants which reduce wear. Other objects will be disclosed hereinafter.

In accordance with the present invention it has been discovered that di-esters of dihydric alcohols and unsaturated fatty acids can be readily sulfurized to produce sulfurized diesters having valuable properties which render them valuable as ingredients in mineral oil lubricants.

In general, the compositions of this invention comprise a major proportion of mineral lubricating oil and a minor proportion of the sulfurized ester, as for example 0.1% to 30%. Other ingredients may be present as desired, it being particularly advantageous to have a phosphorus ingredient present. Apparently phosphorus exerts a synergistic effect on the sulfurized neutral esters since the wear resisting properties are greater than would be predicted from the properties of the separate components. Phosphorus may be introduced by reacting the sulfurized ester with a suitable phosphorus component as hereinafter described or added as a separate component. Examples of suitable phosphorus compounds are mono oleyl phosphate, dioleyl phosphate, mono lauryl phosphate, di lauryl phosphate, mono cresyl phosphate, di cresyl phosphate, di cetyl phosphate, and di octyl phosphate.

2

The presence of a small amount of an organic halogen bearing compound is also desirable in the compounding of some types of lubricants.

The esters to be sulfurized are prepared by esterifying dihydric alcohols of the type

$$OH—R—OH$$

where R is an alkylene group which may contain one or more sulfur or oxygen atoms in the chain. Typical examples are alcohols possessing the formula HOC_2H_4OH, $HOC_2H_4SC_2H_4OH$, $OHC_2H_4OC_2H_4OH$, $HOC_2H_4OC_2H_4OC_2H_4OH$ and the like. The alcohols are esterified with long chain unsaturated fatty acids, as for example oleic acid, elaidic acid, erucic acid, linoleic acid, and ricinoleic acid.

The di-esters may be sulfurized in any suitable manner, the sulfurized products being readily soluble and miscible with mineral oil fractions. Sulfurization may be effected by heating the ester with sulfur or a mixture of sulfur and a sulfur halide at 150–200° C. Where the material is then phosphorized, it is preferred to carry out the reaction under milder conditions, say 100-125° C. The phosphorus sulfides, as for example phosphorus pentasulfide or sesquisulfide are satisfactory phosphorizing agents. The following example demonstrates the sulfurization and phosphorization of glycol di-oleate and is not limitative of the invention.

EXAMPLE I

Into a container of suitable capacity there was charged 2268 parts by weight of glycol di-oleate and 193 parts by weight of sulfur. The mixture was heated for 7½ hours at 177–183° C. under an atmosphere of nitrogen. 13 parts by weight of phosphorus sesquisulfide was then added and heating continued for 9½ hours at 105–110° C. The product contained 8.02% sulfur, 0.29% phosphorus and had a neutralization number of 7.12.

The effectiveness of the sulfurized and phosphorized glycol di-esters may be demonstrated by the conventional tests on compositions comprised of these ingredients and a lubricating oil carrying agent. More specifically, a minor amount of the product described in Example I was added to a high viscosity hydrocarbon lubricating oil (Saybolt Universal viscosity of 101 seconds at 210° F.) and samples of the blended lubricant subjected to the Almen pin test described in a paper presented before the 13th Annual Meeting of the American Petroleum Institute, Division of Refining, on November 17, 1932, by H. R. Wolf and H. C. Mougey—see Proc. A. P. I. 1932, pages 118–130. In addition, the material was subjected to the S. A. E. test described in the S. A. E. Journal 39, 23-4 (1936). The results are summarized below:

Percent Added to Oil	Almen		S. A. E. (1,000 R. P. M.; 14.6:1 rubbing ratio; 77-79 lbs./sec. loading rate
	Load, Lbs.	Torque	
10	41	30	100
18	50	35	132

Additionally, the aforedescribed sulfurized and phosphorized glycol di-oleate passed the more important tests forming the basis of U. S. Army Specification 2-105B. Recognition by the Ordnance Department of the need for a universal gear oil specification which would more nearly define a satisfactory lubricant under field operating conditions in all types of automotive gear drives, led through the efforts of the Coordinating Lubricants Research Committee to the formulation and adoption of U. S. Army Specification 2-105B.

One of the important tests under this specification is that designated by the Ordnance Department as AXS-1570 (C. R. C. Designation L-20-545). This test is a high torque low speed axle test and is described in the C. R. C. Handbook 1946, page 469. A good pass was obtained with a solvent refined Mid-Continent oil containing 10% of the sulfurized and phosphorized glycol di-oleate. The composition also passed the high speed axle test designated by the Ordnance Department as AXS-1569 (C. R. C. Designation L-19-645) described page 467 of the C. R. C. Handbook 1946. Thus, the preferred additives have been found to be entirely satisfactory under conditions simulating actual working conditions.

In order further to demonstrate the invention, a large number of sulfurized and phosphorized additives were prepared under different conditions and tested as components of mineral oil lubricating compositions. Again, the examples are to be taken as illustrative of the invention and not limitative thereof.

EXAMPLE 2

Into a glass or glass lined reactor of suitable capacity there was charged 436 parts by weight of glycol di-oleate, 2.5 parts by weight of sulfur monochloride dissolved in 25 parts by weight of mineral oil (S. A. E. 10) and 37 parts by weight of sulfur. The air in the container was replaced by hydrogen sulfide and the mixture heated with stirring for 7 hours at 167-170° C. 2 parts by weight of P_4S_3 was then added and the phosphorizing reaction effected by heating 5 hours at 104-109° C. in an atmosphere of hydrogen sulfide. Analysis gave 7.03% sulfur, 0.27% phosphorus and a neutralization number of 2.4.

EXAMPLE 3

Into a glass or glass lined reactor of suitable capacity there was charged 436 parts by weight of glycol di-oleate, a solution of 2.5 parts by weight of sulfur monochloride in 25 parts by weight of mineral oil (S. A. E. 10) and 37 parts by weight of sulfur. The air in the container was replaced by hydrogen sulfide and the mixture heated with stirring for 7 hours at 169-171° C. 4 parts by weight of P_4S_3 was then added and heating continued for 5 hours at 104-109° C. in an atmosphere of hydrogen sulfide. The product contained 8.59% sulfur, 0.40% phosphorus and had a neutralization number of 4.85.

A series of preparations were carried out in which glycol di-oleate was sulfurized by heating with sulfur in the ratio of 30 parts of sulfur to 436 parts by weight of glycol di-oleate. For the most part the reactions were carried out either under nitrogen or hydrogen sulfide except Examples 4 and 10 which were prepared in air. No significant differences have been observed due to the presence or absence of an inert atmosphere. However, since hydrogen sulfide is evolved in the reaction, there may have been an effective atmosphere of hydrogen sulfide in every case. Phosphorus sesquisulfide was then added and the composition heated to effect phosphorization. The table below illustrates a variety of conditions and ratios under which the reactions may be successfully carried out. In Example 7 there was present in addition to the sulfur a small amount of a solution of sulfur chloride in mineral oil. 3 parts of S_2Cl_2 dissolved in 25 parts of mineral oil was used for 436 parts of glycol di-oleate.

Example	4	5	6	7	8	9	10	11
Time of sulfurization, hours	7.5	7.5	7.5	18	18	7.5	7.5	7.5
Approximate average temperature of sulfurization, °C	170	170	170	170	170	180	180	180
P_4S_3, parts by weight	3	4	8	2	4	2	3	4
Time of phosphorization, hours	5.5	5	5	5	5	5.5	5	5
Approximate average temperature of phosphorization, °C	107	107	107	107	107	107	107	107

Analysis of the compositions of Examples 2-11 gave an average sulfur content of 6.8% and phosphorus ranging from 0.22% in the case of Example 7 to 0.6% depending upon the amount charged. The neutralization number varied from 5.6 to 13.6. These compositions were evaluated as components of gear lubricants under high torque and low speed conditions by an adaptation of the S. A. E. extreme pressure lubricant testing machine.

The machine employed for the test was an S. A. E. extreme pressure lubricant testing machine manufactured by the Highway Trailer Co., Edgerton, Wisconsin. This machine, suitably modified, provides a simple convenient means of imitating the rubbing of gear teeth by rotating two Timken test cups in line contact with each other and in opposite directions, under controlled rotation speeds. For these tests the speed of the main shaft was reduced from 1000 to 264 R. P. M. and the lower shaft drive gears of 20 and 81 teeth replaced with gears of 52 and 49 teeth to change the rubbing ratio from 14.6:1 to 3.4:1. The oil box on both bearing sides was jacketed by brazing a plate over the offset in the oil box casting and both cooling reservoirs were then connected in series to a water coolant source. Other modifications consisted in fitting the bearing shaft on both sides of the oil box with retainer gaskets, replacing the standard steel bearings with special bronze bearings, installing a thermocouple in the test oil with the junction ¼ inch below the bottom test cup, installing a temperature recorder-regulator to be actuated by the thermocouple, installing a solenoid controlled cooling water valve actuated between limits by the temperature regulator, mounting two 200 watt infra red heating lamps focused into the oil box and actuated by the temperature regulator, and installing a shield over the test cups to prevent direct heating of the cups.

Test procedure

Two Timken test cups are weighed to the nearest milligram and fastened in place on their respective shafts. The oil box is positioned in the carriage with knife edges in place; the thermocouple junction is adjusted to one quarter of an inch below the lower cup; the plate holding the oil seal is tightened; the coupling links are inserted on the upper and lower shafts and the oil box locked into position.

A twenty pound scale load is applied by hand and the cup alignment checked for perfect contacting edges and adjusted if necessary. The twenty pound load is released and the water lines are connected.

The oil is to be tested is then added until the lower test cup is half immersed. This oil level is maintained for the duration of the run by adding more oil when necessary. The oil box bearings are lubricated with the oil to be tested.

With the temperature recorder-regulator in operation, the machine is started and the load is taken up to fifty pounds, where it is maintained for a break-in run of one-half hour. At the end of the break-in the load is brought up to 110 pounds by the automatic loading device where it is held constant for fifteen hours, the duration of the test.

The temperature of the test oil is cycled between 200°–250° F. over a fifteen minute period, by the temperature regulator. Immediately after the application of the 110 pound load the rate of coolant water flow and the distance of the two heating lamps from the oil box are adjusted to obtain a smooth symmetrical heating and cooling curve as drawn by the recorder.

face disturbance than does the top ring, a phenomenon for which there are several theoretical explanations.

The inspection terminology used in describing the ring surface is essentially that given in the C. R. C. Designation L–20–545, namely: (a) burnish, (b) smoothing, (c) rippling, (d) ridging, (e) pitting and (f) galling. Burnish is an alteration from the original ground dull surface to a brightly polished surface and is usually accompanied by some alteration in or elimination of the grinding marks. Smoothing is the elimination or near elimination of the grinding marks where the surface finish usually remains dull. Rippling is the formation of transverse surface patterns, dull or shiny, resembling fish scales or ripples on water. Ridging as here used is a longitudinal furrowing or channeling as a result of a wearing force. This is actually a misnomer as grooving would be a more accurate descriptive term. Frequently rippling appears in the base of the groove indicating this may have been the precursor of grooving or ridging. Pitting is the formation of small pit-like cavities. Galling is difficult to describe but refers to a surface alteration which appears to be a slight lengthening, widening, deepening and blackening of individual grinder marks. This may be due to localized chemical attack.

Rating

Rating is the direct result of C. R. C. L–20–545 correlation. By a study of a backlog of samples upon which the "L–20" results were known, a basis for the overall appraisal of the test specimens was established permitting a final classification as an "L–20" pass or failure. A passing test rarely shows a total weight loss of more than 20 mg. and no light ridging. A test rated "fail" usually shows a weight loss of appreciably more than 20 mg. although it may in some cases be appreciably less. However, all of the described surface disturbance conditions may appear and usually do in the more severe failures.

A tabulation of top and bottom test ring observations is shown in the table below:

Oil Additive, Example No.	Percent on Oil	Ring	Ridging	Rippling	Wt. Loss, mg.	Final Rating
2	18	top	3 bands	trace	7	pass.
		bottom	do	do	9	
3	18	top	0	do	6	Do.
		bottom	0	do	8	
4	18	top	0	do	10	Do.
		bottom	0	do	14	
5	10	top	0	do	5	Do.
		bottom	0	do	9	
6	18	top	0	0	5	Do.
		bottom	0	0	17	
7	18	top	0	trace	11	Do.
		bottom	0	0	12	
8	18	top	trace	trace	4	Do.
		bottom	0	do	11	
9	10	top	0	do	7	Do.
		bottom	0	do	10	
10	18	top	0	do	8	Do.
		bottom	0	do	13	
11	18	top	0	do	10	Do.
		bottom	0	do	8	
11	10	top	0	do	4	Do.
		bottom	0	do	8	

Inspection

Upon completion of the test, the test cups are cleaned and reweighed to the nearest milligram for total weight loss, then inspected microscopically, oiled and filed for future reference. The rating of the completed test depends primarily upon the visual inspection of the test cups. In most instances the bottom ring shows more surface disturbance than does the top ring.

A series of preparations were carried out in which glycol di-oleate was sulfurized by heating with sulfur in the ratio of 37 parts by weight of sulfur to 436 parts by weight of glycol di-oleate. Except for Example 13, an atmosphere of hydrogen sulfide or nitrogen was employed. Phosphorus sesquisulfide was then added and the mixture heated to effect phosphorization.

In Examples 12 and 19 glycol di-oleate containing some oleic acid was employed. Thus, the neutralization number of the material employed in Example 12 was 19.9 and in Example 19 it was 13.1. The table below illustrates a variety of conditions and ratios under which the sulfurization and phosphorization have been successfully carried out.

Example	12	13	14	15	16	17	18	19	20	21
Time of sulphurization, hrs	7	7	13.5	7.5	7.5	7.5	7.5	7.5	9	7.5
Approximate ave. temp. of sulphurization, °C	170	170	170	180	180	180	180	180	180	180
P_4S_3, parts by weight	2	4	2.5	1	2	2.5	3	4	2	3
Time of phosphorization, hrs	5	5	10	5	5	5	5	5	5	5
Approximate ave. temp. of phosphorization, °C	107	107	107	107	107	107	107	107	107	126

The sulfur content of Examples 12–21 averaged about 7.6% and phosphorous ranged from 0.14% in Example 15 to 0.47% in Example 19. The neutralization number varied from 3.7 to 10.6, the average being 7.3.

A summary of the modified S. A. E. test described above on oils containing these products is tabulated below:

Oil Additive, Example No.	Percent on Oil	Ring	Ridging	Rippling	Wt. Loss, mg.	Final Rating
12	18	top	0	trace	8	pass.
		bottom	0	do	14	
13	18	top	a few bands	do	6	Do.
		bottom	0	light	13	
14	10	top	incipient	trace	4	borderline. pass.
		bottom	do	light	11	
15	18	top	0	trace	10	Do.
		bottom	0	do	8	
16	18	top	0	0	5	Do.
		bottom	0	trace	8	
16	10	top	0	do	10	Do.
		bottom	0	do	11	
17	10	top	trace	0	11	Do.
		bottom	0	trace	9	
18	10	top	0	do	9	Do.
		bottom	0	do	6	
19	18	top	0 (1 band)	do	5	Do.
		bottom	0	trace (1–2 bands)	8	
19	10	top	1 band edge 0	0	9	Do.
		bottom	0	0	8	
20	18	top	1 band 0	0	12	Do.
		bottom	0	light	10	
21	18	top	light	trace	9	borderline. pass.
		bottom	0	light	17	

As still further embodiments of the invention, glycol di-oleate was sulfurized by heating with sulfur in the ratio of 41 parts by weight of sulfur to 436 parts by weight of glycol di-oleate. Phosphorus sesquisulfide was then added and the mixture heated to effect phosphorization. The conditions of reaction are set forth in the following table. Examples 22 and 25 were prepared by heating in an atmosphere of hydrogen sulfide or nitrogen but no extraneous atmosphere was used in the case of Examples 23 and 24.

Example	22	23	24	25
Time of sulfurization, hrs	7.5	7.5	7.5	7.5
Approximate average temperature of sulfurization, °C	180	180	180	180
P_4S_3, parts by weight	1	2	3	4
Time of phosphorization, hrs	5	5	5	5
Approximate average temperature of phosphorization, °C	107	107	107	107
Sulfur in final product, percent	8.2	8.3	8.4	8.5
Phosphorus in final product, percent	0.11	0.23	0.35	0.46

The sulfur and phosphorus figures given in the above table are in general the average from several identical preparations. The neutralization number varied from 4.5 to 16.6, the average being 10.4.

EXAMPLE 26

Sulfurization and phosphorization of diethylene glycol di-oleate was carried out in at atmosphere of hydrogen sulfide. 436 parts by weight of diethylene glycol di-oleate was heated 7 hours at 169–171° C. with 34.5 parts by weight of sulfur. 6 parts by weight of phosphorus sesquisulfide was then added and heating under hydrogen sulfide continued for 5 hours at 104–109° C. The product was soluble in mineral oil and had a neutralization number of 10.6. Analysis gave 0.80, 0.90% phosphorus and 8.02% sulfur.

EXAMPLE 27

Sulfurization and phosphorization of dithio diglycol di-oleate was carried out in an atmosphere of nitrogen. 250 parts by weight of dithio diglycol di-oleate was heated with 14.9 parts by weight of sulfur for 7½ hours at 178–182° C. 1.5 parts by weight of phosphorus sesquisulfide was then added and heating under nitrogen continued for 5 hours at 104–110° C. The product was diluted with petroleum ether, filtered through a bed of clay and the solvent removed by vacuum stripping up to 95° C./3 mm. An oil soluble product was obtained which contained 11.4% sulfur and 0.16% phosphorus.

The compositions of Examples 22–27 were added to mineral oil and subjected to the modified S. A. E. test described. The results are summarized below:

Oil Additive Example No.	Percent on Oil	Ring	Ridging	Rippling	Wt. Loss, mg.	Final Rating
22	18	top	0	trace	10	pass.
		bottom	0	do	8	
23	18	top	0	do	6	Do.
		bottom	0	do	6	
24	18	top	0	do	8	Do.
		bottom	0	trace-light	13	
24	10	top	0	trace	12	Do.
		bottom	0	do	10	
25	18	top	0	light	7	Do.
		bottom	0	do	7	
26	18	top	0	some pitting	12	borderline.
		bottom	0	light	13	pass.
27	10	top	3 bands 0	0	4	Do.
		bottom	0	trace	10	
27	5	top	0	do	9	Do.
		bottom	0	do	7	

It is evident from the foregoing examples that glycol di-esters of unsaturated fatty acids may be sulfurized and phosphorized under a variety of conditions and that mineral oil fractions containing these products in minor proportion are eminently satisfactory heavy duty lubricants. In addition, the esters may be reacted with sulfurizing and phosphorizing agents in different ratios than those specifically mentioned. Obviously, sulfurized esters may be produced by elimination of the phosphorizing step. For example, 654 parts by weight of glycol di-oleate was heated with 55.5 parts by weight of sulfur under an atmosphere of nitrogen for 7½ hours at 181–186° C. In another typical preparation glycol di-oleate was sulfurized by heating 1275 parts by weight of the ester and 96 parts by weight of sulfur for 8 hours at 181–184° C. The reaction product was then heated with approximately 5% by weight of Attapulgus clay at 100° C. and filtered. Other sulfurizations were carried out in similar manner. The glycol di-oleate was heated with sulfur at a temperature within the range of 180–188° C. for 7½ hours, then heated with Attapulgus clay and filtered through a layer of diatomaceous silica. The series of preparations is summarized in the following table in which the sulfur is expressed as parts by weight per 436 parts by weight of glycol di-oleate.

Example	28	29	30
Sulfur	32.8	37	42.7
Percent Sulfur in product	6.11	7.68	8.2

Copper strip tests showed that the sulfurized products were not corrosive to copper. The tests were conducted by immersing a clean bright copper strip in mineral oil containing 5% of the sulfurized ester and heating 1 hour at 150° C. In addition, S. A. E. 90 grade gear oil lubricant compositions were compounded from a Mid-Continent solvent refine oil as follows:

Composition A:
Oil+6.0% product of Example 28.
2.0% chlorinated kerosene (58–67% Cl).
0.5% mixture of mono- and di-lauryl phosphate.

Composition B:
Oil+10.0% product of Example 29.
2.0% chlorinated paraffin wax (40% Cl).
0.4% mixture of mono- and di-lauryl phosphate.

Composition C:
Oil+6.0% product of Example 30.
2.0% chlorinated kerosene (58–61% Cl).
0.5% mixture of mono- and di-oleyl phosphate.

These compositions were subjected to the modified S. A. E. test to determine their wear resisting properties. The results are summarized below:

Composition	Ring	Ridging	Rippling	Wt. Loss Mg.	Final Rating
A	top	0	0	2	pass.
	bottom	0	0	9	
B	top	incipient	trace	1	borderline.
	bottom	0	0	8	pass.
C	top	0	0	6	Do.
	bottom	0	0	14	

In addition to gear lubricants, other types of compositions may be compounded from the new adjuvants, as for example crankcase lubricants, spindle oils, turbine oils, insulating and transformer oils, slushing compositions, greases, etc. Effective non corrosive cutting oils have been prepared. For instance, the addition of either of 5% or 10% of sulfurized and phosphorized glycol di-oleate to a 100″ paraffin oil provided compositions exhibiting high Oster threading efficiency and high tapping efficiency. Copper corrosion tests were carried out in the usual manner. The strips were bright after either 24 hours at room temperature or 3 hours at 140° F.

While the invention has been described by reference to a large number of representative examples, it will be appreciated that these are by no means the only compositions which may be employed. Satisfactory products have been made containing from 5.8% to 11.4% sulfur. Compositions analyzing from 0.11% to 0.8% phosphorus have been examined and all have proved to be satisfactory. In general the products may be prepared by heating the base with 1–12% sulfur and then with 0.2–2.0% phosphorus sesquisulfide. In some instances substantially neutral products have been prepared but for the most part they exhibit a mildly acid reaction. So far as is known, this is not a critical feature since all of the products proved to be substantially equivalent over the range stated. Products having neutralization numbers up to 18.6 have been examined.

The conditions of carrying out the reaction are also subject to variation. However, in general no advantage is obtained by conducting the sulfurization at higher temperatures or for longer times than those illustrated above. In fact, the products are then generally less satisfactory and contain less sulfur than products prepared under milder conditions. Lower temperatures may be employed where desired in which case it is advantageous to employ a sulfurization catalyst in order to secure a rapid rate of reaction. Small amounts of acidic materials, as for example toluene sulfonic acid, sulfuric acid, phosphoric acid and the like may be employed to catalyze the sulfurization.

Although the preparation of the phosphorized esters by means of phosphorus sesquisulfide has been described in specific examples, it will be understood that other phosphorus compounds may be used such as phosphorus trichloride, phosphorus oxychloride, phosphorus pentasulfide, phosphorus pentoxide as well as elemental phosphorus and other phosphorus compounds.

The additives of this invention not only are not corrosive but possess marked corrosion resisting properties and may be employed in conjunction with other types of additives which would otherwise be corrosive. They are compatible with mineral oil fractions in high proportions and with most other types of materials employed in the compounding of mineral oil lubricants. They may be used in conjunction with such products as chloronaphtha ethyl xanthate, di-trichlorobenzyl trithiocarbonate, di(ethylene glycol mono oleate) malate, and other esters, halogen bearing esters, halogenated hydrocarbons, phosphorus bearing esters and the like. In addition, the additives may be supplied in the form of concentrates or in other words, mixtures of lubricating oil and of additives in which the additives are present in amounts appreciably higher than those ultimately appearing in the mineral oil lubricant, as for example 75 parts of sulfurized ester and 25 parts of mineral oil.

The present invention is limited only by the claims attached hereto as part of the present specification.

What is claimed is:

1. A composition of matter useful as a lubricant consisting essentially of a major amount of mineral oil the lubricating properties of which are enhanced in the respect that the wearing of lubri-

cated metal surfaces is reduced by having incorporated therein in amount effective to reduce wear an additive composition containing 5.8%–11.4% sulfur and 0.11%–0.80% phosphorus supplied essentially by a sulfurized and phosphorized ester of the group consisting of ethylene glycol dioleate, diethylene glycol dioleate and dithio diglycol dioleate obtained by heating with sulfur at 150–200° C. and phosphorizing at 100–125° C.

2. A composition of matter useful as a lubricant consisting essentially of a major amount of mineral oil the lubricating properties of which are enhanced in the respect that the wearing of lubricated metal surfaces is reduced by having incorporated therein 5%–18% based on the oil of a sulfurized and phosphorized di-oleate of a dihydric glycol selected from the group consisting of ethylene glycol, diethylene glycol and dithio diglycol containing 5.8%–11.4% sulfur and 0.11%–0.80% phosphorus obtained by sulfurizing at 150–200° C. and phosphorizing at 100°–125° C.

3. A composition of matter useful as a lubricant consisting essentially of a major amount of mineral oil the lubricating properties of which are enhanced in the respect that the wearing of lubricated metal surfaces is reduced by having incorporated therein 5%–18% based on the oil of sulfurized and phosphorized ethylene glycol dioleate containing 5.8%–8.6% sulfur and 0.11%–0.80% phosphorus obtained by sulfurizing at 150–200° C. and phosphorizing at 100–125° C.

4. A composition of matter useful as a lubricant consisting essentially of a major amount of mineral oil the lubricating properties of which are enhanced in the respect that the wearing of lubricated metal surfaces is reduced by having incorporated therein at least 0.1% by weight based upon the mineral oil of a sulfurized and phosphorized ethylene glycol di-oleate containing 5.8%–11.4% sulfur and 0.11%–0.80% phosphorus obtained by heating the ester with sulfur at 150–200° C. and with a phosphorus sulfide at 100–125° C.

EDWARD S. BLAKE.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,179,067	Smith	Nov. 7, 1939
2,186,646	Lincoln et al.	Jan. 9, 1940
2,211,231	Henderson	Aug. 13, 1940
2,211,306	Whittier	Aug. 13, 1940
2,225,365	Bray	Dec. 17, 1940
2,415,838	Musselman et al.	Feb. 18, 1947
2,422,630	Musselman et al.	June 17, 1947
2,441,587	Musselman	May 18, 1948
2,483,600	Stucker	Oct. 4, 1949
2,541,789	Stucker	Feb. 13, 1951
2,542,161	Stucker	Feb. 20, 1951