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MINERAL OIL LUBRICANT CONTAINING SULFURIZED AND PHOSPHORIZED PROPYLENE AND BUTYLENE GLYCOL ESTERS OF OLEIC ACID

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This invention relates to lubricants and additives and, more particularly, to additives which have the ability to render a blend of lubricating oil with the additive capable of carrying a high load and also showing a low pour point.

In United States Patent 2,211,306, of August 13, 1940, to Whittier, assigned to The Pure Oil Company, there is disclosed and claimed a process for preparing an extreme pressure lubricant additive which involves sulfurizing a fatty body or oil and subsequently phosphorizing the sulfurized product. Such extreme pressure additives have been in successful use for many years, and have proved to be quite satisfactory. However, when made from ordinary fatty oils, such as lard oil, these additives have one disadvantage, namely, the lubricant which is a blend of the additive with a mineral oil does not have as low a pour point as might be desired. In addition to this disadvantage, the lubricants also display a somewhat limited compatibility with Mid-Continent solvent refined oils.

Accordingly, it is an object of the invention to provide an extreme pressure additive which when blended with minerals oils will endow the blend with low pour point characteristics and improved compatibility with Mid-Continent solvent refined oils.

Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

I have discovered that sulfurized and phosphorized extreme pressure additives displaying high load carrying characteristics and low pour points can be prepared in accordance with the method disclosed and claimed in United States Patent 2,211,306, if the fatty body is an ester of a polyhydroxy alcohol and a monoethenoid acid having the general formula $C_nH_{2n-2}O_2$, and containing from about 10 to 24 carbon atoms in the molecule. In particular, I have found that the esters of glycerol and glycols having more than 2 carbon atoms are valuable starting materials. Compounds suitable for the preparation of additives in accordance with my invention include esters of decenoic, myristoleic, palmitoleic, oleic, erucic, and tetracosenoic acids combined with any one of the polyhydroxy alcohols, such as glycol, glycerol, propylene glycol and butylene glycol as typical examples. Although it is preferable, generally, to use compounds which are completely esterified alcohols, those in which only partial esterification has taken place are also suitable, for example, the mono-, di- and tri-

esters of glycerol and mono- and di-esters of glycols can be used.

In preparation of the sulfurized-phosphorized base, the sulfurization can be carried out using flowers of sulfur or a sulfur compound. Similarly, the phosphorization can be accomplished with elemental phosphorus or a phosphorus compound. When the fatty material or ester is cooked with the sulfur or phosphorus compound, it is customary practice to do so in an open kettle while stirring the reactants. However, better results in the form of precise control over the reaction and the product are obtainable when the sulfurization or phosphorization reaction is conducted by blowing air through the reaction mixture at a rate sufficient to make the reaction self-sustaining thermally. This process is described in detail in United States Patent Application, Serial Number 636,286, filed December 20, 1945, by Elmer W. Brennan and Norman D. Williams (now Patent No. 2,483,571).

Instead of using pure polyhydroxy alcohol-mono-ethenoid acid esters, compositions may be used which contain small amounts of polyethenoid acids or esters thereof as well as small amounts of ethanoid compounds. Compositions deviating from pure compounds are exemplified by such products as partially hydrogenated sunflower, corn and rapeseed oils in which the hydrogenation is carried to a point where the acid radicals having more unsaturation than a single double bond are hydrogenated to a single double bond radical. Olive oil is fairly satisfactory as a starting material. In general, the fatty acid content of compositions useful as starting materials in accordance with my invention should be not less than 80 per cent of monoethenoid acids and not more than 10 per cent of acids of greater unsaturation.

In order to demonstrate the invention a composition was prepared by mixing 5 parts by weight of Gulf Coast mineral oil (having a Saybolt viscosity at 100° F. of 200 to 210 seconds, and at 210° F. of 43 to 45 seconds) and 87.6 parts by weight of glycerol oleates composed of approximately 70 per cent by weight of glycerol trioleate, 20 per cent by weight of glycerol dioleate and 10 per cent by weight of glycerol monooleate. The mixture was slowly heated to a temperature of approximately 270° F., whereupon 7.4 parts by weight of finely ground flowers of sulfur was added over a period of about 10 minutes. After the addition of the sulfur was completed the mixture was raised to a temperature of approxi-

mately 330° to 340° F. and held at this temperature with constant agitation. When a copper strip immersed therein for a period of 2 minutes showed no black coating, the reaction was taken to be complete. This required approximately 7 hours. The mixture was then cooled rapidly to approximately 150° F. and slowly to room temperature. To 99.6 parts of the sulfurized base thus prepared was added 0.4 part by weight of finely divided phosphorus sesquisulfide and the mixture heated with constant agitation to a temperature of approximately 220° to 230° F. The heating was continued for a period of approximately 5 hours and the mixture then allowed to cool. The resulting product was non-corrosive to the copper strip test and did not fume when heated to 300° to 350° F. Blends of 18 per cent by weight of the sulfurized-phosphorized product with mineral oil were prepared to obtain compositions corresponding to an 80 S. A. E. and a 90 S. A. E. gravity oil. These blends were tested for viscosity, viscosity index, pour point, and Timken test and compared with similar blends of phosphorized-sulfurized lard oil made in accordance with the specific example set forth in the manner just described in which glycerol oleates were used. The results of these tests are set forth in the following table:

Table I

	Examples					
	#1	#2	#3	#4	#5	#6
Composition, percent By Weight:						
100 GCO[1]	41	82	------	------	------	------
200 GCO[2]	41	------	41	63	------	------
160 GCO[3]	------	------	41	19	------	------
GCO[4]	------	------	------	------	82	------
GCO[5]	------	------	------	------	------	84
S-P Lard Oil	18	------	18	------	------	------
S-P Glycerol Oleate	------	18	------	18	------	------
S-P Ester[6]	------	------	------	------	18	15
Dibenzyl Disulfide	------	------	------	------	------	1
Saybolt Viscosity, @ 100° F	353	308	1,248	924	1,116	1,436
Saybolt Viscosity, @ 210° F	59.8	56.8	91.1	86.1	81.9	89.1
V. I.	116	123	79	98	68	57
Pour, °F	+10	−30	+5	−20	−5	0
Timken Test:[7]						
Load	71	77	68	86	43	33
Beam	39.5	39.5	35.0	38.0	30.0	29.0
S.A.E., @ 750 R.P.M.	------	------	------	------	155	275

[1] 100 Viscosity Gulf Coast Pale Oil.
[2] 200 Viscosity Gulf Coast Pale Oil.
[3] 160 Viscosity Gulf Coast Bright Stock at 210° F.
[4] Blend of Gulf Coast Pale Oil and Bright Stock to desired viscosity.
[5] Blend of Gulf Coast Pale Oil and Bright Stock to desired viscosity.
[6] S-P Ester—Propylene glycol dioleate.
[7] Timken test: load in pounds; beam in thousands of pounds per square inch.

From an inspection of the table, it is apparent that the blends made by sulfurizing and phosphorizing the glycerol oleate had higher viscosity indexes than the sulfurized-phosphorized lard oil blends, and the pour points of the sulfurized-phosphorized glycerol oleate blends were considerably lower. For example, the 90 S. A. E. grade, #4 in the table, had a pour point 30 degrees lower than the 80 S. A. E. grade made from the lard oil, #1 in the table. The Timken tests for the sulfurized-phosphorized glycerol oleate compositions were at least as good as the sulfurized-phosphorized lard oil compositions, and, in general, were superior from a load carrying standpoint.

Blends prepared in accordance with the second and fourth examples in the table were subjected to actual service tests in the transmissions and differentials of a number of different automobiles. After 4,000 to 5,000 miles of operation, the gears showed no evidence of wear, and the lubricant exhibited high stability. Low temperature characteristics of the lubricant were excellent as evidenced by the fact that after the automobile had been allowed to stand outdoors at temperatures approaching minus 10° F. the gears could be shifted with ease.

Additional blends of extreme pressure additives made from sulfurized-phosphorized propylene glycol dioleate and Mid-Continent solvent refined oils were made and tested. It was found that the propylene glycol dioleate, in addition to making a good extreme pressure additive, also displayed unusual compatibility with the Mid-Continent solvent refined oil. In regulating the compatibility of this additive with the Mid-Continent solvent refined oil, it is well to employ a relatively pure oleic acid in the preparation of the ester, because the 5 to 18 per cent of polyethenoid acids occurring in commercial oleic acid detract from the compatibility of the sulfurized phosporized material, and will cause the separation of a small amount of tarry matter from the blends. In the following table, there are summarized the properties of a few typical blends made from propylene glycol dioleate and Mid-Continent solvent refined oils in combination with a few additives:

Table II

	Examples			
	#1	#2	#3	#4
Composition, percent By Weight:				
S-P Base[1]	18	15	15	15
MCSR Oil[2]	82	84	83.5	83.9
Dibenzyl Disulfide	------	1	1	1
Acryloid 150[3]	------	------	0.5	0.1
Saybolt Viscosity @ 100° F	746	764	752	762
Saybolt Viscosity @ 210° F	81.6	82.1	82.9	82.3
V. I.	109	103	110	109
Pour, °F	10	10	−20	5
Channel, °F	------	−10	Below −30	−30
Timken[4] Test:				
Load	------	------	51	------
Beam	------	------	25.0	------
S. A. E. at 750 R. P. M.	------	------	155	------

[1] S-P Base: sulfurized-phosphorized propylene glycol dioleate.
[2] MCSR Oil: Mid-Continent solvent refined oil.
[3] A pour detressant for the oil, available commercially as a polymeric fluid, it is a methyl methacrylate polymer having the following properties: specific gravity, 60/60, 0.89; viscosity at 210° F. 3100 S. U. S.; viscosity at 100° F. 27500 S. U. S.
[4] Timken Test: load in pounds; beam in thousands of pounds per square inch.

It should be noted that blend No. 3, shown in Table II, displays unusual properties which make it perform like an S. A. E. 80–S. A. E. 90 grade lubricant, because the channel and extrapolated viscosity at zero Fahrenheit meet the requirements of the S. A. E. 80 grade, while the viscosity at 210° F. places it in the S. A. E. 90 grade. Not only do the bench tests and graphs of its physical properties point to its unusual nature, but actual field tests indicate it to be a superior lubricant, as the test described below will establish.

A new clean differential unit was installed in a 1946 De Soto sedan in which the axle housing had previously been thoroughly cleaned. The housing was filled with the test lubricant corresponding in composition to No. 3 above, and the car was driven for ten miles at a rate of 30 miles per hour in order to warm the engine and provide a moderate amount of rear axle break in. The car was then driven for 1,000 miles at high speed,

60 to 90 miles per hour. At the end of this period, the rear axle unit operated perfectly quietly and on disassembly, the ring, pinion and differential gear were found to be in essentially their pristine condition, for they showed no trace of scoring.

In preparing the additive in accordance with my invention, sulfurization may be effected by means of elemental sulfur in an amount of from 1 to 10 per cent by weight, and preferably 5 to 8.5 per cent by weight of sulfur based on the sulfurized product. Also the base can be prepared by sulfurizing the ester in accordance with the method disclosed in United States Patent 2,352,818, of July 4, 1944, to Whittier et al., using approximately 5 to 15 per cent by weight of the sulfur chloride based on the ester. The phosphorization step is preferably effected by means of phosphorus sesquisulfide at temperatures of about 220° to 230° F., but other phosphorus compounds, including halides, oxyhalides, sulfides, and oxides such as phosphorus trichloride, phosphorus oxychloride, phosphorus pentasulfide and phosphorus pentoxide, as well as elemental phosphorus and compounds such as tin phosphide, may be used. The amount of phosphorus in the base should not exceed 2 per cent, and preferably should be only a fraction of 1 per cent, for example 0.2 to 0.6 per cent based on the weight of the sulfurized base.

It will be seen, therefore, that by sulfurizing and phosphorizing a fatty body composed chiefly of esters of polyhydroxy alcohols and monoethenoid acids a lubricant additive having high load carrying characteristics and unexpected low temperature characteristics can be obtained. Additives made in accordance with my invention may be used in lubricating oils in amounts ranging from approximately 0.5 to 20 per cent or more by weight of the finished lubricant depending upon the service for which the lubricant is intended. Although additives prepared in accordance with my invention may be blended with all types of mineral lubricating oil, I prefer to keep the amount of high viscosity-index oil, as exemplified by Mid-Continent solvent refined oil, to a minimum except when employing propylene glycol dioleate as the additive, because generally the sulfurized-phosphorized fatty materials have limited compatibility with high viscosity-index oil. The sulfurized-phosphorized propylene glycol dioleate appears to be unique in possessing the additional property of being quite completely compatible with the solvent refined oils.

This application is a continuation-in-part of my application Serial Number 653,438, filed March 9, 1946.

What is claimed is:

1. A lubricant comprising a major portion of a Mid-Continent Solvent Refined petroleum lubricating oil and a minor portion of a composition as the principal additive, effective to improve its load carrying characteristics, which additive consists substantially of a sulfurized and phosphorized ester from the group consisting of propylene and butylene glycol dioleates, the sulfur content of said additive being about 1 to 10 per cent, and the phosphorus content being about 0.2 to 0.6 per cent, said additive being soluble in said oil.

2. A lubricant in accordance with claim 1 in which the ester is sulfurized with sulfur in an amount equal to about 5 to 8.5 per cent by weight of the sulfurized product, and the sulfurized product is phosphorized with phosphorus sesquisulfide in an amount equivalent to 0.2 to 0.6 per cent of phosphorus based on the sulfurized product.

3. A lubricant in accordance with claim 1 in which the petroleum lubricating oil is a blend of Mid-Continent Solvent Refined bright stock and neutral oil, and the additive is a sulfurized-phosphorized propylene glycol dioleate.

4. A compounded mineral oil lubricant in accordance with claim 1 in which the additive is sulfurized and phosphorized propylene glycol dioleate.

5. A lubricant in accordance with claim 4 in which the sulfurized and phosphorized propylene glycol dioleate is present in an amount of about 15 per cent by weight of the total lubricant, and the lubricant contains about 1 per cent of dibenzyl disulfide.

6. A lubricant additive consisting of sulfurized and phosphorized ester from the group consisting of propylene and butylene glycol dioleates, said additive containing about 0.2 to about 0.6 per cent of phosphorus, and about 1 to 10 per cent of sulfur, and being soluble in Mid-Continent Solvent Refined blended oils.

7. A lubricant additive in accordance with claim 6 in which the ester is propylene glycol dioleate.

8. A lubricant additive in accordance with claim 7 in which the propylene glycol dioleate is sulfurized with elemental sulfur, and the sulfurized product is phosphorized with phosphorus sesquisulfide.

9. A lubricant additive consisting substantially of the phosphorized reaction product of sulfur and propylene glycol dioleate mixed with a small amount of mineral oil, said additive being soluble in Mid-Continent Solvent Refined petroleum lubricating oil and prepared by reacting about 5 to 8.5 per cent by weight of sulfur with propylene glycol dioleate, and then reacting the sulfurized product with 0.2 to 0.6 per cent by weight of phosphorus sesquisulfide based on the sulfurized product.

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