

## UNITED STATES PATENT OFFICE

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## LUBRICATING COMPOSITION

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This invention relates to lubricating compositions, and more particularly to such compositions comprising a major proportion of a mineral oil and a minor proportion of a wear-reducing agent. The invention relates also to an antiwear agent for lubricating oils and the process of preparing it.

It is customary to alter the characteristics of the usual mineral oil fractions of petroleum hydrocarbons employed for lubricating purposes, by incorporating therein various substances or additives capable of enhancing such properties of the oil as stability to oxidation, anticorrosivity, non-emulsibility, and the like. However, precaution must be taken in such practice since it is the rule rather than the exception to it that the addition of a substance to the oil to improve it in some one respect usually produces an undesirable result in one or more other respects. Thus, an attempt to improve the antiwear characteristics of a lubricant by incorporating a usual "extreme pressure" (E. P.) agent therein, may decrease the oxidation stability of the lubricant, may produce a corrosive lubricant, and/or may increase the tendency for emulsification which is particularly undesirable in turbine oils, etc. For example, organic chlorides which have been used extensively as extreme pressure agents in lubricants are both emulsifying agents and are corrosive. Certain organic phosphorus compounds which are employed in extreme pressure lubricants also possess both of these disadvantages. Some sulfur-containing E. P. agents possess similar undesirable characteristics. Thus, alpha mercapto stearic acid increases emulsification and decreases oxidation stability, while sulfurized sperm oil increases emulsification and decreases film tenacity of the oil.

It has been known that sulfurized products of derivatives of unsaturated fatty acids, such as their esters as for example in sperm oil, cottonseed oil, etc., impart "extreme pressure" characteristics to lubricants when incorporated therein in amounts greater than 0.1%, and preferably 1% or more. However, such substances are without any substantial effect upon the wear characteristics of lubricants incorporating them in amounts less than 0.1% by weight. Also, it has been known that sulfurized oleic acid, as prepared by the usual process employed for the preparation of sulfurized fatty oils, is too corrosive for use in lubricants in amounts commonly employed for imparting satisfactory extreme pressure characteristics to the lubricant.

It is an object of the present invention to pro-

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vide an organic lubricant having improved antiwear properties but without emulsion-forming or other deleterious properties. It is another object to provide a mineral oil composition having properties which render it especially suitable for use as a lubricant in turbines and similar mechanisms. Still another object is to provide a base substance which may be incorporated in mineral oil compositions to impart desirable antiwear characteristics to them, but which do not impart undesirable properties to such oil compositions.

Now, in accordance with the present invention it has been found that an improved organic lubricant composition can be prepared by incorporating in a suitable lubricating oil base a minor amount of an oil-soluble, liquid, sulfurized product of oleic acid, said sulfurized product being incorporated in the lubricant in an amount less than that normally required for it to function as an extreme pressure agent. It has been found further that a sulfurized product of oleic acid, which is especially suitable for the purpose of this invention, can be prepared by treating oleic acid with a sulfurizing agent under sulfurizing conditions with a molal ratio of sulfur to oleic acid which is greater than one to one and preferably less than two to one.

The sulfurized oleic acid may be prepared in accordance with this invention by reacting oleic acid with free sulfur at temperatures from about 150° C. to about 300° C. Generally, the amount of sulfur used to sulfurize the acid will be the molal equivalent of the unsaturation of the acid employed. However, the preferred molal ratio of sulfur to acid is from about 1.1 to about 1.4 (about 12.4% to 16% by weight sulfur based on the oleic acid). Higher ratios may be employed, but they do not result in any appreciable further improvement over that obtained by using a ratio of about 1.4. Consideration must be given, however, to the fact that with increasing proportions of sulfur to acid the solubility of the resulting sulfurized product in mineral oil decreases.

The following description of a preferred method used in the preparation of a sulfurized oleic acid in accordance with this invention is given for the purpose of illustration:

Oleic acid of a good commercial grade was heated in a suitable vessel to a temperature of about 150° C. The heated oleic acid was blanketed with an inert atmosphere, such as nitrogen, natural gas, etc., and then, for each mol of oleic acid, about 1.2 mols of sulfur flowers (corresponding to about 13.6% by weight sulfur based on the weight of oleic acid) was added to the heated

acid. The mixture was well stirred and maintained at a temperature of about 150° C. to 180° C. for a period of from about 3½ to 4 hours.

To the crude product was slowly added about 20% by weight of Super Filtrol while the temperature was maintained at about 140° C. to 160° C. After all of the clay (Super Filtrol) had been added and well mixed therewith, it was removed by filtration. The filtrate was then treated with an additional 10% by weight of Super Filtrol in the same manner as above and then filtered. The purpose of the clay treatment was to improve the color of the product by removing color bodies in the sulfurized material, which bodies appear to have undesirable sludging and corrosive properties. The exact nature of such color bodies is not known, but it would appear logical to assume that they comprise substances such as higher molecular weight polymerization products, and the like.

The recovered sulfurized oleic acid was a fairly viscous, reddish-yellow colored, clear liquid which was sufficiently soluble in lubricating oil compositions for the purpose of this invention. Analysis indicated a content of chemically combined sulfur which corresponded substantially to the sulfur content of the mixture of oleic acid and sulfur as mixed. Treatment with a solution of cadmium sulfate to form cadmium sulfide with any hydrogen sulfide, and then with mercury to combine with any free (elementary) sulfur indicated the substantial absence of both elementary sulfur and hydrogen sulfide.

The sulfurized oleic acid is incorporated in the lubricating oil base in the form of the free acid. Effective amounts in a turbine oil are in the order of 0.005% to 0.1% by weight of the oil, although quantities of between 0.01% and 0.05% by weight are usually preferred. The small amount of sulfurized oleic acid which is sufficient to accomplish the present purpose is much less than would be required to alter the other properties of the lubricating composition, including properties of other additive agents which may be incorporated therein. Thus, at the low concentration of the sulfurized oleic acid used here in the turbine oils, no resistance to extreme pressure wear (i. e., where seizure occurs) is obtained.

The effectiveness of sulfurized products of oleic acid prepared in accordance with this invention upon the antiwear characteristics of turbine oils was determined by use of the multiple four-ball machine similar in principle to the Boettlinger apparatus described in the publication, *Engineering*, vol. 136, July 14, 1933. This apparatus comprises four steel balls arranged in pyramid formation. The top ball is rotated by spindles against the three bottom balls which are clamped in a stationary ball holder. The balls are immersed in the oil to be tested. Tests were run for two hours at 700 R. P. M. under a 14.1 kilogram load and at 85° F. The diameters of the wear scars worn on the three balls forming the base of the pyramid were then measured, and the average taken as the true indication of wear. Results from tests using a highly refined turbine oil containing 0.25% by weight of di-tertiary butyl p-cresol as an antioxidant and a small but effective amount of a rust preventive agent, and to which was added 0.03% by weight, based on the oil, of various sulfurized products of oleic acid prepared by reacting varying weight ratios of sulfur and oleic acid in accordance with the previously described method of preparing the sul-

furized oleic acid products of this invention, are given below in Table I.

TABLE I

*Antiwear properties of turbine oils containing various sulfurized products of oleic acid*

| Sample No. | Sulfur Used Mol/Mol of Acid | Per Cent Total Sulfur in Product | Scar Diameter (in 1/1000 inch) |
|------------|-----------------------------|----------------------------------|--------------------------------|
| 1          | 1.37                        | 12.8                             | 10.7                           |
| 2          | 1.37                        | 12.9                             | 10.7                           |
| 3          | 1.5                         | 13.8                             | 11.5                           |
| 4          | 1.94                        | 15.8                             | 11.7                           |
| 5          | 2.92                        | 22.2                             | 12.2                           |
| 6          | 2.92                        | 25.8                             | 12.5                           |
| 7          | 2.92                        | 22.7                             | 12.5                           |
| 8          | 1.94                        | 15.8                             | 11.5                           |
| 9          | 2.92                        | 22.2                             | 11.7                           |

(Control: Same oil without sulfurized oleic acid, 22.0 scar diameter in 1/1000 in.)

1 Blend contained only 0.015% of the sulfurized product.

The results given in Table I show that the addition to the turbine oil of the small proportion of the sulfurized oleic acid products prepared according to the method of this invention reduced the scar diameters to a value only about one-half that obtained with the same oil, but which oil did not contain any of the sulfurized oleic acid. The results show also that the ratio of sulfur to oleic acid employed in the preparation of the sulfurized acid preferably should be not more than about two mols of sulfur per mol of acid. However, the results from using larger ratios show a substantial improvement over the oil containing none of the sulfurized oleic acid.

Oleic acid was sulfurized with sulfur in a molar ratio of one to one, following the same procedure as described hereinabove. The results of antiwear tests similar to those reported in Table I, using the resulting sulfurized oleic acid from a 1:1 molar ratio of sulfur to acid, are given below in Table II.

TABLE II

*Wear evaluation of turbine oils containing the product of sulfurizing oleic acid with sulfur in a mol to mol ratio of 1:1*

| Sample No. | Scar Diameter in 1/1000 inch (0.03% wt. blend) |
|------------|------------------------------------------------|
| 1          | 13.2                                           |
| 2          | 15.4                                           |
| 3          | 13.7                                           |
| 4          | 14.6                                           |
| 5          | 11.6                                           |

NOTE: An average total sulfur percentage of 10.2 in sulfurized oleic acid corresponds to a molal ratio of sulfur to oleic acid of one to one.

The results given in Table II demonstrate the advantage of incorporating in a lubricating oil a small amount of the sulfurized product of oleic acid obtained by reacting the acid with sulfur in a molar ratio of one to one. However, the data show that, when the molar ratio of sulfur to oleic acid is limited to 1 to 1, the change in the antiwear characteristics of the oil are not determined entirely by the amount of the sulfurized product added, but that it is dependent in some unknown manner upon the characteristics of the particular sample of sulfurized oleic acid employed.

The substantial constancy of the results given in Table I, in contrast to the variation of the results given in Table II, demonstrates that for

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best results when using sulfurized oleic acid in lubricating oils, the sulfurized acid should be prepared by reacting the oleic acid with more than one molal proportion of sulfur. Furthermore, the improvement in antiwear properties of the oil as evidenced by the comparative scar values, in general, was greater with the sulfurized acids prepared with a mol ratio of sulfur to oleic acid greater than one to one, than the improvement where the ratio was one to one. The results demonstrate, too, that this difference is not attributable to the fact that, with the same weight percentage of sulfurized product, there would be a larger weight percentage of sulfur in the former than in the latter compositions. For example, referring to the data given in Table I, 0.03% wt. of a sulfurized product having a total sulfur content of 12.8% wt. based on the sulfurized acid (sample No. 1) produced a scar diameter of only 10.7 thousandths of an inch, whereas 0.03% wt. of a sulfurized product containing 25.8% wt. of total sulfur resulted in a scar diameter of 12.5 thousandths of an inch (sample No. 6). Also, it will be noted that 0.015% of the sulfurized acid of sample No. 5 resulted in a smaller scar diameter than 0.03% of the same product (see sample No. 9).

Thus, it is seen that the improvement is not a simple function of the amount of sulfur incorporated in the oil composition. It is evident that the improvement depends upon the form of the sulfur in the sulfurized product, which in turn is dependent, at least partially, upon the ratio of sulfur to acid used in the preparation of the sulfurized acid. Analyses of the various sulfurized oleic acid products indicate that substantially all of the sulfur is in the combined form.

Although it is not fully understood why the sulfurized products containing substantially more than about 10.2% sulfur and obtained by reacting more than one molal proportion of sulfur with one molal proportion of oleic acid are antiwear agents superior to the products obtained by using a molal ratio of unity, it appears that the superiority may be associated with a difference in the molecular species in the products. There is evidence that the superior products contain a substantial proportion of a disulfide of a di-acid, that is, a product with a molecular weight twice that of the normal mono-sulfur-oleic acid reaction product whether the mono-product is an epithio type of compound or has some other structure. It is to be understood, however, that the invention is not to be construed as being limited in any way by any theory as to the explanation of the superior antiwear characteristics of the sulfurized oleic acid prepared in accordance with the present invention and with a sulfur to oleic acid mol ratio greater than unity.

The present invention is directed to the use of a small proportion not greater than 0.1% by weight of sulfurized oleic acid in lubricating oil

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compositions to improve the antiwear properties of the composition. However, it is contemplated, and it is within the scope of the invention, to incorporate in the lubricating composition other additives, such as antioxidants, antifoaming agents, pourpoint depressors, viscosity improvers, rust preventives, and the like. It will be understood, of course, that compounds, such as metallic salts, which react with the sulfurized oleic acid, should be avoided.

The sulfurized oleic acid may be incorporated in lubricating compositions having as base components substances other than mineral oils. Examples of other substances which may be utilized are vegetable oils as castor oil, synthetic lubricants as polymerized propylene oxide, and the like, organic silicones, etc.

Thus, in accordance with the foregoing description of the present invention, an improved lubricating composition may be prepared by incorporating in a lubricating oil a minor proportion, not greater than 0.1% by weight, of sulfurized oleic acid, and particularly a sulfurized product of oleic acid prepared by reacting sulfur with oleic acid in a mol ratio of sulfur to oleic acid greater than one to one. The reaction is preferably carried out in an inert atmosphere and the resulting sulfurized product is preferably given a treatment with an adsorbent purifying agent such as filter clay to improve its properties. The sulfurized oleic acid is of utility in lubricating compositions designed for different uses, particular utility being had in connection with turbine oils.

We claim as our invention:

1. A mineral lubricating oil having incorporated therewith from 0.01% to 0.05% of sulfurized oleic acid having a sulfur content of from 12.4% to 25.8%.

2. A turbine oil having incorporated therewith from 0.01% to 0.05% of sulfurized oleic acid having a sulfur content of from 12.4% to 25.8%.

3. As an additive for improving the anti-wear properties of turbine oils, a sulfurized oleic acid having a sulfur content from 12.4% to 25.8% said product being substantially non-corrosive.

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