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SULPHURIZED PRODUCT AND METHOD FOR MAKING THE SAME

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The present invention relates to an improved lubricant addition agent and to a method for making the same, as well as to lubricants containing the addition agent. The agent is of the sulphurized hydrocarbon type and its method of manufacture and use will be fully understood from the following description.

It has been known for many years that sulphur and sulphur compounds are excellent ingredients for oils and greases for the purpose of giving them increased load carrying capacity. The sulphur has been used in its elemental form but this is unsatisfactory because of its limited solubility, so that sulphur compounds are preferable. Of the various compounds used, the active types are preferred, by which is meant those types which will discolor a bright copper strip according to the familiar test of the petroleum industry. Such active materials do not corrode bearings or other metal in the sense that they are corroded by mineral acids and salt solutions, and they may be used without fear of injury to the finest metal bearings.

Heretofore the best active sulphur compounds have been made synthetically by treating fats or fatty oils with free sulphur, for example by heating to sulphurizing temperatures below about 300° F. The temperature and the amonut of sulphur are limited because the reaction is vigorous when it begins and side reactions, such as decomposition and polymerization, occur which are objectionable. These may be minimized by the use of the low temperatures, but not altogether avoided. The fatty materials have other objections which are apparent to those skilled in the art.

The above mentioned sulphurized products are not entirely satisfactory for two reasons. In the first place, it is difficult to make a material consisting mainly of saturated hydrocarbons absorb a sufficient amount of sulphur to carry the heavy loads required at high speeds. It has been found to be difficult, for example, to make a product that will carry the full load of 580 pounds on the S. A. E. testing machine, at a speed of 1,000 R. P. M. or higher. By mixing free sulphur with oils, the speed and load requirements can be met, but the amount of sulphur required is more than can be dissolved in the oil, and sulphur separates out which is highly objectionable. If it is attempted, on the other hand, to increase the degree of sulphurization sufficiently to hold the sulphur in permanent combination the product is lacking in load carrying capacity.

It has now been found that a two step process of sulphurization can be used which would produce a product which is free from most of these difficulties. It is capable, for example, of carrying the full load on the S. A. E. machine at 1,000 R. P. M., and sometimes even higher speeds, and shows no sulphur separation on long standing at average temperatures and temperatures as low as 0° F. The process referred to constitutes two steps; first, the material to be sulphurized, which is referred to herein as the sulphur carrier, is sulphurized either directly with sulphur or with sulphur chloride in a manner which will be described below. This product is not satisfactory for high speeds and loads, as indicated above, but when this preliminarily sulphurized material is blended with mineral lubricating oil and the blend is re-sulphurized with free sulphur, a product is obtained which not only carries the desired load but does this under conditions of high load and high speeds and shows no separation of sulphur on standing.

The so-called sulphur carriers referred to above are organic materials of several different classes, all of which may be described as materials which sulphurize more readily than mineral lubricating oils. Among these materials are the terpenes, such as pine oil and its related products, rosin and purified rosin, partially hydrogenated rosin, and esters of the rosin and hydrogenated rosin acids. Fatty oils and fats, especially lard oil and unsaturated hydrocarbons such as cracked oil or waxes, but preferably dehydrogenated oils and waxes which may be obtained by chlorination and dechlorination, and unsaturated oils made by the polymerization of hydrocarbon olefins such as ethylene, propylene and the butylenes, amylenes or copolymers thereof, and especially polymers of isobutylene may also be used. Of these last mentioned products, the polymers having molecular weights above 1,000 are to be preferred, but it will be understood that dimers, trimers and tetramers having molecular weights well below 1,000 can be used as well.

In carrying out the first sulphurization step, the organic carrier is mixed with a sulphurizing agent, for example free sulphur, in the absence of any saturated hydrocarbon oil. If free sulphur is used, the sulphur is added in a finely divided form, such as flowers of sulphur, in an amount from 2 to 10% or 15% by weight of the carrier material. The mixture is then thoroughly agitated and heated to a temperature in excess of 300° F. With different carrier materials, somewhat different temperatures are required for

initiating the reaction; the range is ordinarily from 300 to 500° F. and it is rarely necessary to go over 450° F. The time of heating may be from about 10 minutes to 1½ hours. For any given material, the time is shorter at the higher temperatures and a portion of the sulphur is evolved as hydrogen sulphide while the remainder is permanently bound to the carrier in chemical form. Sulphurization may be accomplished by heating under superatmospheric pressure, which prevents evaporation of volatile constituents.

If sulphur chloride is employed in the first sulphurization step, a lower temperature is ordinarily preferred, for example from room temperature to 300 or 350°, and the amount is preferably about up to 20%. Care should be taken in the use of sulphur chloride because it is a polymerizing agent as well and it is desirable not to polymerize fats or fatty oils so as to make them insoluble. The product made from sulphur chloride differs somewhat from the material made from sulphur, especially in the fact that it contains a small amount of chlorine, but this has little effect on the subsequent treatment or the behavior of the oil. The preliminarily sulphurized products made by either of the above mentioned methods are then blended with lubricating oils such as heavy distillates, residual cylinder stocks or bright stock. The amount added is usually from 3 to 15%. If the primary product is relatively richer in sulphur, a smaller amount may be added than when the material contains less sulphur. To this blend is now added an additional quantity of free sulphur and the mixture is resulphurized by heating to a temperature from 300 to 500° F. just as described above, for the sulphurization with free sulphur. As before, a time of 10 minutes to one or one and and one-half hours is required. The resulphurization of this material is readily obtained and the heating period is preferably as short as possible in order to effect the incorporation of the additional sulphur. The amount of the sulphur added in this step is from ½ to 2½% by weight of the total blend and care should be taken to effect its complete reaction without excessively long heating which is found to impair extreme pressure qualities. In this way, a very active sulphur product is obtained which is stable against sulphur separation. If all the sulphur is not reacted, then there may be some slight separation at first, but when this material is removed, it is substantially stable and its extreme pressure qualities do not depend on sulphur which is present in a free state. The total amount of sulphur present is from about 3.5% to 10.0% of the product.

The extreme pressure products made as disclosed above are useful as cutting oils or lubricants for other metal fabricating processes such as drawing, stamping and the like. They are excellent gear oils for extreme pressure work for example, in hypoid gears, etc. They also may be mixed with heavy metal soaps such as lead oleate, naphthenate or sulphonate, or the soaps of zinc, nickel, chromium or other metals, to give the properties desirable for special uses. With heavy metal soaps, the sulphurized materials made by the sulphur chloride method described above are not as desirable as those made with free sulphur because of the separation of heavy metal chlorides from the amount of chlorine contained in the original sulphurized product, but this difficulty is completely avoided if free sulphur is used or if specific means are taken to remove the residual chlorine from the products made by sulphurization with sulphur chloride.

The following inspections are characteristic of the products produced by the present process:

Type	I Dechlorinated wax	II Pine oil	III Lard oil
Viscosity @ 100° F.	2178	3657	2275
Viscosity @ 210° F.	149	167	156
V. I.	104	102	105
Sulphur (total)—percent	2.34	3.05	2.25

Example I

Pine oil unadmixed with other ingredients is sulphurized by heating with free sulphur until 23% by weight has been incorporated preferably at greater than atmospheric pressure. To a heavy lubricating oil, 5% of this sulphurized product was then added. This sample was designated as sample I. To a portion of sample I was mixed 2% by weight of flowers of sulphur and the mixture was heated for 10 minutes at 325° F., and then cooled rapidly. This material was designated sample II.

The two samples referred to above were then tested for lubricating qualities first on the Almen machine and both were found to carry the full load of 15 weights. They were then compared by tests on the S. A. E. testing machine having a rubbing ratio of 14.6 to 1 and a loading rate of 83.5 pounds per second at a speed of 1,000 R. P. M. Sample I failed on this test but sample II carried the full load successfully. Both samples were stable when stored for 7 days at 0.° F., showing no more than a slight trace of sulphur separation.

Attempts were made to admix pine oil with mineral oil and sulphurize this mixture. Much of the pine oil was found to vaporize and prolonged heating was necessary to make a sulphur stable product. When so obtained, the product was not capable of passing the S. A. E. test.

When sample II prepared as above was blended with 10% of lead naphthenate, an excellent leaded oil was obtained capable of passing the most exacting of the hypoid lubricant specifications.

Example II

Lard oil was sulphurized to the extent of 8.2% by heating at 350° F. for 15 minutes with flowers of sulphur. A blend containing 5% of this product was made up with a mineral lubricating oil and was designated sample III. Sample IV was made up by sulphurizing a portion of sample III with 2% by weight of additional sulphur and heating for 10 minutes at 350° F. Sample III failed in the test on the S. A. E. machine referred to in Example I, but sample IV carried the full load successfully just as sample II in the first example. This product was likewise sulphur stable.

Example III

Wax was chlorinated to the extent of 20% by weight by blowing the melted wax with chlorine. The chlorinated wax was dechlorinated by heating to 650° F. until no more acid vapors were evolved. To 90 parts of the dechlorinated wax, 10 parts by weight of sulphur were added and the mixture heated to 390° F. until the sulphur had combined.

Five parts of the sulphurized product were now

blended with 93 parts of cylinder oil and two parts of free sulphur. This mixture was agitated and heated to 350°, being held at that temperature for a period of 15 minutes and then quickly cooled. This product passed the test on the S. A. E. machine at a speed of 1140 R. P. M. and showed no sulphur separation on standing for 7 days at 0° F. Many attempts were made to obtain a satisfactory product with one step of sulphurization, but they were unsuccessful either failing to give sufficient extreme pressure properties or because of the continued separation of sulphur on standing.

Example IV

An oil prepared by polymerizing isobutylene was sulphurized by adding 5% of sulphur and heating to 450° F., and maintaining that temperature for 15 minutes. When 10% of this sulphurized polymer oil was blended with mineral lubricating oil, it was found that a product of good color, odor and appearance was obtained. It carried the full load on the Almen machine but failed on the more severe S. A. E. test. When the blend was resulphurized with 2% sulphur, a product was obtained which was entirely satisfactory on the S. A. E. machine and was completely stable to sulphur separation.

The present invention is not limited to any theory of the operation of the process nor to any particular means for effecting sulphurization, but only to the following claims in which it is desired to claim all novelty inherent in the invention.

I claim:

1. An improved method for preparing sulphurized oils which comprises preliminarily sulphurizing an unsaturated organic substance, then blending the preliminarily sulphurized product with mineral oil and resulphurizing the blend with free sulphur by heating with free sulphur.

2. An improved method for preparing sulphurized oils which comprises preliminarily sulphurizing an unsaturated organic material by heating with free sulphur, then blending this product with a major amount of a mineral lubricating oil and resulphurizing this blend by heating with free sulphur at a temperature between about 300 and 500° F., from about ten minutes to one hour, whereby a sulphur stable oil having extreme pressure properties is obtained.

3. Method according to claim 2 in which the initial sulphurization takes place at a temperature from about 300° to 500° F., and with 2 to 10% of free sulphur by weight of the material being sulphurized.

4. Method according to claim 2 in which the two sulphurization steps are accomplished by heating for a period of time in excess of about 10 minutes until the required sulphurization occurs at a temperature from about 300 to 500° F., first with two to 10% of free sulphur by weight of the material being sulphurized, the second sulphurization with ½ to 2½% sulphur by weight, based on the final blended product.

5. Method according to claim 2 in which the two sulphurizations are accomplished by heating for ten minutes to about one hour and a half with free sulphur at a temperature from about 300 to 500° F., the first sulphurization with 2 to 10% free sulphur based on the organic material being sulphurized, the second with an additional ½ to 2½% free sulphur based on the blended product, the amount of sulphur and the proportion of organic material to mineral oil being in proportion to give a finished product with from 3.5 to 10.0% sulphur.

6. An improved method for preparing sulphurized oils, comprising heating a terpene with from 2 to 25% by weight of free sulphur at a temperature from 300 to 500° F., blending the sulphurized terpene with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

7. An improved method for preparing sulphurized oils, comprising heating an unsaturated fatty material with from 2 to 10% by weight of free sulphur at a temperature from 300 to 500° F., blending the sulphurized unsaturated fatty material with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

8. An improved method for preparing sulphurized oils, comprising heating an unsaturated hydrocarbon with from 2 to 10% by weight of free sulphur at a temperature from 300 to 500° F., blending the sulphurized unsaturated hydrocarbon with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

9. An improved method for preparing sulphurized oils, comprising heating an unsaturated hydrocarbon polymer with from 2 to 10% by weight of free sulphur at a temperature from 300° to 500° F., blending the sulphurized unsaturated hydrocarbon polymer with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

10. An improved method for preparing sulphurized oils, comprising heating an olefin polymer with from 2 to 10% by weight of free sulphur at a temperature from 300 to 500° F., blending the sulphurized olefin polymer with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

11. An improved method for preparing sulphurized oils, comprising heating an iso-olefin polymer with from 2 to 10% by weight of free sulphur at a temperature from 300 to 500° F., blending the sulphurized iso-olefin polymer with a major amount of a mineral lubricating oil and reheating the blend with an additional ½ to 2½% of sulphur based on the blend, at 300 to 500° F., until the sulphur is incorporated in a stable combined state.

12. An improved method for preparing sulphurized oils which comprises sulphurizing an unsaturated organic material which is more reactive than mineral oil, blending the product thus formed with a mineral lubricating oil, and sulphurizing the oil thus blended.

13. An improved sulphurized mineral lubricating oil of high load-carrying capacity produced by sulphurizing an unsaturated organic material which is more reactive than mineral oil, blending the product thus formed with a mineral lubricating oil, and sulphurizing the oil thus blended.

14. An improved sulphurized mineral lubricating oil of high load-carrying capacity produced by sulphurizing terpene to form a sulphur carrier, blending the sulphur carrier thus formed with a mineral lubricating oil, and sulphurizing the oil thus blended.

15. An improved sulphurized mineral lubricating oil of high load-carrying capacity produced by sulphurizing an unsaturated hydrocarbon to form a sulphur carrier, blending the product thus formed with a mineral lubricating oil, and sulphurizing the oil thus formed.

16. An improved sulphurized mineral lubricating oil of high load-carrying capacity produced by sulphurizing an olefin polymer to form a sulphur carrier, blending the product thus formed with a mineral lubricating oil, and sulphurizing the oil thus blended.

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