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LUBRICATING OIL

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This invention relates to lubricating oils such as motor oils adapted for lubrication of bearings and cylinders of internal combustion engines, extreme pressure lubricating oils, and cutting oils. It also relates to oil soluble compositions of matter which when added to mineral lubricating oils yield compounded oils possessing improved properties, such as a reduced tendency to cause corrosion of hard metal bearings, improved extreme pressure properties, and improved viscosity characteristics.

In modern internal combustion engines the bearings usually employed are made of hard metallic materials such as cadmium-silver, cadmium-nickel, and copper-lead alloys. While these bearing materials have definite advantages, they have the disadvantage of being susceptible to corrosion under certain extreme conditions, especially by the modern highly refined motor oils. According to the present invention, the tendency of such oils to corrode bearings under extreme conditions of operation is overcome without impairing other desired properties of the oil, such, for example, as high viscosity index.

Another problem that is presented by the design of modern machinery is the necessity for providing lubricating oils capable of withstanding the high pressures encountered between engaged surfaces, such as the hypoid gears used in motor vehicles. Since the ordinary type of hydrocarbon lubricating oil is incapable of withstanding such pressures, there have been developed so-called "extreme pressure lubricants." An extreme pressure lubricant is generally composed of a hydrocarbon lubricating oil and a minor proportion of an ingredient which imparts extreme pressure characteristics to the oil; i. e., characteristics which enable the oil to form between the engaged surfaces a lubricating film capable of withstanding high pressures.

It is an object of the invention to provide lubricating oil compositions containing an additive which imparts to the compositions one or more desirable properties. Another object of the invention is to provide lubricating oil compositions which possess the valuable properties of high refined oils while at the same time having a decreased tendency to cause corrosion of hard metal bearings. A further object of the invention is to provide lubricating oil compositions possessing improved extreme pressure characteristics. Another object of the invention is to provide novel sulfurized products which when added to lubricating oils are adapted to improve the oils in one or more particulars.

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

The lubricating oil compositions of the present invention contain a lubricating oil and an oil soluble sulfurized rubber polymer, preferably a sulfurized rubber polymer which also contains combined chlorine. Depending primarily upon the characteristics of the base oil and the proportions in which the sulfurized rubber polymer is employed, the polymer acts to inhibit bearing corrosion, to impart extreme pressure characteristics to the oil, or to improve other properties of the oil such as the viscosity index.

In my United States Patent No. 2,078,472, I have described a lubricating oil containing a resinous rubber polymer which consists essentially of a reaction product of rubber with a halide or halogen acid of tin or boron. In my United States Patent No. 2,086,399, I have described a method for treating the resinous rubber polymer so as to remove impurities therefrom. When preparing a polymer as described in these patents a substantial proportion of oil insoluble polymer is produced which is not suitable, in some instances, for compounding with oils. In my United States Patent No. 2,199,352, I have described a resinous rubber polymer which is substantially completely oil soluble. This product is preferably prepared by depolymerizing a dispersion of rubber in a suitable aromatic solvent such as benzene, reacting the depolymerized rubber in the presence of a halide or halogen acid of tin or boron to form a resinous polymer, and precipitating and separating the resinous polymer. In this process the depolymerization of the rubber is preferably effected with the use of an agent such as glacial acetic acid, hydrochloric acid, chlor-acetic acid, acidified benzol, sulfur dioxide, hydrogen sulfide, benzoic acid, mercurous chloride, and ammonia. Examples of suitable halides and halogen acids of tin or boron which may be used in the preparation of the rubber polymers described in my prior patents are stannic chloride, stannic bromide, boron trichloride, boron fluoride, fluoroboric acid, chloro-stannic acid, chloro-stannous acid and the corresponding brom acids, anhydrous stannic chloride being preferred.

In accordance with one feature of the present invention a valuable product is prepared from an oil soluble rubber polymer of the class disclosed in my prior patents, preferably the oil soluble polymer described in my Patent No. 2,199,352. By sulfurizing a polymer of this class a product is obtained which is adapted for addition to hydrocarbon oils, such as petroleum lubricating oils,

to improve the properties thereof. The sulfurization of this polymer is preferably accomplished with the use of sulfur chloride.

In preparing an oil soluble sulfurized rubber polymer in accordance with a preferred manner of proceeding, an oil soluble rubber polymer is first prepared as described in my Patent No. 2,199,352. Thus 50 grams of crepe rubber are dispersed in 1500 cc. of benzol (90%) containing 15 cc. of glacial acetic acid. The dispersion is allowed to stand twenty-four hours, and the air is then swept out with a nitrogen stream. To this depolymerized rubber dispersion, there is added 10 cc. of anhydrous fuming stannic chloride. The mixture is allowed to stand twenty-four hours at room temperature. The product is then run into 3500 cc. of 95% ethyl alcohol which effects precipitation of the resinous polymer. The precipitation is completed by stirring for two to three hours. The precipitated polymer is then filtered off, washed free of acid with alcohol, and dried. It will be understood in this connection that it is not necessary to prepare the depolymerized rubber dispersion as a separate step, but that the rubber may be added to the benzol containing the acetic acid and the stannic chloride.

The rubber polymer prepared as above described, which polymer is conveniently referred to as a "depolymerized rubber polymer," is then reacted with sulfur chloride so as to introduce sulfur and chlorine into the product. This is conveniently accomplished by dissolving the depolymerized rubber polymer in an aromatic solvent such as toluene, xylene, or benzol, preferably benzol, and then introducing the sulfur chloride. The reaction takes place easily, and heating is unnecessary. The resulting solution may then be treated as by filtering to remove impurities. In any case the sulfurized polymer is then separated from the remainder of the solution. This may be done by running the solution into a suitable liquid in which the sulfurized polymer is insoluble, preferably an alcohol. The precipitate is then filtered, washed free of acid, preferably with additional precipitating solvent, and dried.

As a specific example of the above procedure, 20 grams of the depolymerized rubber polymer in solution in 500 cc. of benzol is treated with 5 cc. of sulfur chloride. The resulting reaction mixture is permitted to stand for four hours and is then filtered through Filter-Cel. The filtered solution containing a sulfurized rubber polymer is then run slowly into 2500 cc. of 95% ethyl alcohol. As a result of this procedure, the sulfurized rubber polymer is precipitated. The precipitate is filtered, washed with alcohol and dried. The product is a brownish yellow powder, highly soluble in hydrocarbon oils. It contains about 3% sulfur and about 0.42% chlorine.

This sulfurized rubber polymer has varied properties which make it valuable for addition to different types of lubricating oils. For example, by adding the product to a furfural refined Mid-Continent SAE No. 30 lubricating oil in the proportion of 1% by weight, a compounded oil possessing the following properties as compared with the base oil is obtained:

	SAE #30	Compounded oil
Viscosity SU/100° F	513	630
Viscosity SU/210° F	62	70
Viscosity index (Dean & Davis)	87	95+
Lead index	8	30

The "lead index" given above is an arbitrary empirical figure which is the measure of resistivity of the oil to bearing corrosion. It is obtained by multiplying the lead number of the oil by 1,000. The lead number of the oil represents the maximum percentage of lead as lead naphthenate which can be added to the oil without substantial corrosion when the bearing is immersed in the oil and the oil passed therethrough at a temperature of about 325–350° F. for five hours in the presence of air. The amount of corrosion is determined by weighing the bearing before and after the test. For example, if the oil has a lead index of 10, this means that 0.01% of lead as lead naphthenate is the maximum amount which can be added to the oil without substantial corrosion of the bearing. Thus the results given in the above table show that the sulfurized rubber polymer has a high lead index which means that it has the property of inhibiting corrosion by lubricating oils of the type tested. The results given also show that the sulfurized rubber polymer improves the viscosity index characteristics of the oil.

Although the compounded oil described above displays improved viscosity characteristics over the base oil, where it is desired to increase the viscosity index of an oil to a greater extent this may be done by using a larger proportion of the sulfurized rubber polymer. For example, by mixing a furfural refined Mid-Continent SAE No. 20 lubricating oil with 2.6% by weight of the sulfurized rubber polymer a compounded oil possessing the following properties as compared with the properties of the base oil is obtained.

	SAE #20	Compounded oil
Viscosity SU/100° F	347	630
Viscosity SU/210° F	53.3	73
Viscosity index (Dean & Davis)	84	105
Almen value (breakdown, lbs.)	8.7	20.3

It will be noted that the compounded oil is superior to the base oil not only with respect to viscosity index but also with respect to extreme pressure characteristics, as shown by the relative Almen values. Other Almen tests using 1.0% and 0.5% of the sulfurized polymer show that the use of these proportions improves the extreme pressure characteristics to noticeable degrees, although not as much as the proportion used in compounding the oil identified in the table. Thus, by varying the proportions of sulfurized rubber polymer used, it is possible to vary the extreme pressure characteristics of the oil.

A sulfurized rubber polymer that differs from that specifically disclosed above in a higher content of sulfur and chlorine may be prepared as follows. 20 grams of depolymerized rubber polymer is dissolved in 500 cc. of benzol and 10 cc. of sulfur chloride is added to the solution. The resulting mixture is permitted to stand for 24 hours, after which the mixture is run into 2000 cc. of 95% ethyl alcohol. A brownish yellow precipitate, consisting essentially of the sulfurized rubber polymer, is formed. This precipitate is filtered off, washed, and dried. This product, which is a dry powder, contains 5.58% sulfur and 1.87% chlorine. It is made up into a compounded oil containing 2.6% sulfurized rubber polymer, 58.4% SAE #10 oil, and 39.0% SAE #20 oil (furfural refined Mid-Continent lubricating oils). Only a part of the sulfurized rubber polymer dis-

solves in the oil, and to remove the undissolved portion the compound oil is filtered through Filter-Cel at a temperature of 212° F. The filtered compounded oil as compared with the mixed base oil has the following properties:

	Mixed base oil	Compounded oil
Viscosity SU/100° F.	221	240
Viscosity SU/210° F.	47.1	49
Viscosity index (Dean & Davis)	88	99
Almen value (breakdown, lbs.)	9.5	38.9

It will be noted that this sulfurized rubber polymer, which is relatively high in sulfur content, imparts improved extreme pressure characteristics to the oil.

As indicated above, the sulfurized rubber polymer used in making the compounded oil last described, which polymer contains a relatively high proportion of sulfur, is only partly soluble in the hydrocarbon oil. This polymer nevertheless imparts valuable properties to the oil. Hence in speaking of an oil soluble sulfurized rubber polymer in the specification and claims it will be understood that it is not meant that the polymer is necessarily wholly soluble in a hydrocarbon oil, since in some cases the polymer may be only partly soluble. In using a partly soluble sulfurized rubber polymer it is usually advisable to mix the base oil with an amount of polymer in excess of that which it is desired to dissolve in the oil and then to filter the resulting mixture to remove the undissolved portion of the polymer.

From what has been said heretofore, it will be evident that the properties of the sulfurized rubber polymers can be varied by varying the amount of sulfur chloride used in their preparation. In general the sulfurized rubber polymer preferably should not contain more than 10% sulfur by weight, and where a wholly soluble product is desired the product should contain on the order of 2 to 4% sulfur.

The proportions in which the sulfurized rubber polymer is preferably employed will vary depending upon the base oil employed, the object to be attained, and other factors. For example, for inhibiting corrosion or imparting extreme pressure characteristics the sulfur content of the polymer has an important bearing on the amount of polymer used. It may be stated in general that valuable results may be obtained with the use of from 0.1 to 10% of the polymer based on the weight of the base oil. For inhibiting corrosion and improving the viscosity index of an oil it is ordinarily advisable to use from ½ to 5% of a polymer.

As previously indicated, the lubricating oil compositions of the invention may contain base oils of various types depending upon the type of product desired. For example, if a cutting oil is intended to be prepared, then the lubricating oil should be of relatively low viscosity; for example, 60 to 150 Saybolt Universal at 100° F. On the other hand, in making up certain types of lubricating oil compositions, lubricating oils of viscosity from about 170 to 300 up to 1000 at 100° F. may be advantageous. Further, in the preparation of an extreme pressure lubricant, higher viscosity lubricating oils such as oils of the cylinder stock type, having viscosities of about 100 to 200 at 210° F., may be used.

The invention therefore provides lubricating oil compositions which possess valuable properties imparted to them by the oil soluble sulfurized rubber polymers of the invention. The sulfurized polymers which contain combined chlorine apparently possess exceptionally good extreme pressure characteristics because of this chlorine content.

Since changes may be made in the compositions and processes above described without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A lubricating oil composition comprising a lubricating oil and an oil soluble sulfurized rubber polymer.

2. A lubricating oil composition comprising a mineral lubricating oil and an oil soluble sulfurized rubber polymer, said rubber polymer being the reaction product of rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron.

3. A lubricating oil composition comprising a mineral lubricating oil and an oil soluble sulfurized rubber polymer, said rubber polymer being the reaction product of depolymerized rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron.

4. A lubricating oil composition comprising a mineral lubricating oil and an oil soluble sulfurized rubber polymer containing combined chlorine.

5. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer containing not more than 10 per cent of sulfur, said rubber polymer being the reaction product of rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron, said sulfurized rubber polymer also containing combined chlorine.

6. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer containing not more than 10 per cent of sulfur, said rubber polymer being the reaction product of depolymerized rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron, said sulfurized rubber polymer also containing combined chlorine.

7. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer containing combined chlorine, said sulfurized rubber polymer containing not more than 10 per cent of sulfur and being the reaction product of sulfur chloride with an oil soluble rubber polymer which is the reaction product of rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron.

8. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer containing combined chlorine, said sulfurized rubber polymer containing not more than 10 per cent of sulfur and being the reaction product of sulfur chloride with an oil soluble rubber polymer which is the reaction product of depolymerized rubber with a compound selected from the group consisting of the halides and halogen acids of tin and boron.

9. A lubricating oil composition comprising a mineral lubricating oil and 0.1 to 10 percent of an oil soluble sulfurized rubber polymer containing combined chlorine, said sulfurized rubber poly-

mer being prepared by reacting rubber with glacial acetic acid and with stannic chloride to produce a depolymerized rubber polymer, the reaction with the glacial acetic acid and with the stannic chloride being carried out in the presence of benzol, and reacting the depolymerized rubber polymer in solution in benzol with sulfur chloride to produce the sulfurized rubber polymer.

10. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer prepared by reacting rubber with a depolymerizing amount of glacial acetic acid and with stannic chloride to produce a depolymerized rubber polymer, the reaction with the glacial acetic acid and with stannic chloride being carried out in the presence of benzol, and reacting the depolymerized rubber polymer in solution in benzol with sulfur chloride to produce a sulfurized rubber polymer.

11. A lubricating oil composition comprising a mineral lubricating oil and a minor proportion of an oil soluble sulfurized rubber polymer containing combined chlorine, said sulfurized rubber polymer being prepared by dispersing rubber in benzol, adding glacial acetic acid to the resulting dispersion to produce a dispersion of depolymerized rubber, treating the depolymerized rubber in the presence of benzol with stannic chloride, and reacting the resulting product with sulfur chloride to introduce not more than 10 per cent sulfur therein.

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