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EXTREME PRESSURE LUBRICANTS

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This invention pertains to extreme pressure lubricants and compositions for imparting extreme pressure or load carrying properties to lubricating oils. The invention also pertains to a method for preparing extreme pressure agents, incorporating elements such as sulfur, phosphorus, and the like, in such a manner that they will be available for suitable chemical activity under heavy load conditions.

As is well understood in the art, ordinary mineral base lubricating oils and greases which are used to lubricate opposed metal surfaces are likely to fail under extremely heavy load conditions. For example, certain machine elements such as the hypoid gears commonly used in automotive vehicles may be subjected at times to extremely heavy pressures of the order of hundreds of thousands of pounds per square inch. If the film of lubricating oil separating the opposed elements fails, as it is likely to do under such pressure, the surfaces will contact each other directly, generating high temperatures due to friction, with resultant seizure or excessive wear and early failure. Extreme pressure additives containing active sulfur, phosphorus, or chlorine, or two or more of these, are effective to react immediately with the metal surfaces at their higher temperatures to form a protective metal sulfide, phosphide, or chloride film which serves temporarily as a lubricating medium until the normal oil film between the parts can be reestablished. Extreme pressure additives are, therefore, reactive with the metals they lubricate to form extremely thin protective films thereon when the temperature rises due to normal oil film failure.

According to the present invention, it has been discovered that compositions having extreme pressure properties and other desirable properties for use in lubricating oil compositions, and the like, may be prepared from various esters of the alcohols which are derived from ordinary rosin and related materials by hydrogenation. For example, the abietic acid in rosin may be hydrogenated to convert it to an alcohol such as so-called hydroabietyl or dihydroabietyl alcohol. The alcohol so produced may be esterified in a well-known manner (such as by heating under pressure in the presence of a catalyst, while continuously removing water) with a long chain fatty acid which may be either saturated or unsaturated. The unsaturated acids are preferable for subsequent reactions which will be pointed out below. Thus, the oleic acid ester of alcohols derived by the hydrogenation of rosin is a particularly preferred raw material, although other fatty acids such as stearic acid, palmitic acid, lard oil acids, sperm oil acids, synthetic aliphatic acids such as those produced by the oxidation of waxes, olefins, or the aldehydes formed by the oxo reaction between olefins, carbon monoxide and hydrogen. Other and related acids having from 12 to 22 carbon atoms may be used for esterification.

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A commercial product marketed as a hydroabietyl oleate and consisting apparently of a mixture of about 14% of a dehydroabietyl oleate, 37% dihydroabietyl oleate and 41% tetrahydroabietyl oleate, and 8% of unsaponifiable rosin derivatives (terpenes, etc.) was used in the following examples, but it is apparent that related esters would be equally useful and, in fact, the esters of abietic acid with long chain alcohols and the related hydrogenated acid esters of aliphatic alcohols having from 12 to 22 carbon atoms are contemplated as being satisfactory for the purpose of this invention. For example, among the alcohols which may be used are oleyl, lauryl, tetradecyl, sperm oil alcohols, cetyl, stearyl and synthetic alcohols such as those derived by the oxo reaction between olefins, carbon monoxide and hydrogen.

In producing the additive of the present invention, the ester is first reacted with elemental sulfur, for example by heating at a temperature somewhat in excess of 250° F., preferably in the range between 280° F. and about 450° F. The reaction time may vary from about one hour to about ten hours, although by the addition of a sulfurization catalyst such as a sulfur chloride the reaction may be hastened somewhat. The sulfurized product is then reacted with a bi-elemental phosphorus compound, for example P_4S_3, P_4S_7, P_2S_5, PCl_3, PCl_5, P_2O_5, etc. The phosphorizing reaction is suitably carried out by heating at a temperature in the range from about 150° F. to about 300° F. until a product is obtained which is non-corrosive in the copper strip test which will be described below. In general, this may require a reaction time from about one hour to about 24 hours.

The invention will be more fully understood by reference to the following examples.

Example 1

97 parts by weight of the commercial hydroabietyl oleate referred to above were blended with 3 parts by weight of sulfur at a temperature of about 280° F. The mixture thereupon was heated to a temperature of 385° F. and held at the

higher temperature for about two hours. The material was then permitted to cool to a temperature of 210° F. and then there were added 0.5 parts by weight of P_4S_3, the phosphorus sesqui-sulfide being mixed into the composition, and the mixture held at a temperature of 210° F. for twelve hours with continuous stirring. Upon analysis this product showed a sulfur content of 3.12% and a phosphorus content of 0.30%. This material was subsequently added to mineral lubricating oil with test results which are shown in the table below.

In a patent application, Serial No. 712,050, now Patent No. 2,488,618 filed by the present inventor in conjunction with G. M. McNulty on November 25, 1942, there is described a composition derived from rosin or methylated rosin derivatives which, after treatment with a phosphorus sulfide, has extreme pressure properties when used in lubricating oils. The product of the present invention, however, is quite distinct from that described in the co-pending application in that the long chain esters of this present invention do not have the property of depressing the viscosity index of the oils to which they are added. The short chain esters of the prior invention are objectionable in this particular respect, causing a loss of as much as ten points in the viscosity index of the oils to which they are added. This property is of considerable importance where mineral oils of high viscosity index are not readily available, since a viscosity index of at least 85 is considered necessary in the finished lubricant for many purposes.

Example II

91 parts of hydroabietyl oleate of commercial manufacture, as described above, were combined with 9 parts by weight of sulfur at a temperature of 280° F., and the mixture was heated to a temperature of 385° F. The mixture was maintained at that temperature with constant stirring for about 2¾ hours. It was found that this particular product was corrosive to copper when tested as a 10% concentration in mineral lubricating oil for one hour at 250° F. In order to overcome this corrosive property, 19 additional parts by weight of hydroabietyl oleate were added and the mixture was further heated with stirring for 1½ hours at 385° F. The product was then found to be non-corrosive (no blackening) when tested as above.

The sulfurized product was next treated with 0.5 part by weight of P_4S_3 for 12 hours at 210° F. as in Example I. Analysis showed a sulfur content of 6.25% by weight, with a phosphorus content of 0.25%. Results of adding this material to oil are indicated in the table below.

Example III

92 parts by weight of the commercial hydroabietyl oleate of Example I were heated to a temperature between 280° F. and 300° F. and 8 parts by weight of sulfur were added to the heated ester. The temperature was held at about 300° F. for 7 hours while the mixture was stirred constantly. Subsequently, the material was allowed to cool to 210° F. and was thereupon reacted with 0.5 part by weight of P_4S_3 at 210° F. for 12 hours. Analysis showed a sulfur content of 7.81% by weight, and a phosphorus content of about 0.25%.

Example IV

94 parts by weight of the commercial hydroabietyl oleate of Exampe I and 6 parts of sulfur were heated, as in Example I, 0.5 part by weight of P_4S_3 being added after the sulfur treatment. The resulting composition showed an analysis of 5.16% sulfur and 0.26% phosphorus by weight. This material, as well as that of Example III, was tested in a 10% concentration in mineral lubricating oil with and without 1% of tricresyl phosphate, as indicated in the table which follows. The tricresyl phosphate increases moderately the load carrying properties of the lubricant, but it will be understood that it may or may not be used, as desired. The composition of Example II was tested also with 2% of tricresyl phosphate, with moderate improvement in results.

The base oil used in the tests indicated in the following table was a Pennsylvania cylinder stock of 220 S. S. U. viscosity at 210° F. combined with Mid-Continent acid refined lubricating oil of 50 S. S. U. viscosity at 210° F. The two oils were blended to produce an SAE 90 grade lubricant.

Load carrying tests

Additive	Amount Used	Timken Machine			SAE Machine Lbs. carried at 1,000 R. P. M.
		Lbs. Load	Scar Width in 1/64"	Lbs./sq. in.	
	Per cent				
None		10	1.35	9,500	60
Example I	10	33	1.5	28,200	
Example II	10	43	1.5	36,500	
Plus 2% tricresyl phosphate	10	51	1.65	39,600	110
Example III	10	33	1.5	28,200	
Plus 1% tricresyl phosphate	10	43	1.5	36,500	
Example IV	10	51	1.95	33,600	
Plus 1% tricresyl phosphate	10	51	1.8	36,400	110

It will be understood, of course, that compositions of the type referred to above may be added in various quantities to various types of oils, as will be obvious to those skilled in the art. They may be added to relatively light oils, such as oils of automotive engine grades for the purpose of increasing oxidation stability, although normally they will be used more widely in heavier oils such as those of SAE 80, SAE 90 or SAE 140 grade for the lubrication of hypoid gears and other gears where extreme pressure properties are desired. They may also be used in cutting oils, and in soluble cutting oils in conjunction with sodium sulfonates or other appropriate emulsifying agents. For use in gear oils, proportions of 5 to 20% by weight of the additives are preferred, 10% being a common useful proportion. It will be understood, however, that proportions as low as about 1% may be employed,

For concentrates, to be added to oils by the consumer according to his needs, the additive products of this invention may be marketed straight or in 10 to 80% solutions in mineral oil of appropriate grade. The mineral lubricating oils having viscosities between about 35 S. S. U. and 1,000 S. S. U. at 210° F. are preferred and the useful proportions of the additive are ordinarily between 1 and 20% by weight, based on the total composition.

Various conventional additives may be employed in connection with the extreme pressure compound described above, such as thickeners, oiliness agents, oxidation inhibitors, tackiness agents, viscosity index improvers, pour point depressants, and the like. These materials may also be used in greases thickened with soaps, carbon blacks, silica gels and other known grease-forming materials.

In general, the materials to which the present invention is particularly applicable are the cycloaliphatic esters derived from rosin or from abietic acid or alcohol compounds, esterified with a long chain aliphatic material having from about 12 to 22 carbon atoms. As previously indicated, the long chain acid esters of cyclic alcohols are preferable, but the cyclic acid esters of long chain alcohols having the same general structure are also useful.

What is claimed is:

1. A composition consisting essentially of mineral base lubricating oil containing 1 to 20% by weight, based on the total composition, of a sulfurized and phosphorized ester of an abietic compound esterified with an aliphatic compound of 12 to 22 carbon atoms, wherein one of said esterifying compounds is a carboxylic acid and the other is an alcohol, said sulfurized and phosphorized ester being prepared by first combining about 91 to 97 parts by weight of the ester with 3 to 9 parts of sulfur and heating to a temperature between about 280° and 450° F. for a period of 1 to 10 hours, and thereafter treating the sulfurized product with about 0.5% by weight of a phosphorus sulfide at a temperature between about 150° and 300° F. for a period of 1 to 24 hours.

2. An extreme pressure additive for mineral base lubricants consisting essentially of sulfurized and phosphorized ester of an abietic compound and an aliphatic compound of 12 to 22 carbon atoms, wherein one of said esterifying compounds is a carboxylic acid and the other is a monohydric alcohol, said sulfurized and phosphorized ester being prepared by first combining about 91 to 97 parts by weight of the ester with 3 to 9 parts of sulfur and heating to a temperature between about 280° and 450° F. for a period of 1 to 10 hours, and thereafter treating the sulfurized product with about 0.5% by weight of a phosphorus sulfide at a temperature between about 150° and 300° F. for a period of 1 to 24 hours.

3. An extreme pressure additive for mineral base lubricants consisting essentially of sulfurized and phosphorized aliphatic carboxylic acid ester of hydroabietyl alcohol, wherein the esterifying aliphatic radical has between 12 and 22 carbon atoms, said sulfurized and phosphorized ester being prepared by first combining about 91 to 97 parts by weight of the ester with 3 to 9 parts of sulfur and heating to a temperature between about 280° and 450° F. for a period of 1 to 10 hours, and thereafter treating the sulfurized product with about 0.5% by weight of a phosphorus sulfide at a temperature between about 150° and 300° F. for a period of 1 to 24 hours.

4. The method of preparing an extreme pressure composition which comprises esterifying a hydrogenated rosin alcohol with an unsaturated fatty acid having a chain length of about 12 to 22 carbon atoms, heating about 91 to 97 parts by weight of said ester with about 3 to 9 parts of sulfur to a temperature of about 280° to 450° F. for a period of 1 to 10 hours, and thereafter reacting the sulfurized ester with about 0.5 part by weight of a phosphorus sulfide at a temperature of 150° to 300° F. for a period of 1 to 24 hours to incorporate both sulfur and phosphorus into said composition without rendering said composition corrosive to copper at moderate temperatures.

5. A composition consisting essentially of about 1 to 20 parts by weight of sulfurized and phosphorized hydroabietyl oleate diluted with about 80 to 99 parts of mineral base lubricating oil and about 10 to 20% of tricresyl phosphate, based on the weight of the sulfurized and phosphorized hydroabietyl oleate to form a lubricant having high load carrying properties, said sulfurized and phosphorized hydroabietyl oleate being prepared by first combining about 91 to 97 parts by weight of the ester with 3 to 9 parts of sulfur and heating to a temperature between about 280° and 450° F. for a period of 1 to 10 hours, and thereafter treating the sulfurized product with about 0.5% by weight of P_4S_3 at a temperature of about 210° F. for about 12 hours.

6. Composition as in claim 1 containing 5% to 20% of said sulfurized and phosphorized ester.

7. Composition as in claim 1 containing about 10% of said sulfurized and phosphorized ester.

8. Composition as in claim 1 containing about 10% of said sulfurized and phosphorized ester and about 1% to 2% of tricresyl phosphate.

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