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LUBRICANT

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This invention relates to improvements in hydrocarbon lubricating oils and, more particularly, to improvements in the lubricating properties of such oils. The invention includes a novel addition agent having the effect of improving the film strength and oiliness of a hydrocarbon lubricating oil when incorporated in the oil and also includes an improved lubricant comprising a hydrocarbon lubricating oil containing the addition agent of my invention.

One of the major requirements of a lubricating oil is its ability to maintain a lubricating film between two adjacent metal surfaces moving with respect to one another. When the pressure exerted between these adjacent moving parts is not excessive, ordinary lubricating oils are capable of maintaining a satisfactory lubricating film by virtue of the favorable viscosity characteristics of the oil. In such a case the viscosity of the oil is of primary importance and the film strength, oiliness and affinity of the oil for metal surfaces are of but secondary importance.

In the development of the modern internal combustion engine, characterized by ever increasing power for an engine of a given size, there is a marked tendency toward the use of high pressures in the engine bearings. This high pressure is further exaggerated during the break-in period of the engines. High bearing pressures tend to squeeze out a thin film of lubricating oil to such a point that the friction between the moving parts is greatly increased and even to such a point that direct metal to metal contact occurs. The importance of maintaining an efficient lubricating film, particularly during the break-in period of an engine, has placed a greater demand upon the lubricating characteristics of hydrocarbon oils so that satisfactory viscosity characteristics are no longer sufficient to insure proper lubrication. These further lubricating characteristics, such as film strength, oiliness and affinity of the oil for metal surfaces are thus becoming of increasing importance.

With the increasing importance of film strength, oiliness and affinity of an oil for metal surfaces, addition agents have been suggested for the purpose of improving or imparting these characteristics to a lubricating oil. Organic acids having long straight carbon chains, halogenated organic compounds and organic phosphorus compounds have been recommended for this purpose. Many of these compounds appear to have a real effect upon lubricating oils although other practical considerations frequently have been overlooked. Thus, many addition agents have been suggested for increasing the film strength of an oil although these compounds have a serious detrimental effect on other properties of the oil such, for example, as the stability and corrosiveness of the oil. Furthermore, many of the proposed addition agents are difficultly soluble in lubricating oils. The ultimate in an addition agent of this type is one which not only materially enhances the lubricating properties of an oil within a wide range of solubility but which further has no deleterious effect upon the other physical properties of the oil and, in fact, may even substantially improve these other physical characteristics of the oil.

I have discovered that alkylated triphenyl phosphates in which the alkyl groups on the phenyl radicals contain about ten or more carbon atoms have the effect, when incorporated in hydrocarbon lubricating oils, of materially increasing the film strength and oliness of the oil as well as the affinity of the oil for metal surfaces. I have discovered that tri(p-lauryl phenyl) phosphate is particularly effective in improving these lubricating properties of hydrocarbon lubricating oils. A compounded lubricating oil containing such an addition agent is further characterized by substantially the same stability as the original uncompounded oil as well as by a marked reduction in the corrosiveness of the oil. The addition agent of my invention is readily soluble in lubricating oils so that it may be incorporated in such oils in amounts ranging from 0.5% to 3.0% by weight of the oil. I have found, however, that about 1.0% of the addition agent by weight of the oil is generally sufficient to impart to the oil the desired characteristics.

Tri(p-lauryl phenyl) phosphate may be prepared by phosphating p-lauryl phenol. The lauryl phenol may be prepared according to the method described by Liebman (berichte der deutschen Chemische Gesellschaft, 14, 1842; 15, 150) which comprises reacting lauryl alcohol with phenol in the presence of anhydrous zinc chloride.

In preparing the tri(p-lauryl phenyl) phosphate I first prepared lauryl phenol by mixing one part by weight of anhydrous phenol having a boiling point at atmospheric pressure of 350° to 355° F. with 2.13 parts of commercial lauryl alcohol having a boiling point of 302° to 305° F. at 21 mm. pressure, this commercial product containing over 96% lauryl alcohol. Approximately 2.5 parts by weight of anhydrous zinc chloride were then added to the mixture.

The temperature of the mass was brought to about 360° F. by the end of one-half hour and was maintained at this temperature for an additional hour. The heating was then discontinued and the cooled mass was broken up with dilute hydrochloric acid followed by washing with water to remove soluble zinc salts. The oily product was then dried and distilled at atmospheric pressure to a temperature of 450° F. during which distillation the fraction removed between 370° to 430° F. vapor temperature was separately collected. This fraction was finally redistilled at 14 mm. pressure to collect a purified fraction removed between 370° to 405° F. vapor temperature. A phthalic anhydride test for group positions indicated that the lauryl phenol thus prepared contained meta and ortho lauryl phenol with p-lauryl phenol predominating. The molecular weight of the lauryl phenol thus prepared was 265 as compared with the theoretical molecular weight of 262.

Tri(p-lauryl phenyl) phosphate was prepared by dissolving 3 parts by weight of the lauryl phenol obtained as described above in about 2 parts by weight of benzol and about 1 part by weight of redistilled pyridine having a boiling point at atmospheric pressure of 235° to 241° F. 0.6 part by weight of phosphorous oxychloride ($POCl_3$) was then slowly added to this mixture. The temperature of the reaction mass was held at about 100° F. by means of a cold water bath. After all of the phosphorous oxychloride had been added the reaction mass was refluxed for a period of about 3 hours following which the cooled mass was thoroughly washed with water and the solvent benzol was removed by distillation up to 300° F. The remaining product was a viscous brown oil comprising tri(p-lauryl phenyl) phosphate. Analysis of this product showed that its molecular weight was approximately 1050 as compared to the theoretical molecular weight of 830. The phosphorus content of the product was 5.24% as compared to 3.74% calculated for the pure compound. The product thus prepared was apparently impure and is believed to contain an undetermined percentage of a high molecular weight reaction product of lauryl phenol and phosphorous oxychloride.

Comparatively pure tri(p-lauryl phenyl) phosphate was prepared from the lauryl phenol obtained as described above by reacting the lauryl phenol with phosphorous oxychloride in the presence of anhydrous magnesium chloride. After refluxing this mixture of compounds for approximately 9 hours at the end of which period a temperature of 370° F. was attained, the reaction mass was cooled and washed with hydrochloric acid to remove magnesium compounds. The product was finally washed with water and then with a dilute solution of sodium hydroxide in the presence of benzol which was added as a diluent. Benzol was removed from this washed product and the product was then distilled at 0.4 mm. pressure. A pale yellow oil was obtained by separating the fraction removed between 570° and 640° F., this product comprising comparatively pure tri(p-lauryl phenyl) phosphate. The molecular weight of this product was 830 and its phosphorus content was 3.87%.

I have found that tri(p-lauryl phenyl) phosphate, in either the pure or the impure form, possesses salient film strength and oiliness characteristics as determined by numerous carefully conducted tests in an accurately calibrated hydrophil balance. Experience has shown that an addition agent having a favorable film rigidity as indicated by the results of a hydrophil balance test are effective agents for increasing the film strength of lubricating oils in which these agents have been incorporated. The tests on the hydrophil balance were made by comparing the film rigidity of the addition agent of my invention with those of pure tri p-cresyl phosphate and mixed tricresyl phosphates, agents generally accepted as capable of increasing the film strength of lubricating oils. In testing each of these compounds the individual compounds were dissolved in a volatile solvent, namely, twice-distilled benzene, and these solutions of the various compounds were then studied in the hydrophil balance. By means of the hydrophil balance there may be determined the area covered by each addition agent, measured in square meters per gram of addition agent, at various film pressures, measured in dynes per centimeter, within a film pressure range of zero pressure to the maximum pressure at which a thin film will exist. From these data there may be obtained a numerical value for the compressibility of a monomolecular film of each addition agent calculated in accordance with the formula

$$\frac{\frac{(a_0-a_1)}{a_0}}{f_1-f_0}$$

in which a_0 and a_1 are the areas (in square meters per gram) at film pressures of f_0=zero and f_1=a pressure intermediate zero and the maximum film pressure, respectively. By taking the reciprocal of this compressibility a high value corresponds to a favorable film rigidity whereas a relatively low value corresponds to a poor film rigidity. A representative comparison of the "film strength" of each addition agent may be obtained by adding together the maximum film pressure and the reciprocal of compressibility for each of the addition agents. The "film strength" of the impure tri(p-lauryl phenyl) phosphate is 88.4 and 66.3 for the pure tri(p-lauryl phenyl) phosphate as compared to 25.3 for pure tri p-cresyl phosphate.

The actual effect of the addition agent of my invention on a hydrocarbon lubricating oil is apparent upon consideration of machine tests made on a lubricating oil containing the addition agent. These tests comprise the Timken wear test and the Faville-LeVally breakdown test. The Timken wear test was conducted on each sample of oil with a Timken test machine for an 8 hour period with a lever load of 14 lbs. The area of wear on the test block of the Timken machine was measured at the end of this 8 hour period. The pressure in pounds per square inch was calculated from the area of wear and the lever load on the machine. The Timken pressure value thus obtained is inversely proportional to the amount of wear so that a high pressure value represents a relatively small amount of wear. The Faville-LeVally test machine measures the point, expressed in pounds pressure applied in the machine, at which a film of lubricating oil breaks down between two metal parts, one part moving with respect to the other. The results of these tests are shown in the following table. The tests were made on a double solvent treated lubricating oil having an A. P. I. gravity of 27.9, a viscosity of 1498 seconds Saybolt at 100° F., a viscosity of 122.9 seconds Saybolt at 210° F., a viscosity index of 108 and a pour point of 5° F. Similar tests were made upon this base oil con-

taining 1% by weight of the pure tri(p-lauryl phenyl) phosphate and also on the base oil containing 1% by weight of the impure tri(p-lauryl phenyl) phosphate.

Table I

Test	Base oil	Oil+1.0% impure tri (p-lauryl phenyl) phosphate	Oil+1.0% pure tri (p-lauryl phenyl) phosphate
Timken wear test, pounds/sq. in.	5000	----------	8000
Faville-LeVally breakdown, pounds	500	1000	1000

The results of these tests show that 1% of either the pure or impure tri(p-lauryl phenyl) phosphate increases the film strength and oiliness of this particular lubricating oil as well as the affinity of the oil for metal surfaces. The pure addition agent has no appreciable effect upon the resistance of the oil to oxidation whereas the impure addition agent slightly lowers the resistance of the oil to oxidation. Both the pure and the impure addition agent markedly diminish the corrosiveness of the base oil on cadmium-silver alloy bearings. For example, the impure addition agent reduced the loss of weight of the bearing, during a corrosion test conducted at 350° F. for a period of 12 hours, from 694 mg. loss for the base oil to 2 mg. loss for the compounded oil containing 1% by weight of the impure addition agent.

I attribute the superior film strength, oiliness and affinity for metal surfaces imparted to hydrocarbon lubricating oils by the addition agent of my invention to the molecular structure of the addition agent. I offer this theory merely as an explanation of the effectiveness of the addition agent and not as any limitation to my invention. The vertical orientation of the closely packed long alkyl chains of the molecule with respect to a horizontal film surface tends to increase the cohesiveness of the film due to the molecular attraction between adjacent alkyl chains. The freedom with which these alkyl chains may orient themselves is responsible for the increased oiliness of the addition agent in that it permits a high degree of flexibility of the molecules in a thin film between moving metal surfaces. The length of the alkyl chains increases the molecular thickness of the film and tends to prevent direct metal to metal contact between the moving metal surfaces. The grouping of the several benzene rings increases the surface area of each molecule so as to maintain a large surface area per molecule even under high film pressure. The inorganic phosphate radical is responsible for the increased affinity of the addition agent for metal surfaces. Thus, the cumulative effect of these features in the molecular structure of the addition agent of my invention may account for the salient improvements in the lubricating properties of an oil in which the addition agent has been incorporated.

I claim:

1. The method of improving the lubricating properties of a hydrocarbon lubricating oil which comprises incorporating in the oil a small proportion of an alkylated triphenyl phosphate in which each alkyl group contains ten or more carbon atoms.

2. The method of improving the lubricating properties of a hydrocarbon lubricating oil which comprises incorporating in the oil a small proportion of tri(p-lauryl phenyl) phosphate.

3. The method of improving the lubricating properties of a hydrocarbon lubricating oil which comprises incorporating in the oil about 1.% of tri(p-lauryl phenyl) phosphate by weight of the oil.

4. An improved lubricating oil which comprises a hydrocarbon lubricating oil containing a small proportion of an alkylated triphenyl phosphate in which each alkyl group contains ten or more carbon atoms.

5. The method of improving the lubricating properties of a hydrocarbon lubricating oil which comprises incorporating in the oil a small proportion of the reaction product of lauryl phenol and phosphorous oxychloride.

6. An improved lubricating oil which comprises a hydrocarbon lubricating oil containing a small proportion of tri(p-lauryl phenyl) phosphate and a small proportion of a high molecular weight reaction product of lauryl phenol and phosphorous oxychloride.

7. An improved lubricating oil which comprises a hydrocarbon lubricating oil containing a small proportion of tri(p-lauryl phenyl) phosphate.

8. An improved lubricating oil which comprises a hydrocarbon lubricating oil containing about 1.0% by weight of tri(p-lauryl phenyl) phosphate.

9. An improved lubricating oil which comprises a hydrocarbon lubricating oil containing a small proportion of the reaction product of lauryl phenol and phosphorous oxychloride.

10. An addition agent for incorporation in hydrocarbon lubricating oils which comprises an alkylated triphenyl phosphate in which each alkyl group contains ten or more carbon atoms.

11. An addition agent for incorporation in hydrocarbon lubricating oils which comprises tri(p-lauryl phenyl) phosphate.

12. An addition agent for incorporation in hydrocarbon lubricating oils which comprises a mixture of tri(p-lauryl phenyl) phosphate and a high molecular weight reaction product of lauryl phenol and phosphorous oxychloride.

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