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LUBRICATING OIL COMPOSITIONS, CONSTITUENTS THEREOF, AND METHODS OF MANUFACTURING THE SAME

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Our invention relates to the preparation of addition agents which, when added to lubricating oils in relatively small amount, produce lubricant compositions of advantageous character, to compositions containing such agents in admixture with petroleum lubricating oils, and to methods of preparing such agents.

During the past few years there have been developed a considerable number of addition agents for lubricating oils, which are effective to improve the lubricating value and performance characteristics of oils to which these agents are added in small amount (usually in such amount as to produce compositions having the primary physical characteristics, such as viscosity, color and the like, of the lubricating oil bases). Among these addition agents are a number of oil-soluble esters of phosphoric and phosphorous acids, for example tricresyl phosphate and triphenyl phosphite, as well as alkyl phosphates and phosphites. Most or all of these compounds possess value from one or more standpoints as addition agents for lubricants; on the other hand, most of the compounds of this type which have been developed in the past are also subject to definite disadvantages or limitations in use. The phosphates, in general, are stable and effective to increase the load-carrying properties of petroleum lubricants to which they are added. They are usually designated as "mild EP agents," for the reason that they impart some "extreme pressure" characteristics to lubricating oils. The phosphites, in general, are on the other hand somewhat less stable and less effective to increase load-bearing characteristics, but when added to certain lubricating oils, possess the property of inhibiting corrosion of sensitive metal alloys, particularly under high-temperature conditions. The aryl and alkaryl phosphates and phosphites have definite advantages. However, the less highly alkylated members of this group possess limited solubilities in petroleum lubricating oils, especially in the more highly refined and more highly paraffinic oils of highest grade.

In the copending application Serial No. 100,786, filed September 14, 1936, of Cantrell & Turner, there are set forth and described lubricating oil compositions comprising petroleum lubricating oils in admixture with a relatively small amount of an addition agent prepared by reacting a phenol-olefin condensation product with phosphorus oxychloride. This agent, constituting primarily an alkylated aryl phosphate, represents, from most standpoints, a highly useful and advantageous addition agent for lubricating oils. Its ability to contribute extreme-pressure characteristics is good, it is highly soluble in even the most highly refined lubricating oils, it is stable, and lubricating oil compositions containing relatively small amounts of this agent withstand oxidation, as measured by the commonly employed Sligh oxidation test, to a satisfactory extent. However, this reaction product of phosphorus oxychloride and phenol-olefin condensation product tends normally to be too dark in color for general use; the addition thereof to lubricating oils, even in small amounts up to 2 per cent by weight of such oils, results in an undesirable darkening or discoloration. It is possible to obviate this to some extent by subsequently refining methods, but that involves additional manipulation and expense and is not wholly satisfactory.

We have found that a new and improved addition agent for petroleum lubricating oils can be prepared by reacting a phenol-olefin condensation product or alkylated phenol with phosphorus oxychloride, in the presence of a small or catalytic amount of phosphorus sesquisulfide (P_4S_3). The reaction product thus obtained is exceptionally light in color, stable, highly effective as an extreme pressure agent, having a mild inhibiting value with respect to the corrosion of sensitive metal alloys, such as cadmium-silver, copper-lead and cadmium-nickel bearing alloys, and when added to petroleum lubricants, produces lubricating compositions resistant to oxidation and yielding low Sligh values. This product is also exceptionally useful as a means of preventing piston-ring sticking in internal-combustion engines, and for that purpose may be added either to the crankcase lubricant or to the fuel supplied to such engines; in the latter case, amounts of as little as 0.001 per cent of the fuel are effective.

Where corrosion of sensitive metal alloys, in bearings or the like, is a problem, our invention also contemplates the addition to a lubricating oil of a relatively small amount of a mixture predominating in the light-colored phosphate reaction product of our invention, in admixture with a relatively small amount of a phosphite ester, preferably an alkylated aryl phosphite such as the product obtained by reacting a phenol-olefin condensation product or alkylated phenol with phosphorus trichloride. Such an admixture of addition agents is especially advantageous for the purpose of contributing extreme pressure, anti-ring sticking and anti-corrosion properties to lubricating oils, when added thereto.

The raw material employed in preparing our

improved addition agent is, as has been set forth hereinabove, a condensation product of a phenol and an olefin, and constituting primarily a highly alkylated phenol or a mixture of such compounds. Such alkylated phenols are in themselves powerful antioxidants and represent, partly on account of their insolubility in water and dilute alkali solution, desirable addition agents for petroleum lubricating oils. Such antioxidants and methods of preparing the same are disclosed, for example, in the prior copending application of Stevens & Gruse Serial No. 702,258, filed December 13, 1933 (now Patent No. 2,061,111, patented Nov. 17, 1936), and in the copending applications of Troy Lee Cantrell, Serial No. 64,413, filed February 17, 1936, and Serial No. 99,488, filed September 4, 1936 (now Patent No. 2,149,759, patented March 7, 1939).

In general, such condensation products or antioxidants are prepared by reacting a phenol or a mixture of phenols with an olefin or mixture of olefins, in the presence of sulfuric acid or other condensing agent, or under any other conditions effective to promote alkylation of the phenolic material. Various phenolic materials may be employed, for example phenol itself, any one or more of the cresols, and certain of the xylenols. Ordinary phenol and para-cresol are most advantageous.

The alkylating material may be any olefin effective, under the conditions employed, to produce alkylation products in which the alkylations are of secondary or preferably tertiary type; olefins having 3 to 8 carbon atoms per molecule are useful. Butylenes, amylenes and refinery gases or distillates containing such olefins are especially suitable as olefinic starting materials.

Ordinarily we prefer to alkylate phenol or para-cresol or a phenolic mixture containing either or both of these materials with refinery gases containing isobutylene, in the presence of from 1 to 10 per cent of sulfuric acid having a strength of 60 per cent or higher, and to continue the alkylation until the phenol undergoing reaction has increased in weight to from 2 to 4 times the weight of the original phenolic material. The product thereby obtained is then washed with water and with caustic soda solution not exceeding 15 per cent by weight NaOH, or an alkaline agent of equivalent strength.

It is also advantageous to distil the raw condensation product before reacting the alkylated phenol material thereby obtained with the phosphorus-containing reagent, to secure a relatively concentrated "heart cut" amounting to from 60 to 70 per cent of the crude raw material.

Although some alkali-insoluble secondary type alkylated phenols may be present, the constituents most desired are di- or tri- tertiary alkyl phenols, of which 2,4,6-tri-tertiary-butyl phenol and 2,6-di-tertiary-butyl-4-methyl phenol are examples. However, the exact constitution of the materials thus prepared will, of course, vary with the nature of the materials employed, and especially where the phenolic and olefinic raw materials are crude or mixed in character, the final product is to a certain extent obscure in constitution, and our invention is not limited to any particular chemical compound, beyond the requirement that it constitute a condensation product of a phenol and an olefin, insoluble in water and in 15 per cent aqueous NaOH solution or the equivalent thereof.

As aforesaid, the addition agent of our invention is prepared by reacting a condensation product or antioxidant of the character described hereinabove with phosphorus oxychloride, in the presence of a small or catalytic amount of phosphorus sesquisulfide.

By governing the proportions of the antioxidant raw material and the phosphorus-containing reagents, satisfactory finished products containing from 1.0 to 7.0 per cent of phosphorus (in terms of diluent-free alkylated phenol contained in the starting material) may be prepared. Final products containing from 4 to 6 per cent by weight of phosphorus are, however, most advantageous; these are sufficiently active, and they are more soluble in highly paraffinic oils and more stable in storage than products containing higher percentages of phosphorus.

In general, the alkylated phenol raw material is treated with from 5 to 40 per cent by weight of phosphorus oxychloride and with from 0.1 to 2.0 per cent by weight of phosphorus sesquisulfide, but for the manufacture of inhibitors of the highest grade, it is desirable to employ from 20 to 30 per cent by weight of phosphorus oxychloride and from 0.1 to 0.25 per cent of phosphorus sesquisulfide (assuming the antioxidant starting material to be relatively concentrated and pure in character).

In effecting the reaction, the antioxidant starting material is first dried to remove any substantial amount of moisture which may be present therein, and the desired amount of P_4S_3 is then added to the moisture-free antioxidant followed by the addition of the required amount of $POCl_3$. The mixture is vigorously agitated by suitable means as the addition of the phosphorus-containing reagents progresses. During the addition period, there is a copious evolution of HCl, and for this reason it is well to add the phosphorus-containing reagent well below the surface of the liquid to avoid loss of this reagent in the evolved gas. When the requisite amount of phosphorus reagent has been added, the temperature of the mixture is slowly raised to a temperature of about 550° F., and the mixture is maintained at this elevated temperature until there is no further evolution of HCl, and preferably until the chlorine content of the product is less than 0.25 per cent. The resultant material, after cooling, represents the finished agent of our invention and, as such, is ready for addition to lubricating oils without further purification. The following example will serve to illustrate our invention.

In the preparation of the material of this example there was employed a phenol-olefin antioxidant, prepared in the manner set forth hereinabove, and having the following physical properties:

Gravity: °API	16.1
Viscosity, SUV 100° F	63.4
Flash, OC °F	85
Fire, OC °F	163
Pour °F	−30
Color, NPA	1.0
Distillation, gasoline, ASTM method:	
Over point °F	381
End point °F	528
10% at °F	417
50% at °F	472
90% at °F	508

1000 parts by weight of this material were then reacted with 262 parts by weight of $POCl_3$ and 3 parts by weight of P_4S_3, the temperature of the mixture being raised to 550° F. after the addi-

tion of the phosphorus-containing reagent, and the mixture being maintained at this temperature for five hours.

There were obtained 987 parts by weight of a material having the following physical properties:

Gravity: °API		0.7
Viscosity, SUV at 100° F		2083
Color, NPA		2.25
Appearance		Clear
Sulfur	per cent	0.15
Chlorine	do	0.03
Phosphorus	do	5.57

It will be observed that in adding material of this character to a lubricating oil, the amount added will vary in accordance with the degree of effect desired and the purposes to which the oil is to be put. For crank-cases and engine oils amounts of from 0.1 to 5 per cent, usually around 1 per cent, by weight are suitable, whereas in the preparation of gear lubricants considerably larger amounts up to 25 per cent by weight on the lubricant base may be employed.

In a typical example, one part by weight of alkaryl phosphate, prepared as set forth in Example I, was added to 99 parts by weight of a highly refined lubricating oil of 60 SAE classification. The thereby compounded oil was found to be greatly increased in its ability to stand high-bearing loads and to be substantially improved with respect to its tendency to develop a temperature increase in the lubrication of bearings maintained under moderately high-bearing pressures. Whereas the oil alone failed to carry a 16-pound load for 15 minutes on the Almen testing machine, the compounded oil successfully withstood a lever load in excess of 32 pounds, representing a unit bearing load of 16,000 pounds per square inch for a time in excess of 15 minutes.

The compounded oil was almost exactly identical with the initial oil base in respect to specific gravity, viscosity, flash and fire test, and color. It had a carbon residue of 0.33 per cent as compared with 0.36 per cent for the uncompounded oil. The Sligh oxidation number of the initial oil was only very slightly increased (from 1.0 to 2.0) by the addition of the improved agent and the neutralization number was likewise only very slightly increased.

Increasing the relative amount of phosphorus sesquichloride employed tends to yield a product somewhat more effective, when added to petroleum lubricating oil, in increasing the load-bearing characteristics of the oil, but having a higher Sligh oxidation number. Thus, a material similar to that set forth under Example I hereof but prepared by reacting 1000 parts by weight of the same antioxidant starting material with 262 parts by weight of $POCl_3$ and 13 parts by weight of P_4S_3, when added in the same amount to the same lubricating oil base referred to in Example I gave a lubricant composition capable of sustaining in excess of 18,000 pounds per square inch unit load on the Almen testing machine, but having a Sligh oxidation number of 11.

It will therefore be evident that the relative amount of P_4S_3 employed will be governed by whether high "extreme-pressure" characteristics or high resistance to oxidation constitutes the dominant factor in determining the value of the final lubricant composition.

As indicated hereinabove, the alkaryl product of our invention may be advantageously employed in admixture with a relatively small amount of an oil-soluble phosphite ester, for example an alkylated aryl phosphite prepared by reacting the phenol-olefin condensation product described hereinabove with phosphorus trichloride, as set forth and described in the prior copending application of Cantrell & Turner, Serial No. 99,662, filed September 5, 1936. We have successfully employed mixtures containing these phosphate and phosphite materials in proportions ranging from 4:1 to 9:1, respectively, and in particular have found that the addition of 0.36 per cent of the phosphate inhibitor of our invention plus 0.04 per cent by weight of the aforesaid alkaryl phosphite reaction product to a petroleum lubricating oil yielded a lubricant composition extraordinarily free from ring-sticking and bearing corrosion tendencies, as compared with the uncompounded oil.

The advantages of our addition agent are evident in comparison with tri-cresyl phosphate, which is perhaps the most widely used phosphorus-containing addition agent. As compared with tri-cresyl phosphate, our addition agent is simpler and easier to prepare, requiring no final distillation, it is a more effective extreme-pressure agent than tri-cresyl phosphate, it is more soluble in hydrocarbon oils, particularly the high refined oils, and it is more stable in the presence of water. It also possesses a more effective inhibiting action with respect to corrosion-sensitive bearing alloys than is true of tri-cresyl phosphate, although, as has been indicated, it is less effective for this purpose than most phosphites, and is best employed (where this problem is serious) in admixture with a relatively small amount of a phosphite of similar character. Our addition agent is also of such character, when properly prepared, as to enable oils compounded with it successfully to withstand corrosion in the Sligh oxidation test.

It will be apparent to those skilled in the art that our invention is not limited to the details or examples given hereinabove but may variously be practiced and embodied with in the scope of the claims hereinafter made.

What we claim is:

1. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and a phenol in the presence of a catalyst and treating at least a portion of the resultant product with phosphorus oxychloride in the presence of a catalytic amount of phosphorus sesquisulfide.

2. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises treating a phenol selected from the class consisting of water-insoluble secondary and tertiary alkylated phenols with phosphorus oxychloride in the presence of a relatively small amount of phosphorus sesquisulfide, the amount of the phosphorus-containing reagents being such as to effect the formation of a final phosphate inhibitor product containing from 1 to 10 per cent of phosphorus.

3. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting a phenol selected from the class consisting of secondary and tertiary alkylated phenol with phosphorus oxychloride in the presence of a catalytic amount of phosphorus sesquisulfide, and heating the resultant mixture until the chlorine

content of the product is less than 0.25 per cent.

4. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and a phenol in the presence of sulfuric acid, neutralizing the resultant product with dilute alkali solution, distilling the neutralized alkali-insoluble product to recover a fraction at intermediate boiling range, and reacting said fraction with a mixture of phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide.

5. An improvement agent for hydrocarbon oils comprising a light colored reaction product of a phenol selected from the class consisting of water-insoluble secondary and tertiary alkylated phenols and a mixture of phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide.

6. An improvement agent for hydrocarbon oils comprising a light colored reaction product of a water-insoluble tertiary alkylated phenol and a mixture of phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide, said agent containing from 1 to 10 per cent of phosphorus and not more than 0.25 per cent of chlorine.

7. An improvement agent for hydrocarbon oils comprising a mixture of products obtained by reacting water-insoluble tertiary alkylated phenol with a mixture of phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide, and with phosphorus trichloride, respectively.

8. The method of obtaining a light-colored phosphate reaction product of a water-insoluble tertiary alkylated phenol and phosphorus oxychloride, which comprises conducting the reaction in the presence of a quantity of phosphorus sesquisulfide relatively small with respect to the quantity of phosphorus oxychloride present.

9. In combination, a small amount of a light-colored reaction product of a water-insoluble tertiary alkylated phosphate, phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide, and a hydrocarbon oil.

10. The method of prevention or reducing ring-sticking in internal combustion engines, which comprises introducing into the cylinders of such an engine a small quantity of an aryl phosphate comprising the reaction product of a water-insoluble tertiary alkylated phenol, phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide.

11. An improved lubricant for internal combustion engines comprising a major amount of a hydrocarbon lubricating oil having incorporated therein a minor amount of an aryl phosphate reaction product of a water-insoluble tertiary alkylated phenol, phosphorus oxychloride and a relatively small amount of phosphorus sesquisulfide.

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