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LUBRICATING OIL COMPOSITIONS, INHIBITORS THEREFOR, AND METHODS OF MANUFACTURING THE SAME

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Our invention relates to lubricating oils and more particularly to lubricating oil compositions containing an oil-soluble agent or agents effective to inhibit or mitigate the normal corrosive or destructive action of lubricating oil deterioration products upon certain types of bearing metals under certain conditions of use, said agent or agents also having the properties of imparting so-called "extreme pressure" characteristics to the lubricating oil compositions, and also being effective to reduce or eliminate undesirable oxidation changes in the oil.

Despite the many technological advances made in the art of refining and applying lubricating oils and in the composition of bearing materials, modern lubricating oils and bearings often fail to perform satisfactorily. It is well known in the art that straight petroleum lubricants have fairly well defined limits of bearing speeds, pressures, and temperatures within which they will give acceptable service. These limitations are often exceeded in modern designs, resulting in machines that cannot be satisfactorily lubricated by straight mineral oils. These modern designs are justified by engineers in their efforts to provide machines to conform to the ever-increasing demand for compactness, speed, power and acceleration in modern engines. Many modern designs have already exceeded the above-mentioned limits wherein straight petroleum lubricating oils perform acceptably; therefore, it is necessary to provide lubricating compositions that extend and widen the limits formerly associated with straight lubricating oils.

Moreover, highly paraffinic oils having excellent viscosity-gravity constants, volatilities, carbon residue values, and resistance to sludging and oxidation, and hence of high value for use under relatively mild lubricating conditions, sometimes tend to be even less satisfactory than the less highly paraffinic oils, when the ordinary limits of temperature, pressure, and bearing speed are exceeded. This may be due in part to the fact that the deterioration products of paraffinic constituents are more active than those resulting from naphthenic or other nonparaffinic constituents, and it may be due also to the fact that the nonparaffinic constituents have some inhibiting effect upon either the deterioration of the paraffinic constituents or upon the behavior of products resulting from such deterioration, at high temperatures and pressures and in the presence of certain metals. However, the inhibiting value of the nonparaffinic constituents is low per unit concentration, and they are less satisfactory with respect to viscosity-gravity constant, carbon residue, and similar criteria of lubricating quality than the paraffinic constituents. A more satisfactory solution of the problem would be to substitute for the nonparaffinic constituents removed in the more drastic refining treatments or absent because of the highly paraffinic nature of the original stock, some inhibiting or mitigating agent which would be far more effective per unit concentration and hence less detrimental with respect to the other physical properties which also affect the ultimate lubricating value of the oil.

Improved bearing metals have recently been developed which are mechanically advantageous under many operating conditions. These bearing metals include binary and ternary alloys of cadmium, silver, copper, lead, and nickel; as examples of such improved bearing metals frequently employed at the present time we may mention cadmium-silver, cadmium-silver-copper, cadmium-nickel-copper, and copper-lead alloys. However, such alloys are more subject to chemical attack than babbitt and other bearing alloys used in the past, and their use at high temperatures, high speeds, and high pressures is sometimes accompanied by a deterioration of the oils employed for their lubrication, which in turn may destroy the bearings. The exact mechanism of this action is no doubt complicated and is perhaps not fully understood; it is quite possible that some of the metals present in the bearings tend to promote such deterioration, and that other metals present are subject to attack from the deterioration products. Whatever the cause or the mechanism, the result is that the combina-

tion of drastic lubricating conditions and alloy bearings of the general nature indicated frequently causes trouble; the bearings may be badly etched or corroded, and the quality of the oil may be rapidly deteriorated.

It has been observed in some cases that the more highly paraffinic oils are apt to cause more difficulty in this respect than less paraffinic oils. It is highly desirable, therefore, to provide means whereby the oils may be so improved as to give satisfactory operating results under the conditions noted, and this is especially true insofar as concerns the more highly paraffinic oils, which should and do command a premium in price.

Moreover, it is well known that all hydrocarbon oils are more or less subject to changes through oxidation, resulting in undesirable deterioration, acid formation, and increase in carbon residue, viscosity, sludging, and the like. Such oxidative changes may become more rapid or more far-reaching in extent in the presence of metals such as those employed in modern bearings, for example those of the general class mentioned above.

In order to meet these problems and to provide more satisfactory lubrication under the conditions indicated, various improvement agents have been incorporated in hydrocarbon oils prior to their sale and use. Some of these are extremely effective but too expensive for general use. Others, while having satisfactory inhibiting or mitigating characteristics, are unsatisfactory for other reasons. A primary requisite of any such improvement agent is good oil-solubility under service and marketing conditions; moreover, since solubilities vary in different types of oils, the improvement agent should be capable of being added in the requisite amount to oils of different characters.

The improvement agent should also be highly effective per unit concentration in the lubricating oil compositions; otherwise it would be necessary to add such an amount of the improvement agent as to substantially modify many of the desirable physical properties of the lubricating oil itself. The lubricating oils in which the improvement agents are incorporated have been carefully refined to meet exacting specifications, and if it is necessary to incorporate therein a relatively large amount of some agent differing in physical properties from the oil itself, the resulting composition may prove unsatisfactory for the very purposes for which the lubricating oil was prepared. In general, it is desirable that the improvement agent should be effective at concentrations not exceeding one or two per cent by weight of the lubricating oil, although somewhat higher concentrations may occasionally be justified for special purposes.

It is, therefore, an object of our invention to provide an improvement agent or inhibitor for addition to hydrocarbon lubricating oils, having a high degree of solubility in such oils, even the more highly refined or more highly paraffinic oils, and having a substantial inhibiting or mitigating effect upon the destructive action of lubricating oils upon alloy bearing surfaces under actual conditions of use where such destructive action would otherwise take place, and which when added to hydrocarbon oils will not result in sludging or forming deposits at ordinary temperatures upon metallic packaging materials such as tin plate, terne plate and the like, or other common metal surfaces.

It is also an object of our invention to provide an improvement agent or agents of the character indicated herein, having the property of imparting substantial extreme-pressure characteristics to hydrocarbon oils when incorporated therein.

Another object of our invention comprises the provision of an improvement agent or agents for addition to hydrocarbon oils, having effective anti-oxidant and stabilizing properties and capable of substantially retarding increases in viscosity, carbon residue, acidity and sludging of both highly paraffinic and less highly paraffinic oils.

A further object of our invention is to provide improved lubricating compositions comprising hydrocarbon lubricating oils having certain improvement agents incorporated therein.

A still further object of our invention is to provide a method or methods of manufacturing improvement agents having desirable characteristics for addition to mineral oils.

Our invention has for further objects such additional operative advantages and improvements as may be found hereinafter to obtain.

We have found that advantageous improvement agents or inhibitors may be prepared by reacting phosphorus sesquisulfide with certain anti-oxidants, said anti-oxidants comprising water-insoluble reaction products obtained by reacting phenols with olefins. Such anti-oxidant materials and methods of preparing the same are disclosed in the prior co-pending application of Stevens and Gruse, Serial No. 702,258, filed December 13, 1933, Pat. No. 2,061,111, Nov. 17, 1936, and the copending applications of Troy Lee Cantrell, Serial No. 64,413, filed February 17, 1936, and Serial No. 99,488, filed September 4, 1936, to which reference may be made for further details. The disclosures of the copending applications referred to hereinabove constitute in effect a part of the disclosure of the present application, in so far as relates to the preparation of anti-oxidant materials, which are used as starting materials in preparing phosphorus-containing and sulfur-containing improvement agents in accordance with our present invention.

Referring, for example to the aforesaid application of Troy Lee Cantrell, Serial No. 99,488, there is disclosed a process of manufacturing anti-oxidants wherein a phenol is mixed with from 1 to 10 percent sulfuric acid having a strength of from 60 to 100 per cent, or even fuming sulfuric acid, and an olefin or a mixture of olefins is passed, preferably in the vaporous or gaseous phase, through the liquid mixture until the phenol undergoing reaction has gained in weight from 100 to 200 per cent or thereabouts, followed by washing the products so obtained with water and caustic soda solution, the concentration of which does not exceed 15 per cent. Various phenols may be employed; for example, phenol (C_6H_5OH) itself, the three cresols

(C_6H_4—CH_3—OH)

and certain xylenols (C_6H_3—$(CH_3)_2$—OH), or crude cresylic acid may be employed. The phenolic starting material should be as free as possible from pyridine bases; such pyridine bases may be removed by conventional methods such as washing with acid or by distillation.

As olefinic material there may be employed individual olefins themselves, mixtures of olefins or mixtures of olefinic and non-olefinic materials. By way of example, the olefinic material may be butylenes, amylenes, refinery gases contain-

ing normally gaseous olefins (ethylene, propylene, butylene) in varying amount, and cracked distillates or other relatively low-boiling hydrocarbon mixtures containing normally liquid olefins, and in some instances also containing substantial amounts of dissolved normally gaseous olefins.

Where the reaction is conducted with the olefin in the gaseous phase, the product is relatively highly concentrated with respect to effective anti-oxidant material and may not require distillation or concentration for the purpose of isolating the latter. On the other hand, when the reaction is conducted with the olefinic material in liquid phase, and especially where the concentration of olefin in the starting material is comparatively low, the anti-oxidant phenol-olefin reaction product may be relatively dilute, comprising, for example, a solution of such anti-oxidant in gasoline-like polymers or unreacted liquid hydrocarbons. In such case, the anti-oxidant material may be, and preferably is, concentrated by distillation or otherwise as set forth in the above mentioned co-pending applications, prior to treatment with phosphorus sesquisulfide as described herein.

The exact chemical and structural nature of the anti-oxidant material as thus prepared and employed as a starting material in the manufacture of our improved addition agents is largely obscure. Although we have been able to identify certain types of compounds in these anti-oxidant materials, it will be realized that especially since mixtures of various phenols and mixtures of various olefins are frequently employed in the manufacture of these anti-oxidants, the number of possible chemical compounds is large and varied. In general, they differ from the simple alkylated phenols in that they are insoluble in dilute caustic soda solution and in that they are good anti-oxidants and gum-inhibitors, whereas simple alkylated phenols are not. In general, also, the alkylations, in such instances as they occur, are of secondary and tertiary types; the methods set forth in the above co-pending applications do not produce normal or primary alkylation linkages. Alkylated phenols with normal or primary linkages are undesirable (except as regards cresols and the like, used as phenolic raw material for the preparation of the anti-oxidants), due to the fact that both such materials and their products of reaction with phosphorus sesquisulfide tend to be relatively insoluble in high gravity lubricating oils. It is possible that certain alkylated phenols of normal or primary linkage might be satisfactory as anti-oxidant starting materials provided the chains were long enough, say chains of four carbon atoms or more, on account of the closer resemblance in structure of such compounds to paraffinic lubricating oil constituents. However, this is doubtful and such compounds would be expected to be of prohibitive cost.

We have identified as constituents in the various anti-oxidant materials prepared as set forth hereinbefore such compounds as follows:

Ortho-isopropyl phenol
Ortho-tertiary butyl phenol
2.4-ditertiary butyl phenol
Ortho-isoamyl phenol
Ortho-tertiary amyl phenol

In addition to the above listed compounds, similar derivatives of various homologues of mono-, di- and poly-hydroxy phenols may be present. It may be remarked, however, that while some of the constituents of such anti-oxidants may be identified, it is difficult or impossible to identify all of the constituents of any one anti-oxidant material of the character indicated, and it is equally impossible to say which particular compound or type of compound may be of most importance. As a matter of fact, we have not been able to isolate or identify any single constituent or to recover any fraction of the concentrated anti-ioxidants prepared in accordance with the aforesaid Cantrell application, Serial No. 99,488, which constituent or fraction has an anti-oxidant value as high as that of the total concentrated product. Nor for the purposes of our present invention is it necessary so to do; the fact remains that anti-oxidants may be prepared in the manner set forth herein and in the aforesaid co-pending applications, and such materials comprise suitable starting materials for the manufacture of phosphorus-containing and sulfur-containing improvement agents or inhibitors in accordance with our present invention. Certain of the constituents of the anti-oxidant starting materials which are not in themselves effective as anti-oxidants are, nevertheless, capable of being converted by reaction with phosphorus sesquisulfide to yield phosphorus- and sulfur-containing materials useful as inhibitors and extreme-pressure agents.

We prefer to employ as initial starting material anti-oxidants prepared as set forth above and in the aforesaid co-pending applications and having physical properties within the following ranges:

Gravity_____°A. P. I.__	15.0 to 25.0
Specific gravity, 60°/60° F__	0.0659 to 0.9042
Viscosity, S. U. V. at 100° F_____Sec__	150 to (solid)
Color_____	Water white to 7 (NPA)
Pour point (liquids only) °F__	0 to 30
Melting point (solids only)_____°F__	80 to 225

Our invention in its broadest aspects, however, is not limited to the preferred initial starting material mentioned hereinabove, but contemplates the manufacture of inhibitors of the general class described from any alkylated phenols so long as such alkylated phenols possess definite anti-oxidant properties, are insoluble in water, insoluble or only slightly soluble in dilute alkali, and are permanently soluble up to 5 per cent in paraffin oils. It is a requisite of such alkylated phenols, however, insofar as the present process is concerned, that the compounds shall contain one or more secondary or tertiary carbon linkages, or both.

The anti-oxidant value of this initial starting material should be such that the addition of 0.01 per cent by weight thereof to standard gasoline stock having an oxygen stability period (E. G. C. method) of, say, 120 minutes, will raise the oxygen stability to at least 240 minutes. Less potent anti-oxidants are unsuitable as starting materials.

The character of the final phosphorus- and sulfur-containing inhibitor will, of course, vary with the character of the phenolic and olefinic material employed in the manufacture of the anti-oxidant starting material, with the extent of

absorption of the olefin, and with the amount of phosphorus and sulfur subsequently introduced. All of these factors are very intimately inter-related. These are the primary factors, but it will be obvious that there are numerous secondary factors, for example the degree of purification and decolorization of the anti-oxidant starting material.

Naturally, it is to be expected that the viscosities, specific gravities and other physical characteristics of the particular phenols employed will have a corresponding effect upon the product, to some extent at least.

When cresylic acid, ortho-cresol and meta-cresol, and the like are used in the manufacture of the anti-oxidant, we prefer to limit the olefin absorption to around one mol per mol of the phenolic material, i. e., to give a water-insoluble product representing roughly 135 to 150 per cent by volume of the original phenol, in order ultimately to secure inhibitors that are sufficiently soluble in the higher gravity oils; the result of carrying the absorption of olefin farther is to make the anti-oxidant product less capable of absorbing the desired amount of phosphorus and sulfur.

When the anti-oxidant starting material is prepared from phenol (C_6H_5OH) itself, e. g., "90% phenol", the degree of absorption of olefin may be carried farther, for example to about two mols of olefin per mol of phenol (based on the assumption that the olefin is made up entirely of C_4 hydrocarbons).

The preferred olefins are those containing from three to eight carbon atoms per molecule; the higher the molecular weight of the olefin the more viscous the final phosphorus and sulfur containing product will be. Olefins containing more than eight carbon atoms per molecule tend to reduce the phosphorus and sulfur contents of the final inhibitor product. Ethylene (C_2H_4), on the other hand, is insufficiently reactive, requiring the use of fuming sulfuric acid and does not sufficiently reduce the acidity of the original phenol.

The best olefin starting materials are those containing from three to five carbon atoms per molecule, especially butylene; fractions obtained from gases produced in the pyrolysis of hydrocarbon oils and rich in olefins of this approximate range represent advantageous and available raw materials.

After the reaction between the phenol and olefin has been carried to the desired degree of completion, the product is washed with water and dilute caustic soda in the manner set forth hereinabove and in the aforesaid co-pending applications. The resultant water-insoluble anti-oxidant material is then preferably dried. The drying may be accomplished by filtering this material through adsorbent clay or the like, the effect of which is to dehydrate and decolorize. Or, the drying may be accomplished by heating the anti-oxidant material to about 400° F. in suitable apparatus; this procedure dehydrates and tends to darken the anti-oxidant material.

The dry anti-oxidant may then be treated directly with phosphorus sesquisulfide, or it may first be distilled to separate undesirable low-boiling and high-boiling constituents, respectively. Thus we may distill under a vacuum of from −11 in. to −28 in. Hg., to recover a fraction distilling over between 400° and 550° F., which fraction may then be treated with phosphorus sesquisulfide. The lower boiling material, and sometimes also the residue, may be recycled for further reaction with the olefins in the presence of sulfuric acid, or used as an anti-oxidant.

As aforesaid, we prepared our improvement agents by reacting anti-oxidants of the general character described above with phosphorus sesquisulfide. The reaction is conducted by mixing phosphorus sesquisulfide with the anti-oxidant material in the desired amount and heating the mixture until volatile sulfur compounds are no longer evolved. We find it is ordinarily desirable to heat the mixture to from 450° to 550° F., and to maintain it at that temperature for several hours, for this purpose.

We have found that, using concentrated anti-oxidant starting material, prepared as set forth in the aforesaid co-pending application of Troy Lee Cantrell, Serial No. 99,488, filed Sept. 4, 1936, relatively small amounts of phosphorus sesquisulfide are required, for example not more than 10 per cent by weight; in most cases the anti-oxidant material will not absorb more than a few per cent of phosphorus sesquisulfide. The products ordinarily contain up to 3 per cent by weight of the combined phosphorus and sulfur, the phosphorus and sulfur being present in substantially 2:1 proportion. It is not necessary to fully saturate the anti-oxidant material with the reagent in order to obtain useful products; highly desirable materials may be prepared by limiting the amount of phosphorus sesquisulfide to a point short of completion of reaction of the phosphorus sesquisulfide with all of the anti-oxidant present, as shown in Example 2 hereinbelow. When this is done, the product, while possessing excellent extreme-pressure properties and corrosion inhibiting value, retains to a considerable extent the anti-oxidant value of the original starting material. It may be remarked, however, that even where all of the anti-oxidant is fully reacted with phosphorus sesquisulfide, the product will still possess excellent anti-oxident properties.

It will be readily understood that there are no absolute fixed lower limits with respect the percentages of phosphorus and sulfur in the final compound. Products containing less than about 0.5 per cent of phosphorus and 0.25 per cent of sulfur are, however, apt to be insufficiently effective for general application.

The product obtained as indicated hereinabove may be used directly as an inhibitor for addition to hydrocarbon oils, in amounts which will ordinarily range from 0.25 to 2.0 per cent by weight of the oil. It is one of the advantages of our invention that the products are very light in color and ordinarily do not require decolorization, although wherever an extremely light product is desired, the material may be decolorized by conventional means, as for example by filtration through absorbent clay or the like. Filtration may also be employed to remove impurities and any unreacted sesquisulfide, mechanical filters being suitable for the latter purpose.

The following examples will serve to illustrate our invention in some of its more specific embodiments:

Example 1

(a) Preparation of anti-oxidant starting material

20 gal. of "90% phenol" were mixed with 5 per cent of 94.5% sulfuric acid (c. p.). Olefin gas, composed primarily of C_4 hydrocarbons, was then introduced in close contact with the phenol-acid mixture until the volume of the reaction

mixture increased to about 45 gal. This product was then washed with 10 gal. of 10 per cent caustic soda, and later with 10 gal. of water. After washing, the recovered product, amounting to about 40 gal., was distilled under a vacuum of 11 to 12 in. Hg. The distillate was then cut into three fractions. That fraction distilling over at vapor temperature between 300° and 550° F. had the following properties:

Gravity	°A. P. I.	17.9
Viscosity, S. U. V.—		
100° F.	seconds	212
210° F.	do	37.0
Pour point	°F.	0
Color	N. P. A.	2

(b) Preparation of final inhibitor

95 parts by weight of the above distillate were warmed to 120° F., and 5 parts by weight of phosphorus sesquisulfide were then added. The mixture was heated to about 500° F. and held at that temperature for 5 hours. It was then cooled to around 250° F. and filtered. The resulting material had the following properties:

Gravity	°A. P. I.	12.1
Viscosity, S. U. V. at 210° F.	seconds	38.5
Color	N. P. A.	2.0
Phosphorus	percent by wt.	1.52
Sulfur	do	0.7

EXAMPLE 2

In this example, a distillate prepared as set forth in Example 1 (*a*) above was employed, except that in this instance the distillate had the following properties:—

Gravity	°A. P. I.	16.8
Viscosity, S. U. V. at 100° F.	seconds	185
Color, Saybolt		−13

97 parts by weight of this distillate were treated with 3 parts by weight of phosphorus sesquisulfide, the procedure being the same as that described in connection with Example 1 (*b*). The resulting product had the following properties:—

Gravity	°A. P. I.	12.5
Viscosity, S. U. V. at 210° F.	seconds	36.9
Color	N. P. A.	1.0
Phosphorus	percent by wt.	1.1
Sulfur	do	0.5

These inhibitors, when added to hydrocarbon oil in amounts corresponding to from 0.25 to 2.0 per cent by weight of the oil, strongly inhibit corrosion of metal alloy bearings, such as those of silver, cadmium, copper and nickel, under conditions where highly paraffinic oil alone would cause such corrosion. They are extremely effective as regards contributing extreme-pressure properties and do not tend to deposit out of lubricating oil compositions containing them, at least until such time as they are required at the point of application. They are permanently soluble in hydrocarbon oils of high viscosity. Moreover, these inhibitors have excellent anti-oxidant properties and they are substantially free from any tendency to hydrolyze. They are especially useful as improvement agents for addition to turbine oils, spindle oils, and other lubricating oils intended to be used for the lubrication of high-speed machinery.

The following tables will serve to illustrate the effectiveness of our inhibitors and the value of lubricating compositions containing them.

TABLE I

	Untreated oil	Oil containing our inhibitor (prepared as in Example 1)
Make-up, percent by weight:		
Lubricating oil	100	99
Inhibitor	0	1
General properties:		
Gravity, A. P. I.	32.4	32.2
Specific gravity, 60°/60° F.	0.8633	0.8644
Lb./gal., 60° F.	7.188	7.198
Viscosity, S. U. V., seconds—		
100° F.	182.5	178.7
210° F.	45.9	45.7
Viscosity index	103	105
V-G constant	0.805	0.807
Flash, OC—°F.	410	405
Fire, OC—°F.	475	480
Pour Point, °F.	0	0
Color, N. P. A.	1.50	1.50
Sulfur, percent	0.05	0.09
Phosphorus, percent	Nil	0.01
Carbon residue, percent	0.03	0.05
Almen test:		
Lever load, pounds	10	22
Journal speed, R. P. M.	600	600
Rubbing speed, ft./min.	40	40
Unit load, lb./sq. in.	5000	11000
Lubricant temperature, °F—		
Initial	88	88
Final	105	130
Special oxidation and corrosion test:		
Time oxidized, hours	48	48
Oil bath temperature, °F.	347	347
Air rate, cubic centimeters per hour	2000	2000
Quantity of oil, cubic centimeters	300	300
Cadmium-silver bearing—		
Weight before test, g.	35.8670	35.9161
Weight after test, g.	35.5260	35.9143
Loss in weight, g.	0.3410	0.0018
Appearance	Etched	Good

TABLE II

	Untreated oil	Oil containing our inhibitor (prepared as in Example 2)
Make-up, percent by weight:		
Lubricating oil	100	99
Inhibitor	0	1
General properties:		
Gravity, °A. P. I.	32.4	32.2
Specific gravity: 60°/60° F.	0.8633	0.8644
Lb./gal., 60° F.	7.188	7.198
Viscosity, S. U. V., seconds—		
100° F.	182.5	178.2
210° F.	45.9	46.0
Viscosity index	103	109
V-G constant	0.805	0.806
Flash, OC—°F.	410	405
Fire, OC—°F.	475	485
Pour point, °F.	0	0
Color, N. P. A.	1.50	1.50
Sulfur, percent	0.05	0.08
Phosphorus, percent	0	0.01
Carbon residue, percent	0.03	0.03
Almen test:		
Lever load, pounds	10	22
Journal speed, R. P. M.	600	600
Rubbing speed, ft./min.	40	40
Torque, lb./ft.	15	40
Unit load, lb./sq. in.	5000	11000
Lubricant temperature, F.—		
Initial	88	84
Final	105	185
Special oxidation and corrosion test:		
Time oxidized, hours	48	48
Oil bath temperatures, F.	347	347
Air rate, cubic centimeters per hour	2000	2000
Quantity of oil, cubic centimeter	300	300
Cadmium silver bearing—		
Weight before test, g.	35.8670	36.2191
Weight after test, g.	35.5260	36.2211
Change in weight, g.	−0.3410	+0.0019
Appearance	Etched	Good

The lubricating oil referred to in the tests listed in Tables I and II was S. A. E. 10 grade oil which had been previously treated with aluminum chloride.

The "Special Oxidation and Corrosion Test" referred to in the foregoing tables is conducted as follows: An alloy bearing shell of certain commonly used standard dimensions is submerged in 300 cc. of the oil or oil composition in a 400 cc. Pyrex beaker and heated in a thermostatically controlled oil bath to 175° C. (347° F.), and air, at the rate of 2000 cc. per hour, is bubbled through the oil in contact with the bearing shell. At the end of 48 the loss of weight and the condition of the bearing shell are determined, the bearing shell being washed free of oil and dried before weighing. When determining the effectiveness of various improvement agents, the usual procedure is to run a "blank" test simultaneously with the oil composition being tested, employing for that purpose a sample of the untreated oil.

In this test it is advantageous to employ commercial bearing shells. These shells comprise a suitable metal backing faced with the alloy bearing metal. In this way, the actual bearing face is subjected to severe deteriorative conditions. By comparison of the results of such tests with actual service tests, we have found them to be in substantial agreement as to the suitability of particular lubricants.

In the tests given in Tables I and II, we employed so-called "cadmium-silver" bearings of the following approximate composition:

Metal	Percent
Cadmium	98
Silver	1
Copper	1

In these tests the loss in weight, while not extremely high when expressed as "per cent loss", is, nevertheless, very significant as the bearing shells used have an alloy facing of only 0.008 to 0.012 in. thickness on a highly resistant backing and the observed losses in the reported tests often represent a loss of the order of 10 per cent of the alloy facing.

Various modifications in the operating procedures mentioned hereinabove will suggest themselves to those skilled in the art. For example, we have described washing the phenol-olefin reaction product with water and dilute caustic soda solution to effect neutralization and removal of the acid or acids (e. g., sulfuric acid and sulfonic acids) remaining in the reaction mixture after the introduction of the olefins has been discontinued. Such neutralization and removal may be effected in other ways, as by extraction with aqueous alcohol, contact with solid alkalis such as calcium or sodium carbonates, or by contacting the reaction mixture with solid adsorbents such as fuller's earth, activated carbon, or the like.

Wherever the expression "highly paraffinic oil" is employed herein and in the claims hereinafter made, it is in general intended to indicate lubricating oils conforming in physical properties to oils prepared from Pennsylvania crudes; these "highly paraffinic oils" are either oils derived from Pennsylvania crudes or oils which have been refined or blended to approach or even exceed the former oils in paraffinicity. Where various materials are referred to as being soluble in such paraffinic oils, this expression is intended to mean that such materials may be incorporated into such oils in amounts up to 10 per cent, without producing any haziness nor cloudiness in the appearance of the resultant compositions, at least under atmospheric temperatures and under the ordinary conditions to which such oil compositions are subjected in storage and handling prior to their actual use as lubricant.

While we have described our invention hereinabove with reference to various preferred forms and embodiments, and with reference to various specific examples, it will be understood that our invention is not limited to the details of such illustrative embodiments or examples but may be variously practiced and embodied within the scope of the claims hereinafter made. Moreover, while we have in certain instances specifically given certain preferred ranges and proportions, it will be understood that our invention is not limited thereto and that such preferred ranges and proportions are in general selected for particular products and particular purposes; variations in proportions and in the methods of preparation result in products of different characteristics, such products having individual advantages and utilities.

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 sesquisulphide.

2. 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 sesquisulphide to obtain a final inhibitor product containing from 0.5 to 2.0 per cent by weight of phosphorus.

3. 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 sesquisulphide, to obtain a final inhibitor product containing from 0.25 to 1.0 per cent of sulphur.

4. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting phosphorus sesquisulphide with a water-insoluble reaction product of a phenol and an olefin, said product having anti-oxidant properties when added to a hyrdocarbon oil.

5. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting phosphorus sesquisulphide with a water-insoluble reaction product of a phenol and an olefin, said product having anti-oxidant properties when added to a hydrocarbon oil, the reacting being carried to such an extent as to incorporate sufficient phosphorus and sulphur into the final product to give the final product the property of inhibiting the corrosion of bearing metals by hydrocarbon oil, when added to such oil, while retaining to such a substantial extent the anti-oxidant value of the aforesaid phenol-olefin reaction product.

6. The method of preparing an oil-soluble organic compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and phenol in the presence of sulphuric acid, neutralizing the resultant product, distilling the neutralized product to recover a fraction of intermediate boiling range, and re-

acting said fraction with phosphorus sesquisulphide.

7. An improvement agent for hydrocarbon lubricant oils, comprising a phosphorus-sesquisulphide reaction product of a water-insoluble secondary or tertiary alkylated phenol.

8. An improvement agent for hydrocarbon lubricant oils, comprising a phosphorus-sequisulphide reaction product of a water-insoluble secondary or tertiary alkylated phenol, said product containing a total of from 0.75 to 3 per cent of combined sulphur and phosphorus.

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