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METHOD OF MANUFACTURING INHIBITORS FOR LUBRICATING OIL COMPOSITIONS

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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 combination 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, viscocity, 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 satisfactorily high degree of solubility in hydrocarbon oils, even the more highly refined or more highly paraffinic oils, having a satisfactory 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 or moderately elevated temperatures upon metallic packaging metals 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 desirable 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 desirable anti-oxidant and stabilizing properties and effective to retard increase 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 hereinafter be found to obtain.

We have found that extremely effective improvement agents or inhibitors of the general character indicated can be prepared by reacting phosphorus pentachloride with certain anti-oxidants, said anti-oxidants comprising water-insoluble reaction products obtained by reacting phenols with olefins. Such anti-oxidants 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, (now U. S. Patent No. 2,061,111, patented November 17, 1936) and the co-pending 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 had for further details. The disclosures of the co-pending applications referred to constitute in effect a part of the disclosure of the present application insofar as relates to the preparations of such anti-oxidant materials which are used as starting materials in preparing improvement agents in accordance with our present invention.

Referring, for example, to the aforesaid co-pending application, Serial No. 99,488, there is disclosed a process of manufacturing anti-oxidants wherein a phenol is mixed with from 1 to 10 per cent of sulfuric acid having strength of from 60 to 100 per cent, or even fuming sulfuric acid, and an olefin or 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 product 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 acids also 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 material. By way of example, the olefinic starting material may be butylenes, amylenes, refinery gases containing normally gaseous olefins (ethylenes, propylenes) in varying amounts, 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.

When 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 when the concentration of olefins 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 use in the process described herein.

The exact chemical and structural nature of the anti-oxidant materials, as thus prepared and employed as 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 also 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-copending 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 pentachloride 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, 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 the most important. 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-oxidants 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 purpose of our present invention is it necessary to do so; 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 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 pentachloride to phosphorus-containing materials useful as inhibitors.

As aforesaid, we prepare our addition improvement agents or inhibitors by reacting anti-oxidants, as described herein, with phosphorus pentachloride. The general procedure is as follows: The anti-oxidant material, which should preferably be dry, is warmed if necessary to reduce its viscosity and powdered phosphorus pentachloride is slowly added in predetermined amount, the mixture being stirred as the reaction proceeds. The temperature is slowly raised to 350°–450° F., or thereabouts, and maintained at this elevated temperature for a suitable time in order to drive off the hydrogen chloride resulting from the reaction, and which is copiously evolved during the early stages of the reaction. The mixture is then cooled. The prodouct thus prepared may be filtered to remove insoluble impurities by means of a mechanical filter, or if it is desired to lighten the color of the material, it may be treated with a suitable solid adsorbent material such as fuller's earth, charcoal, acid-treated clay or the like. Wherever the material as initially prepared is of relatively high viscosity, it may be diluted with a suitable hydrocarbon liquid of lower viscosity in preparation for the filtration-decolorizing step. By way of example, we may employ a light naphtha as diluent, the use of naphtha having the advantage that such naphtha may be readily removed after the filtration operation by distillation. Or, we may employ as diluent a low-viscosity oil similar to the oil to which the inhibitor is to be added eventually; in such case it is unnecessary to remove the diluent prior to incorporating the inhibitor in the lubricating oil.

The amount of phosphorus pentachloride added will vary over a considerable range, depending upon the desired characteristics of the final product and the degree of concentration of the anti-oxidant. Where the anti-oxidant material is relatively highly concentrated and the phosphorus pentachloride is added in sufficient amount to react fully with all of the anti-oxidant present, the products tend to be of high viscosity. It is desirable to add sufficient phosphorus pentachloride to give a product containing from 1 to 5 per cent by weight of phosphorus, assuming the original anti-oxidant material to be free or relatively free from diluent. However, we find that the best results are obtained by limiting the amount of phosphorus pentachloride added to give products containing from about 2.0 to 4.0 per cent of phosphorus. Products containing phosphorus well within this preferred range are effective enough to be economical, and their physical properties, such as viscosity, solubility in oil, color and the like, make them highly suitable as addition agents, especially for incorporation in highly paraffinic oils. Moreover, by limiting the amount of phosphorus pentachloride added to a

point short of completion of the reaction with all of the anti-oxidant, we obtain final products comprising mixtures of the phosphorus-containing inhibitor and some of the original anti-oxidant material, and having especially advantageous properties. The unreacted anti-oxidant serves as a blending agent and also contributes anti-oxidant and stabilizing properties, so that the products thus prepared are very soluble in hydrocarbon oils and, while effective as inhibitors, also have high anti-oxidant and stabilizing values and are themselves stable to an advantageous extent.

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

Gravity: °API	15 to 25
Specific gravity:	
60°/60° F	0.9659 to 0.9042
Viscosity, SUV at 100° F.: seconds	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 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 starting material should be such that 0.01 per cent by weight thereof added 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 for the process of the present invention.

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

Naturally, it is to be expected that the viscosities, specific gravities, and other physical characteristics of the particular phenol employed will have a corresponding effect upon the product, to some extent at least; this effect may not, however, always hold true where the degree of olfin absorption varies over comparatively wide limits and where the percentages of phosphorus in the final compound also varies.

When cresylic acid, ortho-cresol, 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 to ultimately secure inhibitors that are sufficiently soluble in higher gravity oils.

When the anti-oxidant material is prepared from phenol (C_6H_5OH) itself, e. g. "90 per cent 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 three to eight carbon atoms per molecule; the higher the molecular weight of the olefin the more viscous the final product will be. Olefins containing more than eight carbon atoms per molecule tend to reduce the phosphorus content of the final inhibitor product. Ethylene 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 olefinic starting materials are those containing from three to five carbon atoms per molecule, especially butylenes; fractions obtained from gaseous products of 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 resulting water-insoluble anti-oxidant material is then preferably dried. The drying may be accomplished by passing the material through absorbent clay and 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. and treating it with a dry inert gas, in suitable apparatus. This procedure dehydrates but tends to darken the anti-oxidant material.

The dry anti-oxidant may be then treated directly with phosphorus pentachloride, or it may first be distilled to separate undesirable low-boiling and high-boiling constituents, respectively. Thus, we may distill under a vacuum from −11 in. to −28 in. Hg, to recover a fraction distilling over between 300° to 550° F., which fraction may then be treated with phosphorus pentachloride in the manner described. The lower boiling material and sometimes also the residue may be recycled for further reaction with olefin in the presence of sulfuric acid, or used as anti-oxidant.

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 per cent phenol" were mixed with 5 per cent by weight of 94.5 per cent H_2SO_4 (c.p.). Olefin gas, composed primarily of C_4 hydrocarbons, was then introduced into close contact with the phenol-acid mixture until the volume of the reacting mixture increased to about 45 gal. This product was 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 then distilled under a vacuum of 11 to 12 in. Hg. The distillate was cut into three fractions. That fraction distilling

over at vapor temperatures between 300° and 550° F. had the following properties:

Gravity: °API	16.8
Viscosity, SUV at 100° F.: sec.	185
Color: Saybolt	−13

(b) Preparation of final inhibitor

83 parts by weight of the above distillate were treated with 17 parts by weight of phosphorus pentachloride, and the resulting material had the following properties:

Gravity: °API	8.3
Viscosity, SUV at 100° F.: sec.	946
Color, NPA	(Dark)
Phosphorus: per cent by weight	2.62

EXAMPLE 2

80 parts by weight of an anti-oxidant fraction similar to that described in Example 1(*a*) above were treated with 10 parts by weight of phosphorus pentachloride, yielding an inhibitor product having the following properties:

Gravity: °API	11.4
Viscosity SUV at 100° F.: sec.	480
Color, NPA	(Dark)
Phosphorus: per cent by weight	1.76

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 the oil alone would cause such corrosion. Oil compositions containing them also exhibit marked extreme-pressure characteristics. These inhibitors are stable at ordinary or moderately elevated temperatures 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 paraffinicity. Moreover, these inhibitors have excellent anti-oxidant properties, the anti-oxidant properties rising in proportion to the amount of unreacted starting material remaining in the final product. They are not subject to hydrolysis to any detrimental extent; the organic products of such hydrolysis as may occur are in themselves anti-oxidants and non-corrosive materials.

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 wt.:		
Lubricating oil	100	99.0
Inhibitor		1.0
General properties:		
Gravity: °API	28.1	27.9
Specific gravity: 60°/60° F.	0.8866	0.8877
Viscosity, SUV: seconds—		
100° F.	295	299
210° F.	51	51.4
Viscosity index	90	90
V-G constant	0.827	0.828
Flash, OC: °F.	430	425
Fire, OC: °F.	495	490
Pour point: °F.	0	0
Color, NPA	4.25	4.25
Phosphorus: Percent by wt.		0.03
Carbon residue: Percent by wt.	0.07	0.09
Almen test:		
Lever load: lb.	8	16
Journal speed: RPM	600	600
Rubbing speed: ft./min.	40	40
Unit load: lb./sq. in.	4000	8000
Lubricant temp.: °F.—		
Initial	90	85
Final	105	130
Special oxidation and corrosion test:		
Time oxidized: hr.	48	48
Oil bath temperature: °F.	347	347
Air rate; cc. per hr.	2000	2000
Quantity of oil: cc.	300	300
Oxidized oil:		
Gravity: °F.	27.1	27.4
Viscosity, SUV: seconds—		
100° F.	341	330
210° F.	53.3	53.1
Carbon residue: Percent	0.52	0.48
Neutralization No.	0.80	0.77
Sludge: Percent	0.45	0.31
Cadmium-silver bearing:		
Weight before test: g.	27.5090	27.3311
Weight after test: g.	27.4000	27.3340
Change in weight: g.	−0.1090	+0.0029
Appearance	etched	good

TABLE II

	Untreated oil	Oil containing our inhibitor (prepared as in Example 2)
Make-up: Percent by wt.:		
Lubricating oil	100	99.0
Inhibitor		1.0
General properties:		
Gravity: °API	32.4	32.3
Specific gravity: 60°/60° F.	0.8633	0.8639
Viscosity, SUV: seconds—		
100° F.	182.5	179.6
210° F.	45.9	46.0
Viscosity index	102	107
V-G constant	0.805	0.805
Flash, OC: °F.	410	410
Fire, OC: °F.	475	475
Pour point, °F.	0	
Color, NPA	1.5	1.75
Phosphorus: Percent by wt.	0	0.02
Carbon residue: Percent	0.03	0.05
Almen test:		
Lever load: lb.	10	16
Journal speed: RPM	600	600
Rubbing speed: ft./min.	40	40
Unit load: lb./sq. in.	5000	8000
Lubricant temp.: °F.—		
Initial	70	77
Final	120	135
Special oxidation and corrosion test:		
Time oxidized: hr.	48	48
Oil bath temperature: °F.	347	347
Air rate: cc. per hr.	2000	2000
Quantity of oil: cc.	300	300
Oxidized oil:		
Gravity: °API	30.8	31.0
Viscosity, SUV: seconds—		
100° F.	232	229
210° F.	51	50
Carbon residue	0.51	0.46
Neutralization No.	1.30	1.25
Cadmium-silver bearing:		
Weight before test: g.	36.2480	36.7710
Weight after test: g.	36.0970	36.7739
Change in weight: g.	−0.1510	+0.0029
Appearance	etched	good

The lubricating oil used in the tests given in Table I was an SAE 20 grade oil which had been previously solvent refined; this is a moderately highly paraffinic oil. The oil used in the tests given in Table II was an SAE 10 grade oil which had been previously treated with aluminum chloride; this is a highly paraffinic oil.

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 and 96 hours, 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 treated 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 the foregoing tables 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.

In addition to the preparation of inhibitors comprising reaction products of phosphorus pentachloride alone with anti-oxidants of the general class described, our invention contemplates mixtures of such inhibitors with reaction products obtained by treating such anti-oxidant material with other phosphorus-containing and sulfur-containing reagents. Particularly effective mixtures may be obtained, for example, by mixing inhibitors prepared as set forth hereinbefore with inhibitors comprising organic esters of phosphorus acids, such as inhibitors prepared by reacting phosphorus trichloride with anti-oxidant material of the general class described herein above and as set forth in our co-pending application, Serial No. 99,662, filed September 5, 1936. The combination of both trivalent and pentavalent compounds in such mixtures is especially advantageous in that such combinations tend to possess a wider range of effectiveness than is true of either class of compounds alone, and possibly also because the pentavalent phosphorus compounds tend to have a stabilizing effect upon the trivalent phosphorus compounds.

Furthermore, advantageous and effective composite inhibitors may be prepared comprising mixtures of inhibitors prepared as set forth hereinabove with inhibitors prepared by reacting anti-oxidant materials of the character described with suitable reagents containing sulfur, or containing both phosphorus and sulfur. For example, inhibitors prepared as set forth hereinabove may be used in admixture with inhibitors prepared by reacting anti-oxidants of the class described with sulfur chloride, as described in our co-pending application, Serial No. 100,956, filed September 15, 1936, or with inhibitors prepared by reacting anti-oxidant material of the class described with phosphorus pentasulfide, or with a mixture of phosphorus penasulfide and phosphorus trichloride, as disclosed in our co-pending application, Serial No. 100,382, filed September 11, 1936. Such mixtures, containing both phosphorus and sulfur, are of especial value for particular uses and often exhibit characteristics which could not be predicted from the characteristics of the individual constituents themselves.

With reference to all of the above mixtures, they may be prepared either by separately treating anti-oxidant with the individual reagents noted, or they may be prepared by treating anti-oxidant material directly with a mixture of any two or more of the various reagents noted; however, in the latter case, due to reactions which may take place during or prior to the reaction with the anti-oxidant, the character of the final products may be different from those obtained by simply blending individually prepared inhibitors of the different types. So far as we have been able to ascertain, all of these composite inhibitors, prepared in either of the above manners, are useful and effective, although they vary with reference to their value for particular purposes, e. g., as inhibitors, extreme-pressure agents, and as anti-oxidants or stabilizers; each has particular advantages with respect to particular uses.

Various modifications in the operating procedure mentioned hereinabove will suggest themselves to those skilled in the art. For example, we have described washing the phenol-olefin reaction product or anti-oxidant 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 lime or sodium carbonate, 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 latter 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 used as lubricants.

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 phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting phosphorus pentachloride with a water-insoluble reaction product of a phenol and an olefin having anti-oxidant properties when added to a hydrocarbon oil, the reaction being carried to such extent as to incorporate sufficient phosphorus 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 preserving to a substantial extent the anti-oxidant value of the aforesaid phenol-olefin reaction product.

2. The method of preparing an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises passing a gaseous olefin into contact with a phenol in the presence of sulfuric acid until the reacting mixture has increased in volume from 30 to 250 per cent on the original phenol, neutralizing the resultant anti-oxidant product, and reacting at least a portion of the washed anti-oxidant product with phosphorus pentachloride to obtain a final oil-soluble material containing not more than about 5 per cent of phosphorus.

3. The method of preparing an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises passing a gaseous olefin into contact with a phenol in the presence of sulfuric acid until the phenol-acid mixture has absorbed from one to two mols of olefin per mol of phenol, washing the resultant anti-oxidant product with water and dilute alkali, and reacting at least a portion of the washed anti-oxidant product with phosphorus pentachloride.

4. The method of preparing oil-soluble organic compounds suitable as improvement agents for highly paraffinic lubricating oils which comprises reacting an olefin and a phenol in the presence of a catalyst, washing the resultant product with water and dilute alkali, treating at least a portion of the product with phosphorus pentachloride, and regulating the degree of absorption of olefin in the initial reaction stage with reference to the specific chemical character of the phenol and olefin, to secure an intermediate water-insoluble product which, when treated in the subsequent reaction stage with phosphorus pentachloride in the required amount to introduce from 1 to 5 per cent of phosphorus into the aforesaid intermediate product, will yield a phosphorus-containing product soluble in highly paraffinic oil.

5. The method of preparing oil-soluble organic compounds suitable as improvement agents for highly paraffinic lubricating oils, which comprises reacting an olefin and a phenol in the presence of sulfuric acid, washing the resultant product with water and dilute alkali, treating a portion of the product with phosphorus pentachloride, treating a second portion with phosphorus trichloride, and blending the resultant reaction products to obtain a final product soluble in highly paraffinic oil and containing a total of not more than about 5 per cent of phosphorus.

6. The method of preparing an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and a phenol in the presence of sulfuric acid, and treating at least a portion of the resultant product with a mixture of phosphorus pentachloride and phosphorus trichloride.

7. The method of preparing an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and a phenol in the presence of sulfuric acid, and treating at least a portion of the resultant product with a mixture of phosphorus pentachloride and phosphorus pentasulfide.

8. The method of preparing an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils, which comprises reacting an olefin and a phenol in the presence of sulfuric acid, and treating at least a portion of the resultant product with a mixture of phosphorus pentachloride and sulfur chloride.

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