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MINERAL OIL COMPOSITION AND IMPROVING AGENT THEREFOR

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This invention has to do in a general way with viscous mineral oil compositions of the lubricant and dielectric types which have been improved in one or more of their various properties by having admixed therewith a minor proportion of a mineral oil-improving agent. More specifically, the invention is concerned with the production of a novel class of mineral oil-improving agents and with the production of improved mineral oil compositions of the viscous type containing one or more of these novel improving agents.

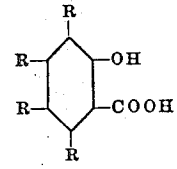
It is well known to those familiar with the art that the deteriorating effect of oxidation and continued use upon a mineral oil fraction manifests itself in various ways, depending upon the source of the oil—that is, the crude from which it is derived—the refining treatment to which the oil has been subjected, and the particular conditions under which the oil is subjected to oxidation. Motor oils, for example, especially those refined by certain solvent-extraction methods, tend to oxidize when subjected to high temperatures and form products that are corrosive to metal bearings. This corrosive action may be severe with certain bearing metals such as the hard metal alloys of the cadmium-silver and copper-lead types, and the class of improving agents contemplated herein are particularly useful as inhibitors of oxidation and the attending bearing corrosion in oils of this character.

The oil-improving agents contemplated herein also find valuable application in the field of motor-lubrication as inhibitors of the formation of materials which lead, on accumulation, to the sticking of piston rings and the filling of the slots in oil rings.

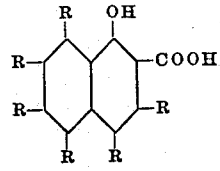
Certain of these improving agents are also useful in oils which have been refined for turbine or transformer use, particularly those which have been highly refined, to retard the deterioration of such oils and the attending development of acid or sludge which takes place under the conditions of use.

Although the general class of compounds or reaction products contemplated herein finds application principally in the field of oxidation inhibitors, and particularly as improving agents for internal combustion engine lubricants, it is to be understood that these improving agents may effect improvement in other respects or properties, such as load-carrying capacity, and, as indicated above, certain members of the class, at least, are effective acid inhibitors for highly refined turbine and transformer oils. In this same connection our invention contemplates, as an especially preferred group or type of improving agents falling within the general class, compounds or reaction products which are multifunctional in that they possess in addition to the inhibiting properties mentioned above, the property of improving the pour point of the oil to which they are added.

The oil-improving agents contemplated herein have as their characterizing constituent a reaction product obtained by reacting a phosphorus pentahalide with an aromatic hydroxycarboxylic acid which we may represent by the general formulae:

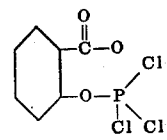


and



wherein the R's represent radicals selected from the group consisting of hydrogen, alkyl, aryl, aralkyl and alkaryl radicals. The foregoing reaction, whereby we obtain a subgroup of compounds encompassed by the invention and a first reactant for obtaining the remaining compounds contemplated herein, may be represented by the following equation wherein the ortho-hydroxy acid is used for purposes of illustration:



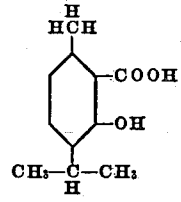


or

Because of uncertainty as to the molecular structure of this reaction product we prefer to identify it by its empirical formula $C_7H_4O_3Cl_3P$ or merely as a reaction product instead of indulging in speculation as to the structural formula. It will be observed that in the foregoing illustrative equation and reaction the aromatic hydroxycarboxylic acid used was an unsubstituted ortho-hydroxybenzoic acid (salicylic acid), and while the ortho-hydroxybenzoic acid (both sub-

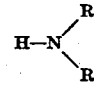
stituted and unsubstituted) and phosphorus pentachloride are considered preferred reactants for obtaining this sub-group of compounds, it is to be understood that the invention includes mono- and poly-cyclic aromatic hydroxycarboxylic acids in general and phosphorus pentahalides as initial reactants for obtaining this particular group of reaction products which may be used as oil-improving agents or as initial reactants for obtaining additional improving agents encompassed by the present invention.

As an example of a substituted ortho-hydroxybenzoic acid which may be reacted with a phosphorus pentahalide, we may mention thymotinic acid (methyl isopropyl salicylic acid) having the general formula:



These two acids, salicylic acid and thymotinic acid, will be used herein to illustrate the manner of synthesizing the various oil-improving agents and to demonstrate their effectiveness in mineral oil compositions.

As has been pointed out above, the reaction products obtained by reacting a phosphorus pentahalide with a mono- or poly-cyclic, substituted or unsubstituted aromatic hydroxycarboxylic acid constitute one group of oil-improving agents contemplated by the present invention. Another group of related oil-improving agents is obtained by taking the product of the foregoing reaction as a first reactant and reacting such product with a compound selected from the group consisting of ammonia, organic compounds containing replaceable hydrogen, and compounds containing replaceable metal atoms. Representative of the derivatives from reaction products of the type first mentioned above which are contemplated herein as oil-improving agents are those obtained by reacting the PCl_5-aromatic hydroxycarboxylic acid reaction product with materials containing "active" or replaceable hydrogen atoms, such as: ammonia or amines (compounds having the general formula



in which the Rs represent hydrogen, alkyl, aryl, aralkyl, or alkaryl radicals); and alcohols and mercaptans having the general formula R'XH, in which R' represents an alkyl, aryl, aralkyl or alkaryl radical, and in which X represents oxygen or sulfur. Inclusive of "second" reactants containing replaceable metal atoms may be mentioned the corresponding metal derivatives of the foregoing compounds, such as alcoholates, phenylates, mercaptides, etc.; also metal salts or derivatives of organic acids such as metal carboxylates, thiocarbonates, thiocyanates, cyanides, etc.

As has been previously noted, this invention contemplates as an especially preferred group of oil-improving agents those which are of multifunctional activity. Such reaction products are obtained by first condensing the phosphorus pentahalide with an aromatic hydroxycarboxylic acid (preferably an orthohydroxy acid) and then reacting the product thus obtained with an alkyl-substituted hydroxyaromatic compound in which the alkyl substituent is derived from a high molecular weight aliphatic hydrocarbon. For example, a multifunctional oil-improving agent of this type may be obtained by reacting the first reaction product with a wax-phenol obtained by reacting phenol with a chlorinated petroleum wax in the presence of a Friedel-Crafts catalyst. The details in procedures which may be conveniently followed in synthesizing oil-improving agents of the type contemplated herein, together with further details as to the physical properties and behavior of these reaction products in mineral oil will be best appreciated from the following examples.

EXAMPLE I

Synthesis of PCl_5-Aromatic Ortho-Hydroxy Carboxylic Acid Reaction Products

(a) PCl_5-salicylic acid reaction product

One mol of salicylic acid and one mol of phosphorus pentachloride were mixed together in a large flask fitted with a stirrer and reflux condenser. The mixture was heated on a water bath to a temperature not exceeding 80° F. and stirred until HCl evolution ceased. Hydrogen chloride evolution commenced when the reactants were mixed and became quite vigorous at the elevated temperature. The resulting product was a light-colored liquid which fumed in contact with moist air and will be hereinafter referred to as the "Salicylic-PCl_5 product."

(b) PCl_5-thymotinic acid reaction product

Following the same procedure described above, equal molecular proportions of thymotinic acid and phosphorus pentachloride were reacted together to yield a brown liquid product which will be hereinafter referred to as "Thymotinic-PCl_5 product."

(c) PCl_5-betahydroxy-alpha-naphthoic acid reaction product

Fifteen grams of betahydroxy-alpha-naphthoic acid and 22½ grams of PCl_5 were stirred together without external application of heat. A spontaneous reaction occurred, accompanied by a temperature rise from 28° C. to 42° C., forming a dark oil. This was taken up in 100 cc. of petroleum ether and 10 cc. of benzene and filtered. The solvents were partially removed in a vacuum dessicator, yielding a white crystalline solid with a melting point slightly above room temperature. This product will be identified herein as "Hydroxy-naphthoic-PCl_5 product."

The procedure followed in Examples *a* and *b* above was essentially that of Anschütz and Moore, Annalen 239, 314 (1887), and the method described in Example *c* was essentially that of Rabé, Ber. 22, 392 (1889).

EXAMPLE II

As we have previously pointed out, the products obtained by reacting PCl_5 with an aromatic ortho-hydroxy carboxylic acid (typified by Examples *Ia* and *Ib* above) may be reacted with a compound selected from the group consisting of ammonia, organic compounds containing reactive hydrogen and compounds containing reactive metal atoms, to yield additional oil-improving agents within the general class contemplated herein. The following examples illustrate reaction products of this last-mentioned type in which "Salicylic-PCl_5 product" and "Thymotinic-

PCl_5 products" have been reacted with compounds of the type represented by the formula



and R'XH above referred to and metallic derivatives such as alkali dithiocarbonates (xanthates), alkali thiocyanates and alkali cyanides.

(a) *"Thymotinic-PCl_5 product" and dibutylamine*

The "thymotinic-PCl_5 product" prepared from 39 grams (0.2 mol) of thymotinic acid and 42 grams (0.2 mol) of phosphorus pentachloride was added with stirring to a solution of 155 grams (1.2 mols) of dibutylamine in 100 grams of benzene. After the exothermic reaction had subsided, the benzene solution was filtered free of amine hydrochloride. The benzene was removed from the filtrate by vacuum distillation on the water bath. The residue was taken up in petroleum ether, filtered to remove more precipitated amine hydro-chloride, and the product, a dark-colored oil, recovered by vacuum distillation of the petroleum ether on the water bath. The product of this reaction will be hereinafter referred to as "Material from Example II*a*."

(b) *"Thymotinic-PCl_5 product" and monoamylamine*

In essentially the same manner as in the preceding example, II*a*, the product resulting from the reaction of 19.4 grams (0.1 mole) of thymotinic acid and 20.8 grams (0.1 mole) of phosphorus pentachloride was allowed to react with 60 grams (0.7 mole) of monoamylamine. The reaction was carried out in petroleum ether instead of benzene. Otherwise it was analogous to the Example II*a*; the excess amine was removed by vacuum distillation. The material was a brown, viscous oil weighing 35 grams and will be hereinafter referred to as "Material from Example II*b*."

(c) *"Salicylic-PCl_5 product" and dibutylamine*

A solution of 27.5 grams (0.1 mol) of the "salicylic-PCl_5 product" in 50 cc. benzene was added dropwise with stirring to a solution of 77.5 grams (0.6 mol) of dibutylamine in 100 cc. benzene during 3 hours. The mixture was filtered free of amine hydrochloride and the benzene removed by vacuum distillation on the water bath. This residue was freed from the last traces of amine hydrochloride by solution in petroleum ether, filtration and removal of the petroleum ether by vacuum distillation. The residue, a brown moderately viscous oil, weighed 45 grams. This product analyzed 5.74 per cent phosphorus, 6.81 per cent nitrogen and 0.31 per cent chlorine. Theoretical composition of $C_{31}H_{68}O_3N_3P$ is 5.63 per cent phosphorus and 7.62 per cent nitrogen. The product of this reaction will be hereinafter identified as "Material from Example II*c*."

(d) *"Salicylic-PCl_5 product" and N-amylaniline, in presence of pyridine*

A solution of 27.3 grams of the "salicylic-PCl_5 product" in 50 cc. of benzene was added during 25 minutes to a stirred solution of 50 grams of N-amylaniline and 25 cc. pyridine in 80 cc. benzene. The temperature rose spontaneously from 78° to 140° F. After stirring for an additional hour the temperature had dropped to 84° F. The mixture was filtered free from hydrochloride and the dark red filtrate refluxed for an hour. The cooled, filtered solution was washed with water and dried over anhydrous sodium sulfate. The solvent was removed by vacuum distillation on the hot water bath, leaving as the product 65 grams of a dark red, sticky oil, which will be hereinafter referred to as "Material from Example II*d*."

(e) *"Salicylic-PCl_5 product" and crude ricinoleic amine ("Castor amine")*

A solution of 27.3 grams of "salicylic-PCl_5 product" in 50 cc. benzene was added during 20 minutes with stirring to a solution of 85 grams of "Castor amine" (crude ricinoleic amine) and 30 cc. of pyridine in 200 cc. of benzene. The reaction was decidedly exothermic. After stirring for 2.5 hours longer the mixture was almost solid because of hydrochloride, which had separated. About 500 cc. of benzene was added and the mixture filtered. The solid was washed down with more benzene. The combined benzene filtrates were water-washed and the benzene was removed by vacuum distillation on the hot water bath, leaving a dark red, sticky oil, which will be hereinafter identified as "Material from Example II*e*."

(f) *"Salicylic-PCl_5 product" and ammonia*

This material was prepared in the oil merely by dissolving the calculated amount of "salicylic-PCl_5 product" in the oil to be tested, saturating for about an hour with ammonia and filtering off the precipitated ammonium chloride. The product of this reaction will be hereinafter referred to as "Material from Example II*f*."

(g) *"Salicylic-PCl_5 product" and tertiary amyl phenol*

A mixture of 68.5 grams (0.25 mol) of "salicylic-PCl_5 product" and 123 grams (0.75 mol) of "pentaphen" (commercial tertiary amyl phenol) in 150 cc. of benzene was refluxed for 3 hours until HCl evolution had substantially ceased. The benzene was then removed by vacuum distillation, leaving the product as a dark brown, viscous residue, which will be hereinafter referred to as "Material from Example II*g*."

(h) *"Salicylic-PCl_5 product" and 2-ethyl hexanol*

Thirty-nine grams of 2-ethyl hexanol and 27.3 grams of "salicylic-PCl_5 product" were mixed without solvent. Immediate reaction ensued, accompanied by a copious evolution of hydrogen chloride. The mixture was heated to 90° C. with stirring and held at that temperature for 1.5 hours. The mixture was then blown with dry nitrogen gas at 90° C. to free it from occluded HCl and to remove any excess 2-ethyl hexanol. The product was a straw-yellow, mobile liquid, and will be hereinafter referred to as "Material from Example II*h*."

(i) *"Salicylic-PCl_5 product" and p-tertiary amyl phenol disulfide*

A mixture of 1 gram of "salicylic-PCl_5 product" and 4.3 grams of p-tertiary amyl phenol disulfide was stirred and heated for an hour (until HCl evolution ceased) on a hot water bath. The product was a dark red oil, which will be hereinafter identified as "Material from Example II*i*."

(j) *"Salicylic-PCl_5 product and wax-phenol*

A mixture of 136 grams of "diwax-phenol" (obtained by Friedel-Crafts condensation of chlorinated paraffin wax and phenol and containing about 0.22 mol of phenolic hydroxyl) and

20 grams of "salicylic-PCl_5 product" was heated with stirring to 150° F. and 6 grams of anhydrous aluminum chloride gradually added. Evolution of gaseous HCl started immediately. The mixture was heated with stirring during 30 minutes to a temperature of about 350° F. and was held at that temperature for about 15 minutes. The reaction mixture was cooled, taken up in 250 cc. of benzol and washed with water. The solution was then diluted with petroleum ether and clarified by filtration. After evaporating to a volume of around 300 cc. and drying with anhydrous sodium sulfate, the solvent was removed by vacuum distillation on a water bath, leaving the product as a dark brown, viscous and tacky residue. This product, which will be hereinafter referred to as "Material from Example II*j*," is multifunctional in that it possesses the property of being an effective pour point depressant for viscous mineral oil fractions in addition to the oxidation-inhibiting property which characterizes the remainder of these oil-improving agents.

(*k*) *"Salicylic-PCl_5 product" and amyl mercaptan*

A solution of 27.3 grams of "salicylic-PCl_5 product" and 33 grams of amyl mercaptan in 100 cc. benzene was stirred and refluxed for 7 days, until the slow HCl evolution had ceased. The solvent was then removed by vacuum distillation on the water bath. The residue was extracted with petroleum ether. Evaporation of the petroleum ether extract yielded a red oil analyzing 5.47 per cent phosphorus, 21.98 per cent sulfur, and 0.57 per cent chlorine. Theoretical composition for $C_{22}H_{37}S_3O_3P$ is 6.51 per cent phosphorus, and 20.2 per cent sulfur. This product will be hereinafter identified as "Material from Example III*k*."

(*l*) *"Salicylic-PCl_5 product" and potassium ethyl xanthate*

A solution of 27.3 grams of "salicylic acid-PCl_5 product" in 70 cc. of benzene was added during 7 minutes to a stirred suspension of 48 grams of potassium ethyl xanthate in 150 cc. of benzene. The reaction was exothermic, the temperature rising from 80° to 99° F. The mixture was then refluxed for 1.5 hours. The mixture turned dark red in color and a finely divided precipitate (potassium chloride) separated out. The mixture was filtered when cold. It was noted that the solution was red when viewed through thick layers, but green in a thin layer. The solution was evaporated under vacuum on a hot water bath, leaving 27 grams of a dark red liquid, which will be identified herein as "Material from Example III*l*."

(*m*) *"Salicylic-PCl_5 product" and potassium thiocyanate*

A solution of 27.3 grams of the "salicylic-PCl_5 product" in 70 cc. of benzene was added during 45 minutes to a stirred suspension of 29.1 grams potassium thiocyanate in 150 cc. of benzene. The temperature of the reaction mixture rose only three degrees, from 80 to 83° F., and the solution colored light brown. After refluxing for an hour the solution became bright red. The mixture was filtered. The filtrate fumed, indicating the presence of unreacted acid chlorides. More potassium thiocyanate (10 gms.) was added and the mixture stirred and refluxed for 1½ hours. The mixture was filtered and the benzene removed by vacuum distillation on the hot water bath, leaving a dark red oil weighing 14 grams, which will be hereinafter identified as "Material from Example II*m*."

(*n*) *"Salicylic-PCl_5 product" and potassium cyanide*

To a suspension of 19.5 grams of potassium cyanide in 100 cc. of benzene was added with stirring, during 25 minutes, a solution of 27.3 grams of "salicylic-PCl_5 product" in 50 cc. of benzene. The temperature of the reaction mixture rose spontaneously from 80° to 96° F. during the course of the reaction. The mixture was stirred and refluxed for 45 minutes. Some unreacted chloride was still present, so an additional 10 grams of potassium cyanide was added and the refluxing and stirring continued for 2 hours. The reaction mixture was then filtered and the solvent removed from the filtrate by vacuum distillation on the water bath, leaving a light brown non-viscous liquid residue, which will be hereinafter identified as "Material from Example II*n*."

(o) *"Hydroxynaphthoic-PCl_5 product" and dibutylamine*

A solution of 23 grams of "hydroxynaphthoic-PCl_5 product" in 100 cc. of benzene was added during 30 minutes to a solution of 78 grams of dibutylamine in 80 cc. of benzene. The reaction was exothermic, the temperature of the reaction mixture rising from 30° C. to 70° C. After stirring for two hours the mixture was filtered free from solid amine hydrochloride and the filtrate heated to reflux for two hours. The benzene residue was taken up in petroleum ether and the resultant solution washed with dilute hydrochloric acid and then with distilled water. After drying over sodium sulfate the petroleum ether was removed by distillation.

IMPROVEMENT OF MINERAL OIL FRACTIONS

As was pointed out above, the compounds or reaction products contemplated herein are effective to inhibit the corrosive action of mineral oil fractions, such as solvent-refined oil, normally corrosive to hard metal alloy bearing metals typified by cadmium-silver and copper-lead alloys. In this same regard, our invention contemplates, in addition to mineral oil fractions containing the improving agents contemplated herein, a method for lubricating alloy bearings which involves the use of a lubricant containing one or more of these improving agents to provide the lubricant film.

To demonstrate the effectiveness of the improving agents contemplated herein as inhibitors of corrosive action of the type above referred to, samples of motor lubricating oil and oil blends containing representative improving agents were tested by suspending a 6-gram section of a hard metal alloy bearing in a 30-gram sample of the oil or oil blend and heating same to about 175° C. for 22 hours while bubbling a stream of air against the surface of the bearing. The weight loss in milligrams of the bearing section is interpreted as a measure of the corrosiveness of the oil. In each case, a sample of the oil containing the addition agent was run concurrently with a sample of the blank oil, and each companion sample contained a bearing section. The results obtained with blends of the various reaction products from the several examples above are listed in Table I below. In all cases, except the test run with "Material from Example II*a*" the alloy bearing section was from a cadmium-

silver bearing and the oil was a commercial S. A. E. 20 solvent-refined motor oil. The oil containing the product from Example IIa was an S. A. E. 60 aero engine oil, and the bearing section was taken from a copper-lead alloy bearing.

Table I

Improving agent added to oil	Weight in oil	Weight loss in milligrams	
		Blend	Blank
Salicylic-PCl_3 product	0.25	1	35
Material from Example IIa	0.25	0	30
Material from Example IIb	0.25	4	55
Material from Example IIc	0.10	0	69
Material from Example IId	<0.10	0	49
Material from Example IIe	<0.10	14	35
Material from Example IIf	0.25	0	35
Material from Example IIg	0.25	1	37
Material from Example IIh	0.25	6	46
Material from Example IIi	0.10	0	35
Material from Example IIj	1.00	1	44
Material from Example IIk	0.10	0	69
Material from Example IIl	<0.10	0	47
Material from Example IIm	<0.10	0	49
Material from Example IIn	0.10	0	49
Material from Example IIo	0.10	0	27

In addition to the foregoing motor oil test, typical improving agents contemplated herein were blended with motor oil and subjected to an accelerated engine operation test to evaluate their ability to prevent ring-sticking, etc., in engine operation. The engine employed in the test was a standard C. F. R. "knock test" engine and the test involved operating the engine first with the oil and then with the oil blend at an approximate speed of 1200 R. P. M. with the throttle set just below detonation, using a compression ratio of 7:1 and a jacket temperature of 400° F.

The test runs were normally 28 hours in length with an inspection at 14 hours. The following inspections were made:

I. The piston:
- (a) Degrees of ring-sticking (0° being an entirely free ring and 360° a totally stuck ring)
- (b) Per cent of filling of oil slots
- (c) Deposits (grams)

II. Used oil:
- (a) Kinematic viscosity (K. V.) at 210° F.
- (b) Neutralization number (N. N.)

The results obtained are listed in Table II below, where "Oil A_1" and "Oil A_2" are the motor oil blanks and oils B_1 and B_2 are the same oil containing 0.5 per cent of the "Material from Example IIc" and 1.0 per cent of "Material from Example IIa" respectively.

Table II

Oil	Hours	Degrees stuck					Slots percent filled			Total deposits	Used oils	
		1	2	3	4	5	3	4	5		210° F. K. V.	N. N.
Oil A_1	14	0	0	0	0	0	5	5	**Tr			
	28	360	0	360	360	90	80	80	50	11.5	29.94	1.6
Oil B_1	14	0	0	0	0	0	0	0	0			
	28	0	0	0	0	0	0	0	0	10.5	30.81	2.2
Oil A_2	14	0	0	90	90	0	40	15	5			
	28	90	*T	360	360	15	65	50	20	12.22	28.67	1.5
Oil B_2	14	0	0	0	0	0	Tr	Tr	Tr			
	28	0	0	0	0	0	Tr	Tr	Tr	10.51	26.73	1.45

*Tacky.
**Trace.

As was also indicated hereinabove, certain of the improving agents contemplated herein are effective to inhibit the deteriorating effects of oxidation upon highly refined oils of the type used in turbines, transformers and the like. To demonstrate effectiveness in this regard a very highly acid-refined oil of the transformer type and blends containing same were used. The oil had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Viscosity of 69 seconds at 100° F. The test (known as a Modified German tar test) was conducted by heating oil samples to 120° C. and bubbling oxygen gas through the oil for a period of 70 hours and then determining the neutralization number of the oil as an indication of the amount of acidic oxidation products formed. Although all of the improving agents tested were effective to inhibit the corrosive action of solvent-refined motor oils and were effective to inhibit ring-sticking in the operation test, some of these same agents failed to show particular promise as inhibitors for highly refined oils of the turbine and transformer types. Certain of these agents, however, were highly effective in this regard and the results obtained with these products in the test and oil referred to above are listed in Table III below.

Table III

Oil sample	Neutralization number
Blank	20–25
Blank+<0.10% Material from Example IId	0.04
Blank+0.10% Material from Example IIi	0.04
Blank+0.25% Material from Example IIj	0.04
Blank+0.10% Material from Example IIk	0.03
Blank+<0.10% Material from Example III	0.61

The ability of the improving agents contemplated herein to increase the load-carrying capacity of lubricants has been demonstrated with the material from Examples IIc and IIo. An S. A. E. 60 aero engine oil failed in the Almen test at a load of 4000–6000 pounds at a speed of 200 R. P. M., as compared with a blend of the same oil containing 1.0 per cent of "Material from Example IIc," which passed the test at 30,000+pounds. Using a gear oil of 80 to 90 seconds Saybolt viscosity at 210° F., the load limit in the Almen test at a speed of 600 R. P. M. was 4000 pounds and this same oil containing 5.0 per cent of "Material from Example IIo" passed the test at 30,000 pounds.

To demonstrate the effectiveness of the preferred multifunctional reaction product (material from Example IIj) as a pour point depressant, blends were prepared from a conventional motor lubricating oil having an A. S. T. M. pour test of +20° F. A blend of this oil containing only 0.1 per cent of the "Material from Example IIj" had a pour point of −10° F., and the same oil containing 1 per cent of this same material had a pour point of less than −35° F.; reductions in

pour point of 30° and more than 55° respectively.

The amount of improving agents which may be used in the oil will vary more or less with the oil and the conditions of use, but in general the desired improvement can be effected with amounts ranging from about 0.01 per cent to about 10 per cent.

It is to be understood that while we have herein described certain preferred procedures for synthesizing improving agents of the type contemplated by this invention and have designated certain illustrative reactants which may be employed, the invention is not confined to the specific detailed procedural operations or reactants described but includes within its scope whatever changes fairly come within the spirit of the appended claims.

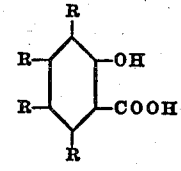
We claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting a phosphorus pentahalide with an aromatic hydroxycarboxylic acid and then reacting the product thus obtained with a compound selected from the group consisting of: ammonia, organic compounds containing replaceable hydrogen and compounds containing reactive metal atoms.

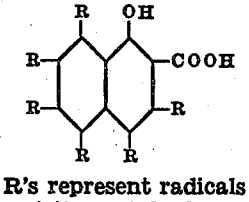
2. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting a phosphorus pentachloride with an aromatic orthohydroxycarboxylic acid and then reacting the product obtained from the foregoing reaction with a compound selected from the group consisting of: ammonia, and organic compounds containing replaceable hydrogen atoms and organic compounds containing replaceable metal atoms.

3. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with a compound selected from the group consisting of ammonia, organic compounds containing replaceable hydrogen atoms and organic compounds containing replaceable metal atoms.

4. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with a compound selected from the group having the general formulae:



and



in which the R's represent radicals selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, and alkaryl radicals and then reacting the product thus obtained with a compound selected from the group consisting of ammonia, organic compounds containing replaceable hydrogen atoms and organic compounds containing replaceable metal atoms.

5. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with an organic compound containing a replaceable hydrogen atom.

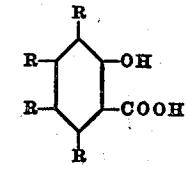
6. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with a wax-substituted hydroxyaromatic compound.

7. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with wax-substituted phenol.

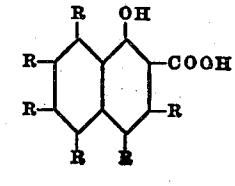
8. The method of lubricating relatively moving metallic bearing surfaces having the corrosion susceptibility of hard metal alloys of the cadmium-silver type which comprises maintaining between the bearing surfaces a lubricant film having as a primary lubricating constituent the combination of a major portion of a mineral oil normally corrosive to alloys of the cadmium-silver type and a minor proportion of a reaction product obtained by first reacting a phosphorus pentachloride with an aromatic ortho-hydroxycarboxylic acid and then reacting the reaction product thus obtained with a compound selected from the group consisting of: ammonia, organic compounds containing replaceable hydrogen atoms and organic compounds containing replaceable metal atoms.

9. A mineral oil-improving agent comprising a reaction product obtained by first reacting a phosphorus pentahalide with an aromatic ortho-hydroxy-carboxylic acid and then reacting the reaction product thus obtained with a compound selected from the group consisting of ammonia, organic compounds containing replaceable hydrogen and organic compounds containing replaceable metal atoms.

10. A mineral oil-improving agent comprising a reaction product obtained by first reacting phosphorus pentachloride with an hydroxyaromatic acid selected from the group consisting of acids having the general formulae:



and



in which the R's represent radicals selected from the group consisting of: hydrogen, alkyl, aryl, aralkyl and alkaryl radicals,and then reacting the reaction product thus obtained with a compound selected from the group consisting of ammonia, organic compounds containing replaceable hydrogen and organic compounds containing replaceable metal atoms.

11. A mineral oil-improving agent comprising a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with a compound selected from the group consisting of ammonia and organic compounds containing replaceable hydrogen and organic compounds containing replaceable metal atoms.

12. A mineral oil-improving agent comprising a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with an organic compound containing a replaceable hydrogen atom.

13. A mineral oil-improving agent comprising a reaction product obtained by first reacting phosphorus pentachloride with an ortho-hydroxybenzoic acid and then reacting the product thus obtained with a wax-substituted hydroxy-aromatic compound.

14. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an aromatic hydroxycarboxylic acid and then reacting the product thus obtained with an alcohol.

15. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an aromatic hydroxycarboxylic acid and then reacting the product thus obtained with a mercaptan.

16. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of a reaction product obtained by first reacting phosphorus pentachloride with an aromatic hydroxycarboxylic acid and then reacting the product thus obtained with an amine.

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