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LUBRICATING OIL

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This invention relates to the treatment of hydrocarbon products such as mineral oil to improve their characteristics, and particularly to the addition to petroleum lubricating oil of certain materials which improve their ability to resist the deteriorating effect of oxidation and their ability to lubricate bearing surfaces which are subjected to extreme pressures such as are now commonly encountered in the newer types of machinery.

Moderately refined oils, such as motor oils and other moderately refined lubricating oils and moderately refined turbine oils normally used under conditions of exposure to oxidation in the presence of metals, oxidize, giving rise to sludge and/or acidic oxidation products frequently corrosive to the metals which they encounter in use, as for example bearing metals in automotive use, and copper and copper alloys in turbine use. It has now been found that stabilization of these oils against such oxidation effects may be conveniently accomplished either by addition to the oils of certain materials which substantially retard the oxidation of the oils, whether or not metal is present, or by the addition of certain other materials which apparently have the ability to inhibit the catalytic effect of metals in promoting oxidation reactions and thus prevent the formation of sludge and/or acidic constituents and the like under normal conditions of use and achieve an equally good practical result, although materials of this latter class may be incapable of inhibiting oxidation of oils in the absence of metals. This invention has to do with stabilizing compounds which appear to be of this latter class, not heretofore known to be effective for this purpose, and with oils stabilized by the use of these compounds.

Recent changes in automotive engine design, tending toward higher bearing pressures, higher rotative speeds, higher engine temperatures, and the like, have occasioned departure from the use of the usual bearing metals such as babbitt. The newer bearing metals are of different nature, than those less recently developed and while harder, are in general more susceptible to destructive agencies of a corrosive nature. Typical of these newer bearings are those composed of a cadmium-silver alloy supported upon a steel back, which are now widely installed in certain makes of automobiles. Others of these relatively new bearing metals which may be mentioned are copper-lead alloys, copper-lead-tin alloys, cadmium-nickel alloys, cadmium-zinc alloys, cadmium-zinc alloys modified by the presence of

lead, antimony, or both, and a general class of alloys consisting mainly of lead and hardened with calcium, barium, potassium, antimony, and the like, known generically as "high lead babbits."

These changes in engine design have been concurrent with marked advances in methods of refining lubricant oils for automotive use. The demand for oils having lesser changes in viscosity with temperature change; i. e., higher viscosity index (frequently designated as V. I.), has been met by refining lubricants intended for motor oils by certain solvent refining or solvent extraction processes, wherein advantage is taken of the selective solvent power for hydrocarbons of various types which is possessed by certain liquid reagents, for example, dichlorodimethyl ether, cresylic acid, phenol, chloraniline, chlorophenol, phenetidine, benzyl alcohol, nitrobenzene, benzonitrile, furfural, aniline, benzyl acetate, liquid sulphur dioxide, mixtures of liquid sulphur dioxide or aniline with benzol, and the like. Those solvent refining processes are designed to concentrate in the desired lubricant fraction those compounds of a "paraffinic" nature possessed of the ability to suffer only a small change of viscosity with change of temperature, and to reject the compounds of "naphthenic" nature which do suffer such change of viscosity to such a marked degree. These refining processes have provided a supply of an oil of quite desirable general characteristics definitely far superior to any oil previously produced from mixed base or asphaltic crudes, and superior to a like, though lesser, degree over oils previously produced from paraffin base crudes.

It has been found that the solvent refined motor oils referred to above are definitely corrosive to the newer bearing metals referred to above under normal conditions of automotive use, due to oxidation during use, sometimes resulting in bearing failure after only a few thousand miles of normal driving. It is further known that the same reaction, viz., corrosion of alloy bearing metals such as cadmium-silver, also occurs in good paraffinic base oils which have not been subjected to solvent refining. The higher the V. I. of the lubricating oil, the more pronounced is the tendency to corrosion of the kind referred to above. Generally speaking, the problem is encountered in oils having a V. I. of 75 or higher, and becomes pronounced in oils having a V. I. of 80 to 85 or higher, and very pronounced in oils of 100 V. I. or higher.

Furthermore the present trend in automotive

design toward lower body styles, rapid acceleration, and the use of hypoid gears has increased the unit loadings on rear axles. In some cases the unit pressures encountered become great enough to rupture the oil film of ordinary mineral oil lubricants, with consequent metal to metal contact. In other lines of power transmission and the like, there is a similar tendency toward the use of high unit pressures of a degree which are near or beyond the limit at which mineral oils, alone, will maintain effective lubrication. This invention is therefore specifically concerned with the production of lubricants capable of withstanding the high unit loadings which occur in such instances. Such lubricants are generally spoken of as extreme pressure lubricants.

Extreme pressure lubricants are normally produced by adding to a hydrocarbon lubricant oil a small amount of some characterizing substance which enables it to maintain a lubricant film unruptured under conditions which would cause the breakdown of a film formed of oil alone. Such additive substances are spoken of as E. P. (extreme pressure) bases, or E. P. ingredients. Many commonly used E. P. bases are composed of sulphur dissolved in mineral oil, sulphurized vegetable or animal oils, chlorinated compounds, metallic soaps, and the like. This invention is specifically concerned with the use, as E. P. characterizing ingredients, of compounds new and novel for this purpose, and not heretofore so used or known to be useful for this purpose.

It is an object of this invention to provide an extreme pressure lubricant, together with a base for use in compounding same, which lubricant is superior to lubricants of this class heretofore commonly known, particularly in load-carrying capacity, stability, and maintenance of extreme pressure lubricating properties under sustained conditions of high loading. It is an object of this invention to prepare novel and valuable ingredients and to combine them with hydrocarbon lubricant oils to produce lubricants having high load bearing capabilities, to prepare such ingredients which have good characteristics of stability, which are less corrosive, and which impart a greater influence when present in much smaller amounts than are required with ordinary extreme pressure ingredients. Further objects are the provision of methods of making the ingredient or ingredients, methods of preparing lubricants containing these novel characterizing ingredients, and methods of lubrication making use of the lubricants so produced.

It is an important object of this invention to provide means for satisfactorily inhibiting or preventing corrosion from taking place to a serious degree particularly in oils of relatively high viscosity index. It is also an object of this invention to alter or modify a highly refined motor oil, normally corrosive, by the use of an additive ingredient capable of substantially inhibiting this corrosion. It is a further object of this invention to provide a substantially non-corrosive motor oil of high V. I. Still another object of this invention is to provide an additive reagent or ingredient capable of inhibiting the corrosive properties of these oils. The production of solvent refined oils of low corrosive properties under conditions of automotive use is a major object of this invention, as well as the method of production of such oils which combine a relatively high viscosity index with a relatively low tendency to produce such corrosion.

A further object is the provision of a method of

lubrication making use of oils containing these novel ingredients.

We have found that hydrocarbon oils of the classes defined above can be stabilized against the formation of acidic and/or corrosive and/or sludgebodies by oxidation in the presence of metals by the addition to said oils of a relatively small amount of the substantially stable, oil-soluble, water-insoluble condensation reaction product of a phosphorus trihalide and an organic amine having at least one hydrogen atom attached directly to the nitrogen atom of the amine. We have also found that novel lubricants having exceptional extreme pressure lubricating characteristics can be produced by adding to oil a sufficient quantity of these same materials. The amines which are suitable for the purposes of this invention are as follows: Compounds of the general formula



and



where R is an organic radical preferably selected from the group of aryl radicals consisting of phenyl, naphthyl, anthryl, and their corresponding alkaryl radicals or the group of alkyl radicals consisting of methyl, ethyl, propyl, butyl, amyl, cetyl, and the like. Specific examples of amines suitable for the purposes of the present invention are: Aniline, xylidines, toluidines, naphthylamines, anthramines, xenylamines, cumidines, mesidines, anisidines, monomethyl amine, dimethyl amine, monoethyl amine, diethyl amine, monopropyl amines, dipropyl amines, monobutyl amines, dibutyl amines, monoamyl amines, diamyl amines, monocetyl amines, dicetyl amines, methyl ethyl amine, ethyl propyl amines, propyl butyl amines, butyl amyl amines, methyl propyl amines, methyl butyl amines, methyl amyl amines, ethyl butyl amines, ethyl amyl amines, propyl amyl amines, butyl amyl amines, and also cycloalkyl amines such as cyclohexyl amine, and the like.

The above-mentioned substantially stable oil-soluble, water-insoluble condensation reaction products are adapted, as we have discovered, to be added directly to or dissolved in a hydrocarbon oil for the purpose of inhibiting or eliminating the normal tendency of said oils to corrode the metal bearings and parts hereinbefore mentioned. To stabilize the said oils against the accelerating action of metals on the deteriorating effects of oxidation reactions under normal conditions of use and/or handling and/or storage and to increase the ability of the oil to withstand high unit loadings. By substantially stable, we mean stable under the normal conditions of use and/or handling and/or storage to which these corrosion inhibitors and oxidation inhibitors are ordinarily subjected, after manufacture, either before they are added to the hydrocarbon oil to be stabilized or after they are added to such an oil.

In carrying out our invention we prefer to proceed in accordance with the following examples: We first prepare the substantially stable oil-soluble, water-insoluble condensation reaction product referred to above in one of the following manners: (1) Six moles (560 grams) of aniline and 700 cc. of benzene are placed in a suitable reaction vessel or flask. One mole (138 grams) of phosphorus trichloride is diluted with or dissolved in 150 cc. of benzene and this solution gradually added to the reaction vessel containing the solution of aniline in benzene. It will be

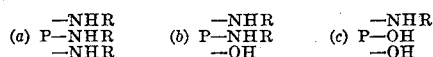
noted that two equivalents of aniline are employed for each equivalent of the phosphorus trichloride. After the phosphorus trichloride in benzene solution has been added to the aniline solution the mixture or solution thus obtained containing the two reactants, i. e. aniline and phosphorus trichloride, is gently heated for about 2 hours at a temperature of about 45° C. to insure complete reaction between the reactants.

The main reaction products formed by this reaction are the oil-soluble, water-insoluble condensation reaction products referred to above and the hydrochloride salt of aniline, the latter compound being substantially less soluble in benzene (and also in oil) than the other reaction products referred to. The reaction mixture thus obtained is next cooled in order to precipitate or crystallize out the hydrochloride salt of the aniline which is then separated by filtration from the remaining reaction product. The amount of hydrochloride salt thus formed and separated from the remaining mixture corresponds to approximately $\frac{1}{2}$ of the aniline employed in the original reaction mixture. The benzene in the filtrate from the hydrochloride salt is next separated by distillation. During this distillation, polymerization of the benzene-soluble, oil-soluble, water-insoluble condensation reaction product occurs resulting in the production of a paste-like solid in the distillation flask. This polymerization product is next washed repeatedly with fresh portions of benzene to remove benzene-soluble impurities, the slight proportion of benzene remaining in the residue being removed by evaporation. The solid residue thus obtained is the polymerized form of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and aniline referred to above and has a melting point between about 142° C. and about 146° C. Although the solubility of this polymerization product in hydrocarbon oils is rather slight, amounting to only about .1%, it is nevertheless quite effective, when dissolved in such oils in this proportion for stabilizing such oils against the accelerating action of metals on the deteriorating effects of oxidation and for inhibiting the corrosion produced by such unstabilized oils on bearing metals as hereinbefore explained.

(2) Six moles (945 grams) of diamyl amine and 700 cc. of benzene is placed in a suitable reaction vessel or flask. One mole (138 grams) of phosphorus trichloride is diluted with or dissolved in 150 cc. of benzene and this solution gradually added to the reaction vessel containing the solution of diamyl amine in benzene. It will be noted that two equivalents of amine are employed for each equivalent of the phosphorus trichloride. After the phosphorus trichloride-benzene solution has been added to the benzene solution of diamylamine the mixture or solution thus obtained containing the two reactants, i. e., diamyl amine and phosphorus trichloride, is gently refluxed for about 30 minutes at a temperature of about 88° C. to insure complete reaction between the reactants. The main reaction products formed by this reaction are the oil-soluble water-insoluble condensation reaction products referred to above and the hydrochloric salt of diamyl amine, the latter compound being substantially less soluble in benzene (and also in oil) than the other reaction products referred to. The reaction mixture thus obtained is next cooled in order to precipitate or crystallize out the hydrochloride salt of the amine which is then separated by

filtration from the remaining reaction product. The amount of hydrochloride salt thus formed and separated from the remaining mixture corresponds to approximately $\frac{1}{2}$ of the diamyl amine employed in the original reaction mixture. The benzene in the filtrate from the hydrochloride salt is next separated by distillation. The residual orange colored oil thus obtained after removal of the benzene solvent is preferably washed with water to remove water-soluble impurities, such as diamyl amine hydrochloride. This water washed product is then preferably subjected to distillation under about 2 mm. mercury pressure to remove the remainder of the water and diamyl amine. However, the unwashed product is also quite effective as an E. P. base in accordance with the present invention.

While we do not desire to limit our invention to any specific formula of the oil-soluble, water-insoluble product hereinbefore described, nevertheless the evidence indicates as will be readily understood by those skilled in the art that this product (in the case of primary amines) corresponds to a composition containing compounds having the following general formulae:



and their polymers, wherein R is an organic radical as defined above; the compounds corresponding to (b) and (c) predominating in the mixture when aryl amines are used and the (a) type predominating when alkyl amines are used. In the case of secondary amines the characters NHR become NR₂ in the formulae.

In preparing the finished hydrocarbon oil composition in accordance with our invention the oil-soluble, water-insoluble condensation reaction product referred to above is intimately incorporated with or dissolved in the oil which is to be stabilized against the accelerating action of metals on the deteriorating effects of oxidation reactions and against its normal tendency to corrode metal bearings, etc., and the product thus obtained may then be employed for the purposes and uses for which the unstabilized oil itself is normally employed, but with the improved results above described.

The condensation reaction product, as produced and described above also constitutes our novel extreme pressure ingredient, and when small amounts are added to or directly dissolved in a proper hydrocarbon lubricating oil, confers upon it a greatly enhanced ability to maintain lubrication under extreme conditions of loading.

It will be understood further that our invention is not restricted to the details of the above examples which are given merely as illustrations of our invention, but that various changes may be made in these details without departing from the true scope of our invention as defined in the appended claims. Thus for example we may substitute in place of the aniline any one of the specific aryl amines belonging to the general class of aryl amines hereinbefore defined or any mixture or combination of such amines. While aniline is preferred, because it is more conveniently obtained, we have found that xylydine is at least as effective in its stabilizing action as aniline. Also we may substitute in place of the diamyl amine any one of the specific amines belonging to the general class of amines hereinbefore defined or any mixture or combination of such amines. Likewise we may substitute in the above examples in place of the benzene solvent

any other suitable solvent for the amine and the phosphorus trihalide, it being understood, of course, that such substituted solvent should be inactive or substantially stable toward the action of the phosphorus trihalide or the amine. Also as will be readily understood by those skilled in the art the reaction between the phosphorus trihalide and the amine may be promoted by heating under pressure if desired and also at other temperatures than those specified in the example. The amine hydrochloride salt, may, of course, be treated with a suitable alkali to liberate the amine in accordance with well-known methods which may be reacted with phosphorus trichloride in accordance with the first steps of the process described in the above example.

Stabilized motor oils

The following data illustrate the inhibiting action of the corrosion inhibitors described above (i. e., the oil-soluble, water-insoluble condensation reaction products of phosphorus trihalides and organic amines). These data are shown in Table I.

Table I

(a)	Loss in weight of bearings in mgs.	
	Inhibited oil (b)	Oil alone (c)
Oil plus 0.10% phosphorus-di-anilide	0	33.2
Oil plus 0.05% phosphorus-di-anilide	2.9	40.0
Oil plus 0.05% phosphorus-di-anilide	3.6	31.5
Oil plus 0.10% phosphorus-di-xylylide	0	23.4
Oil plus 0.05% phosphorus-di-xylylide	1.9	46.3
Oil plus 0.50% phosphorus amyl amide	+2.4	40.4
Oil plus 0.05% phosphorus amyl amide	0	50.2
Oil plus 0.05% phosphorus amyl amide	0	40.7
Oil plus 0.01% phosphorus amyl amide	0	40.7
Oil plus 0.01% phosphorus amyl amide	0	35.5
Oil plus 0.05% phosphorus amyl amide	0	24.2
Oil plus 0.025% phosphorus amyl amide	0	24.2

In the above table the specific corrosion inhibitors employed are designated for convenience as phosphorus-di-anilide, phosphorus-di-xylylide and phosphorus amyl amide, respectively. In obtaining the data shown in Table I a solvent refined motor oil, S. A. E. 20, having a Saybolt viscosity of 56 seconds at 210° F. and a flash point of 420° F. was employed to illustrate the action of these inhibitors. The test used in obtaining these data comprised passing a current of air (2000 ml. per hour) through a 50 ml. sample of oil heated to 347° F. for 22 hours in intimate contact with a sheet of cadmium-silver alloy weighing about 6 grams, the sheet of cadmium-silver alloy being submerged in the oil. In this table the composition of the different mixtures of oil and inhibitor are shown in column (a). The loss of weight of the sheet of cadmium-silver alloy bearing metal caused by the action of the inhibited oil is shown in column (b) and that for the uninhibited oil alone is shown in column (c). It will be noted from the above data that the inhibited oil is radically less corrosive than the uninhibited oil alone.

To further demonstrate the effectiveness of the novel compounds with which this invention is concerned, under actual use conditions, a modified Delco knock test engine was made use of. This engine was operated at a speed of 1600 R. P. M. with an average crankcase temperature of 330° F. in the oil, equipped with cadmium-silver alloy bearings supported upon a steel back. It was first operated using a lubricating oil of S. A. E. 20 type, having a Saybolt viscosity of 56''

at 210° F., and a flash point of 420° F., the oil having been produced by a process of solvent refining, and having a viscosity index of 117. At the end of twenty hours, the engine was torn down, cleaned, and the neutralization number of the oil determined, the loss of weight of the bearing in milligrams determined, and the wear of the bearing in inches determined. Then the engine was reassembled and operated using as a lubricant the same oil inhibited by mixing therewith 0.15% of its weight of phosphorus amyl amide, one of the novel compounds of this invention. Three separate operations, one at twenty, one at forty, and one at sixty hours were made, and at the end of each operation the properties of the oil and the losses of the bearing were determined. The data so derived are reported in the following table:

Table II

Motor oil (S. A. E. 20) alone	Weight loss of bearings in mgs.	N. N.	Wear in inches
Measurements—end of 20 hrs.	32.56	3.2	0.0025
Motor oil (S. A. E. 20) plus 0.15% phosphorus amyl amide	Weight loss of bearings in mgs.	N. N.	Wear in inches
Measurements—			
End of 20 hrs.	146	0.2	0.0001
End of 40 hrs.	162	0.3	0.0002
End of 60 hrs.	1398	0.7	0.0012

In Table III is shown data illustrating the corrosion-inhibiting effect of phosphorus-di-anilide on cadmium-silver alloy bearings obtained by a slightly different test than that employed in obtaining the data shown in Table II above. The test employed in obtaining the data shown in Table III was made by introducing the stabilized oil into the crankcase of a modified Delco knock test engine provided with heaters in the crank case to maintain the oil at a temperature of about 330° F. The bearings were of cadmium-silver alloy on a steel back. The oil employed in this instance was a solvent-refined motor oil of S. A. E. 30. This test was designed to correspond to an accelerated service condition. In Table III the composition of the oil employed and the duration of the test is shown in column (a). The weight-loss of bearings in mgs. is shown in column (b), the neutrality number of the oil at the end of the test is shown in column (c) and the wear in inches of the bearings is shown in column (d).

Table III

(a)	(b)	(c)	(d)
Motor oil (S. A. E. 30) alone	Weight loss of bearings in mgs.	N. N.	Wear in inches
Measurements end of 20 hrs.	150	0.7	0.0002
Measurements end of 30 hrs.	2.2	2.2	0.0002
Measurements end of 40 hrs.	7100	3.1	0.0032
Motor oil (S. A. E. 30) plus 0.10% phosphorus-di-anilide	Weight loss of bearings in mgs.	N. N.	Wear in inches
Measurements end of 20 hrs.	160	0.14	0.0001
Measurements end of 40 hrs.	250	0.60	0.0002
Measurements end of 60 hrs.	330	1.80	0.0003
Measurements end of 65 hrs.	1300	9.60	0.0011

It will be observed from the foregoing data

that as little as .1% of phosphorus-di-anilide dissolved in the motor oil exerts a very pronounced inhibiting effect upon the corrosion of the bearings as indicated by the weight-loss and the wear in inches and also the strong stabilizing effect with respect to the formation of acidic products as indicated by the neutrality numbers in column (c). The neutrality number is indicated in the table as N. N. (Note: N. N. is mgs. KOH necessary to neutralize acids in 1 gram of sample oil.)

It will be noted that the data in Tables II and III likewise show that the inhibited oil of our invention is decidedly less corrosive and more stable with respect to the formation of acidic impurities than the uninhibited oil alone.

Stabilized moderately refined oils

As hereinbefore mentioned, moderately refined oils, such as turbine oils, normally tend to deteriorate by oxidation under normal conditions of use, yielding both acids and sludge. The inhibitory effect of the phosphorus amides or oxidation inhibitors of the present invention upon such oils is illustrated by the data shown in Table IV which data were obtained by heating mixtures or solutions of phosphorus-di-anilide and phosphorus amyl amide dissolved in a turbine oil having a Saybolt viscosity of 152 seconds at 100° F. and a flash point of 385° F. The heating was continued for 3 days at a temperature of 230° F. in contact with metallic copper with exposure to air, in accordance with the procedure known as the Brown-Boveri turbine oil test. In the table the nature of the oil employed in the tests is shown in column (a), the Lovibond color of the turbine oil and of the mixture of oil with phosphorus-di-anilide before aging or heating is shown in column (b), the Lovibond color of the turbine oil alone and of the mixture after aging or heating is shown in column (c), and the so-called neutralization number indicated by N. N. of the oil and oil mixtures employed after aging or heating is shown in column (d). (Note: N. N. is mgs. KOH necessary to neutralize acids in 1 gram of sample oil.)

Table IV

(a)	Before aging Lovibond color	After aging Lovibond color	N. N.
(b)	(c)	(d)	
Turbine oil alone.....	0.4	83	0.12
Oil plus 0.10% phosphorus-di-anilide.....	0.4	3.2	0.01
Turbine oil alone.....	0.4	52	0.10
Turbine oil plus 0.10% phosphorus amyl amide.....	0.4	3	0.07
Turbine oil plus 0.02% phosphorus amyl amide.....	0.4	1.3	0.01
Turbine oil plus 0.005% phosphorus amyl amide.....	0.4	6	0.03
Turbine oil plus 0.001% phosphorus amyl amide.....	0.4	24	0.05

As will be noted from the data shown in Table IV the inhibitory effect or power of phosphorus-di-anilide on the turbine oil is quite pronounced even when the percentage in the oil is as low as $\frac{1}{10}$ of 1%. The inhibitory effect of phosphorus amyl amide on the turbine oil is quite pronounced even when the percentage in the oil is as low as $\frac{1}{1000}$ of 1%.

The following tubular data illustrate the efficacy of extreme pressure lubricants embodying this invention. Oils or lubricants of this type may be tested in the Almen pin test machine, described by Mougey and Almen (Proc. A. P. I. 1931, page 77), wherein a pin is rotated in bear-

ings so designed that increasing pressures may be applied to the lubricated surface. This machine is widely used in such comparative evaluations.

In the following tabulation of results from the Almen pin test machine, column 1 shows the pressure in pounds per square inch applied to the lubricated contact surface. Columns 2 to 7 inclusive show the torque in foot pounds transmitted through the pin of the test machine with the respective described lubricants, and in some cases, indicate failure of lubricant, resulting in seizure of bearing and pin.

1	2	3	4	5	6	7
Weights	Min- eral oil alone	Per cent D. A. P. in mineral oil			M. A. P. in min- eral oil	2% D. A. P. in min- eral oil after 24 hours at 300° F.
		1%	2%	20%		
1,000.....	0.5	0.7	0.8	0.9	0.7	0.7
2,000.....	Seized	.9	1.2	1.1	1.1	1.0
3,000.....		1.2	1.5	1.3	1.3	1.3
4,000.....		1.5	1.7	1.6	1.5	1.6
5,000.....		2.6	3.1	2.8	2.6	2.9
10,000.....		4.2	4.3	4.7	3.7	4.8
15,000.....		5.4	4.8	5.2	4.2	5.8
19,000.....		5.8	4.9	5.4	6.0	5.8
20,000.....		5.5	5.0	5.8	Released	5.9
21,000.....		5.2	5.3	6.1		6.0
22,000.....		5.7	5.8	6.7		6.0
23,000.....		6.0	6.2	Released		6.0
24,000.....	Seized		6.2			6.0
25,000.....		Released				6.0
26,000.....						6.0
27,000.....						Released

In the above tests the oil used in column 2 was an oil of the following characteristics:

Saybolt viscosity 210° F..... 165
Pour point.....°F..... 20

This is an oil of the type normally used in the compounding of extreme pressure lubricants, and as indicated, is quite ineffective when used in the absence of a characterizing ingredient. The oils of tests as indicated in columns 3, 4 and 5 are the same oil as column 1, compounded respectively with 1, 2, and 20% of the reaction product PCl₃ and diamyl amine, designated D. A. P. for brevity. Column 6 shows tests upon the oil of column 1 compounded with 1% of the reaction product of PCl₃ and monoamylamine, designated M. A. P. for brevity. Column 7 shows the persistence of the activity of these compounds under extreme conditions, the oil of column 1 being compounded with 2% of the D. A. P. product and then maintained at 300° F. for 24 hours, after which it was cooled and tested.

It will be observed that extreme pressure lubricants embodying this invention are exceptionally effective.

The proportion of the characterizing ingredients of this invention used in admixture with ordinary hydrocarbon lubricant oil to provide an extreme pressure lubricant may be widely varied. Suggested limits of from 1% to 20% are those which will convert ordinary hydrocarbon lubricants to extreme pressure lubricants capable of withstanding the conditions of use now imposed. Within this range, it is preferable with all compounds of this class to use only the lower concentrations of these ingredients, say approximately 1% to 2% since these ingredients present in these concentrations result in the production of lubricants more capable of withstanding present conditions of loading imposed than do those lubricants now commercially used. Additionally, it may be noted that some of these compounds

are readily soluble only to the low concentration preferably indicated.

The above compounds with which this invention is concerned are compounds which are oil-miscible and water-insoluble. That is to say, they are compounds, which when added to oil form a substantially homogeneous combination with said oil, and they are water-insoluble in the sense that they will fail to be extracted or separated from a homogeneous mixture of the substance and oil when such mixture is brought into immediate contact with such amounts of water or moisture as are ordinarily encountered under normal conditions of storage and/or handling and/or use.

The condensation products of aryl amines and phosphorus trihalides, with which this invention is concerned are not highly oil-miscible in the usual broad sense. They are miscible with oils of the class herein spoken of to the extent of about 0.10% to 0.15% by weight, and since those amounts are suitable for prevention of corrosion according to this invention, the term oil-miscible, when used herein, is used with the understanding that it defines sufficient miscibility for this purpose. The recommended concentration of the novel compounds of this invention for the purpose of preventing corrosion is from 0.10% to 0.01% by weight in oil, the lower concentrations (around 0.02%), being particularly preferred for turbine oils.

The condensation products of amyl amines and phosphorus trichloride are highly miscible in oil, beyond any concentration useful for the purposes of this invention. The maximum percentage recommended for use for the prevention of corrosion according to this invention is about 0.15%, with the preferred concentration being from 0.10% to 0.01% with phosphorus triamyl amide, the lower percentages (around 0.02%), being particularly preferred for turbine oils. Other phosphorus alkyl amides are useful for this purpose in substantially similar proportions.

This application is a continuation in part of the following applications: James et al. Serial Number 83,072, filed June 2, 1936; James et al. Serial Number 83,073, filed June 2, 1936; and James et al. Serial Number 83,074, filed June 2, 1936.

We claim:

1. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an amine having at least one hydrogen atom directly attached to the nitrogen atom.

2. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an amine having at least one hydrogen atom directly attached to the nitrogen atom, said product being present in a proportion sufficient to reduce the tendency of the oil to deteriorate but not sufficient to materially increase the load bearing ability of the oil.

3. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an alkylamine having at least one hydrogen atom directly attached to the nitrogen atom.

4. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an arylamine having at least one hydrogen atom directly attached to the nitrogen atom.

5. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an alkylamine having at least one hydrogen atom directly attached to the nitrogen atom, said product being present in a proportion sufficient to increase the load bearing ability of the oil.

6. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an amine having at least one hydrogen atom directly attached to the nitrogen atom, said product being present in a proportion from about .01 to .15%.

7. A lubricant comprising a hydrocarbon oil and a small proportion of a product of the reaction of phosphorus trichloride and an amine having at least one hydrogen atom directly attached to the nitrogen atom, said product being present in a proportion from about 1 to 20%.

8. A lubricating oil composition comprising a relatively large proportion of a lubricating oil of the type which normally tends to rupture at the surface of contact with a bearing-metal under relatively high bearing pressure, and in intimate homogeneous combination therewith a relatively small proportion, sufficient to prevent such rupture, of the oil-miscible, substantially water-insoluble condensation reaction product of phosphorus trichloride and an alkyl amine having at least one hydrogen atom attached directly to the nitrogen atom.

9. A lubricating oil composition comprising a relatively large proportion of a lubricating oil of the type which normally tends to rupture at the surface of contact with a bearing metal under relatively high bearing pressure, and in intimate homogeneous combination therewith a relatively small proportion, sufficient to prevent such rupture, of the oil-miscible, substantially water-insoluble condensation reaction product of phosphorus trichloride and a secondary alkyl amine.

10. A lubricating oil composition comprising a relatively large proportion of a lubricating oil of the type which normally tends to rupture at the surface of contact with a bearing-metal under relatively high bearing pressure, and in intimate homogeneous combination therewith a relatively small proportion, sufficient to prevent such rupture, of the condensation reaction product of phosphorus trichloride and diamyl amine.

11. A lubricating oil composition comprising a relatively large proportion of a lubricating oil of the type which normally tends to rupture at the surface of contact with a bearing-metal under relatively high bearing pressure, and in intimate homogeneous combination therewith a relatively small proportion, sufficient to prevent such rupture, of the oil-miscible, substantially water-insoluble condensation reaction product of phosphorus trichloride and an alkyl amine selected from the group of alkyl amines consisting of monomethyl amine, dimethyl amine, monoethyl amine, diethyl amine, monopropyl amines, dipropyl amines, monobutyl amines, dibutyl amines, monoamyl amines, diamyl amines, monocetyl amines, dicetyl amines, methyl ethyl amine, ethyl propyl amines, propyl butyl amines, butylamyl amines, methyl propyl amines, methyl butyl amines, methyl amyl amines, ethyl butyl amines, ethyl amyl amines, propyl amyl amines and butyl amyl amines.

12. The method of lubricating relatively moving metal parts wherein unit bearing pressures of high magnitude are developed, which comprises applying to the area of contact between

said parts a mixture of viscous petroleum oil and a small proportion, sufficient to increase the load-bearing capacity of the mixture, of the oil-miscible, substantially water-insoluble condensation reaction product of phosphorus trichloride and an alkyl amine having at least one hydrogen atom directly attached to the nitrogen atom.

13. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use involving the accelerating action of metals and in intimate admixture therewith a relatively small proportion, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and an alkyl amine having at least one hydrogen atom attached directly to the nitrogen atom, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use.

14. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use involving the catalytic action of metals and in intimate admixture therewith a relatively small proportion, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and a secondary alkyl amine, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use.

15. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use involving the catalytic action of metals and in intimate admixture therewith a relatively small proportion, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and diamyl amine, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use.

16. A hydrocarbon oil composition comprising a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use involving the accelerating action of metals and in intimate admixture therewith a relatively small amount, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and an alkyl amine selected from the group of alkyl amines consisting of monomethyl amine, dimethyl amine, monoethyl amine, diethyl amine, monopropyl amines, dipropyl amines, monobutyl amines, dibutyl amines, monoamyl amines, diamyl amines, monocetyl amines, dicetyl amines, methyl ethyl amine, ethyl propyl amines, propyl butyl amines, butyl amyl amines, methyl propyl amines, methyl butyl amines, methyl amyl amines, ethyl butyl amines, ethyl amyl amines, propyl amyl amines, butyl amyl amines, and cyclohexyl amines, the said hydrocarbon oil composition as a whole being further characterized by relatively high resistance toward the deteriorating effects of oxidation under normal conditions of use.

17. A method of lubricating bearing surfaces which comprises maintaining between surfaces, one of which is an alloy selected from the class consisting of cadmium-silver, cadmium-nickel, cadmium-zinc, cadmium-zinc-lead-antimony, copper-lead, copper-lead-tin, and high lead bab-bitt, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small proportion, sufficient only to substantially retard corrosion, of the condensation reaction product of phosphorus trichloride and an alkyl amine having at least one hydrogen atom directly attached to the nitrogen atom.

18. A hydrogen oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount, sufficient to inhibit such deterioration, of the oil-soluble, water insoluble condensation reaction product of phosphorus trichloride and an aryl amine having at least one hydrogen atom attached directly to the nitrogen atom, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use in the presence of metals.

19. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and a primary aryl amine, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use in the presence of metals.

20. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and aniline, said composition being further characterized by a relatively high stability toward deterioration by oxidation under normal conditions of use in the presence of metals.

21. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil of relatively high boiling point normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount, sufficient to inhibit such deterioration, of the oil-soluble, water-insoluble condensation reaction product of phosphorus trichloride and an aryl amine selected from the group of aryl amines consisting of monophenyl amines, diphenyl amines, mononaphthyl amines, dinaphthyl amines, monoanthramines and dianthramines, the said hydrocarbon oil composition as a whole being further characterized by relatively high resistance toward the deteriorating effects of oxidation under normal conditions of use in the presence of metals.

22. A method of lubricating bearing surfaces

which comprises maintaining between bearing surfaces, one of which is an alloy selected from the class consisting of cadmium-silver, cadmium-nickel, cadmium-zinc, cadmium-zinc-lead-antimony, copper-lead, copper-lead-tin, and high lead babbitts, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small proportion, sufficient only to substantially retard corrosion, of the condensation reaction product of phosphorus trichloride and an aryl amine having at least one hydrogen atom directly attached to the nitrogen atom.

23. A method of lubricating bearing surfaces which comprises maintaining between bearing surfaces, one of which is an alloy selected from the class consisting of cadmium-silver, cadmium-nickel, cadmium-zinc, cadmium-zinc-lead-antimony, copper-lead, copper-lead-tin, and high

lead babbitts, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small proportion, sufficient only to substantially retard corrosion, of the condensation reaction product of phosphorus trichloride and an amine.

24. The method of lubricating relatively moving metal parts wherein unit bearing pressures of high magnitude are developed, which comprises applying to the area of contact between said parts a mixture of viscous petroleum oil and a small proportion, sufficient to increase the load-bearing capacity of the mixture, of the oil miscible, substantially water-insoluble condensation reaction product of phosphorus trichloride and an amine.

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CERTIFICATE OF CORRECTION.

Patent No. 2,146,543.

February 7, 1939.

WILLIAM H. JAMES ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, line 70, for the word "tubular" read tabular; page 5, second column, line 45, after the syllable "uct" insert of; page 7, second column, line 17, claim 18, for "hydrogen" read hydrocarbon; page 8, first column, line 5, claim 22, for "copped-lead-tin" read copper-lead-tin; line 20, claim 23, for "codmium-zinc" read cadmium-zinc; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of April, A. D. 1939.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.