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LUBRICATING OIL COMPOSITIONS AND METHODS OF MAKING THE SAME

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This invention relates to improvements in lubricating oil compositions and methods of making the same. More particularly this invention is concerned with lubricating oil compositions of a character adapted to protect ferrous and other metal surfaces to which they are applied, from rust and other types of corrosion, in addition to affording lubrication of such surfaces.

Simple mineral oil films afford limited protection to metal surfaces from rust and other types of corrosion, but do not afford any great protection under severe conditions of use. Many so-called anti-rust lubricating oils have been proposed, consisting of mineral oils with added constituents intended to protect metallic surfaces from corrosion, tarnish or rust.

Most of them are of rather limited applicability, in that while they may afford satisfactory protection to one class of metals, they may be ineffective, or even deleterious, with another class. This shortcoming is serious for example in the case of electric motors, where surfaces of both steel and copper are exposed to corrosive conditions, and in the case of copper-alloy bearings with steel shafting. Moreover many such oils show undue sensitivity to moisture and air and other substances to which they are exposed. It is also found that some compounded oils which are effective as regards preventing rust, are deficient in lubricating properties.

Among the objects of the present invention is the provision of an anti-corrosive lubricating oil composition, of excellent lubricating properties, adapted to protect steel from rusting while being of itself free from tendencies to corrode copper and other metallic surfaces, and being in itself relatively inert and unaffected by air and moisture.

These and other objects of the invention are achieved by the provision of a lubricating oil composition including, as a rust inhibitor, the substantially neutral product obtained by reacting isoamyl octyl acid phosphate with primary fatty amines containing from 8 to 18 carbon atoms; reaction being conducted under conditions such that the reaction product or mixture has a pH value between 5.5 and 7.5.

This composition proves to be very effective as an anti-corrosion lubricant, for metal surfaces in general. It forms a tightly adherent oily film on the metal, protecting the surface from moisture and air. In addition, the composition itself is free from any tendency to attack the metal, by reaction therewith or otherwise. Polished or highly-finished steel surfaces protected by establishing and maintaining the composition on the surfaces thereof, remain bright indefinitely, and copper-alloy bearings (which present a difficult problem in protection from corrosion) are maintained in their highly-finished condition even under unfavorable conditions of use. Copper, aluminum, zinc, tin and their alloys are all effectively guarded against corrosion and are well lubricated.

In general, various improved lubricants, such as household lubricants, machine oils, gun oils, turbine oils, slushing oils, and the like are prepared, by selecting a suitable lubricating oil or base and dissolving the required amount of the inhibitor described in the oil.

The invention finds special utility in the case of relatively light (low viscosity) oils, for lubricating light mechanism such as electric fans, guns, etc. For example, the invention is especially well suited for improving highly refined lubricating oils, of Saybolt Universal viscosity about 60 to 150 at 100° F., oils of 100 viscosity being especially suitable.

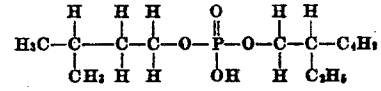
Usually 0.5 per cent or less of the inhibitor is sufficient to impart to lubricating oils adequate rust-inhibiting properties for articles exposed to moisture and air, but as much as 25 per cent by weight on the oil is sometimes incorporated to afford prolonged and complete protection from rust under extremely severe conditions. Such highly concentrated compositions still retain excellent lubricating and other characteristics in addition to affording practically complete rust protection under extraordinary conditions.

The reaction products employed in the present invention are relatively stable compositions under ordinary conditions. At room temperatures some of them are heavy viscous liquids, others soft solids which melt to oily liquids at slightly elevated temperatures. All are relatively non-volatile, and are insoluble in water and more or less water repellant. They are very resistant to hydrolysis. The reaction products are however soluble in oils, both mineral oils and fatty oils. The solubility varies somewhat with the particular oil, but is quite high in general.

In preparing our rust inhibitors, the isoamyl octyl acid phosphate is caused to react with the primary fatty amine in approximately equal molecular ratios, and the reaction is controlled so as to produce substantially neutral reaction mixtures having a pH value within the range 5.5 to 7.5 (as measured with quinhydrone-calomel electrode assembly).

This acid phosphate ester can be readily pre-

pared by known methods and any of the commercial acid esters may be employed. This acid ester is a di-ester of ortho-phosphoric acid and has the following formula:



This compound is also known as 3-methyl-butyl, 2-ethyl-hexyl ortho-phosphate.

The primary fatty amine employed to react with the acid phosphate ester may be represented by the following generic formula:

$$H_2N—CH_2—(CH_2)_n—CH_3$$

wherein n is an even number between 8 and 16. This generic class includes the following members:

Mono-capryl amine, $CH_3(CH_2)_8CH_2NH_2$
Mono-lauryl amine, $CH_3(CH_2)_{10}CH_2NH_2$
Mono-myristyl amine, $CH_3(CH_2)_{12}CH_2NH_2$
Mono-palmityl amine, $CH_3(CH_2)_{14}CH_2NH_2$
Mono-stearyl amine, $CH_3(CH_2)_{16}CH_2NH_2$

We sometimes prepare the rust inhibitors by reaction of the ester with some particular one of these amines, but more usually mixtures of amines of this group are employed, as they afford a somewhat better product than if only one amine is used. One commercially available mixture which we ordinarily employ is so-called "coco amine," made in known ways by conversion of coconut oil fatty acids into the corresponding amines. Coco amine contains a major amount of mono-lauryl amine (the C_{12} amine) with minor amounts of its adjacent homologs. The average molecular weight of coco amine ranges between 200 and 210. A value within this range is considered as the molar weight in reacting with the ester.

The following example illustrates one good way of preparing a rust inhibitor within the purview of the present invention.

Example I.—To a suitable vessel equipped with heating and cooling coils and means for mechanical agitation are added 200 pounds of coco amine, and 281 pounds of isoamyl octyl acid phosphate, commercial grade, are slowly added, slowly so as to keep the temperature of the reaction mixture below 180° F. whereby to avoid splitting out water from the mixture. After the addition of isoamyl octyl acid phosphate, the mixture has a pH of 3.0 and it is brought to the desired pH of 7.2 by adding 20 pounds of coco amine and stirring the final mixture for one hour. This product is a heavy viscous oily material, light amber red in color, with a pleasant odor.

The substantially neutral reaction product obtained in Example I is soluble in mineral oils, as are the amines from which it is prepared. Accordingly, we sometimes prepare concentrated solutions of the rust inhibitor in mineral oil by forming them in situ in the oil. In such processes, the fatty amine is first dissolved in the mineral oil, and then the acid phosphate ester added, the mixture being stirred and maintained at desired temperatures until the reaction is complete and the mixture has a pH value within the specified range. In preparing the oil concentrate, sometimes additional amine is added in the later stages to adjust the pH value as desired. Preparation of such a concentrated rust inhibitor is illustrated in the following example:

Example II.—One hundred pounds of light mineral oil having a viscosity of 100 seconds SUV at 100° F. were added to an iron vessel equipped with an air lance. The temperature of the oil was 80° F. To this oil was added 125 pounds of "coco amine," which was thoroughly mixed with the oil by air agitation. The temperature was 80° F. after mixing the two components. To the above mixture 175 pounds of isoamyl octyl acid phosphate were added over a period of two hours. The mixture was agitated with air during the addition and the temperature rose to 185° F. The pH of the mixture at this stage was 3.4. To increase the pH of the mixture, 5 pounds of coco amine were added, which increased the pH from 3.4 to 4.0. Another 4 pounds of coco amine were added to bring the pH into a higher range, and the pH after this addition was 6.0. Finally 5 pounds more of the coco amine were added to the mixture, which gave a final pH of 6.7. The above mixture, after the final pH adjustment, was added to the mineral oil.

The reaction products prepared as described above may be dissolved in various types of mineral oils and improved anti-rust and non-corrosive oil compositions obtained capable of inhibiting or retarding the rusting of ferrous metals as described.

Example III.—In preparing an oil especially suitable for lubricating household appliances or instruments, the rust inhibitor of the class described is dissolved in a refined paraffinic oil having a viscosity of 85 seconds Saybolt Universal at 100° F. The properties of the untreated oil, and the oil containing 0.01 per cent of the rust inhibitor are as follows:

	Base oil	Improved oil
Gravity, °API	29.5	29.5
Viscosity, SUV, 100° F.	90.5	90.4
Color, Saybolt	+25	+25

These oils were then tested for non-rusting properties by the following test: Thirty-six cc. of the oil to be tested and 4 cc. of water are placed in a 1" x 6" Pyrex test tube, and a polished copper or steel strip is immersed in the oil-water mixture; 2000 cc. of humidified air per hour are bubbled through the mixture, so as to provide mixing of the oil and water. The apparatus is set in a water bath maintained at 122° F. (50° C.) and the original water level in the tube is maintained by additions of fresh water every 24 hours. The test is continued for 12 days, regardless of whether or not the strip shows signs of corrosion. The base oil began to show rust on a steel strip after 6 hours in the test whereas after 12 days the improved oil showed no evidence of rust. Ordinarily an uninhibited oil will tarnish a copper strip within approximately twelve hours, and will attack a steel strip. Generally the addition of as little as 0.05 per cent by weight of a rust inhibitor such as alkylamine isoamyl octyl phosphate, will maintain both the copper and the steel strips free from tarnish and rust for periods up to twelve days, the maximum duration of the test. The test may be carried out with copper, steel, or other metallic strips, such as zinc and tin.

In certain special cases the prevailing conditions are so extreme as to require that a lubricant be extremely highly protective toward metal surfaces. In this case a higher percentage of rust inhibitor is incorporated in the oil.

Example IV.—In preparing one such lubricant, 0.3 per cent of the rust inhibitor was incorporated.

The oil base selected and the improved lubricant made from it have the following properties:

	Base oil	Improved oil
Gravity, °API	28.5	28.4
Viscosity, SUV, 100° F	110	109
Color, NPA	1.25	1.25

This oil is capable of preventing rusting and corrosion of metals under extreme conditions, even in the presence of salt or sea water. In testing it an aqueous solution of salt is substituted for the water employed in the test given above, the procedure otherwise being the same. Both the base oil and the improved oil were tested. The improved oil showed no evidence of corroding either copper or steel after 12 days in either of the above tests, whereas the base oil allowed the steel strip to rust in approximately 8 hours in the fresh water test and in about 3 hours in the salt water test. The copper strips were more slowly attacked, but overnight were coated with a greenish deposit.

The specific embodiments described above are merely illustrative of the practice of this invention and other embodiments thereof may be used as desired; for instance, these rust inhibitors are compatible with various other compounding ingredients and they may be added to blended oil bases or compounded lubricants to obtain other types of improved lubricants. Improved oil compositions can be prepared from base oils containing varying amounts of fatty oils admixed with mineral oil, such blends being especially useful as household lubricants. By the present invention, any of the previously known household or other lubricants containing relatively light lubricating oils can be improved by adding small amounts of our rust inhibitors as described.

The invention is equally applicable to heavy mineral oils, petrolatum oils, greases, and jellies; in fact to any petroleum lubricant or coating oil, in which corrosion-preventive properties are desired. In the claims the term lubricant includes mineral oils, jellies and the like even when used for purposes other than strict lubrication; e. g. slushing oils and gun greases.

One important application of the present invention is to the prevention of rusting in aviation engines after these have been used, either upon aging in intermittent actual service or in storage of engines or planes awaiting completion of assembly, shipment, and other delays after engine break-in. Such rusting is aggravated by the presence in the crankcase and crankcase-oil of moisture, sulfur, oxidation products from petroleum, tetraethyl lead, decomposition products, etc. Attempts have been made to remedy this condition by washing out all motor oil from the crankcase of an engine if it is to be stored for any appreciable time, or adding compounds containing large amounts of oiliness agents and the like. The present invention presents a more economical remedy for these conditions, for corrosion is effectively retarded under such conditions when from 0.5 to 1.0 per cent by weight of our compounds is added to a used motor oil. Adding the highly potent rust preventive compound during the latter part of the break-in period for the new engine, with operation for sufficient time after addition to assure full mixing and coating of parts, will prevent rusting.

Extensive tests in which the pH values of the agent of the present invention as employed in finished oils were varied confirm our discovery that the optimum results for a given amount of the agent in oil are secured when the pH value is maintained within the stated range of 5.5 to 7.5 for the compounding agent. There is usually a slight drop in pH value in the dilute finished oil solution as compared with the values for the compounding agents or mixtures thereof. The finished oil (which usually contains only a small proportion of the dilute compounding agent) should test between 5.0 and 6.0; advantageously around 5.7.

Any substantial departure from the stated range either on the alkaline or acid side gives less desirable results. For example, with an unduly low pH value (acid side) there is some rusting of steel surfaces by our steel strip corrosion test, while compositions with an excessively high value (alkaline side) may produce greenish corrosion effects by the oxidation tests with copper surfaces and the like, although not affecting steel to any appreciable extent. The exact adjustment is attained in preparing the compound (e. g. cocoamine salt of isoamyl octyl phosphate) by reacting the desired molecular proportions of the two agents in the manner described, and after the neutralization or compounding reaction has progressed practically to completion, by testing the reaction product, and making any minor adjustments that are necessary for exact control by adding the required small additional proportion of the amines (if on the acid side of our desired range) or the isoamyl octyl phosphate (if on the alkaline side).

In measuring the pH of the agents of the present invention and oils containing them, which are both substantially water-insoluble, the sample is dissolved in normal butanol (which contains a small amount of water) adjusted exactly to pH 7.0. The butanol acts as a blending agent for the water and the relatively insoluble material, but does not appreciably alter the pH value as it is of pH exactly 7 itself. Measurement is made by electrometric or colorimetric procedures; the results agree closely.

What we claim is:

1. A composition effective as a lubricant for metal surfaces and capable of preventing corrosion thereof in the presence of moisture and air, comprising a petroleum lubricant containing in solution in a proportion sufficient to prevent rusting, a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and a primary fatty amine containing from 8 to 18 carbon atoms, said product having a pH between 5.5 and 7.5 and containing the said acid phosphate and amine chemically combined together in molar ratios between 1:1 and 1:1.1.

2. The composition of claim 1 wherein said amine is cocoamine.

3. The composition of claim 1 wherein said petroleum lubricant contains from 0.01 to 25 per cent of said substantially neutral addition product dissolved therein.

4. A composition effective as a lubricant for metal surfaces and capable of preventing corrosion thereof in the presence of moisture and air, comprising a mineral oil containing in solution from 0.01 to 25 per cent of a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and a primary fatty amine containing from 8 to 18 carbon atoms, said product having a pH between 5.5 and 7.5 and containing the said acid phosphate and amine chemically combined together in molar ratios between 1:1 and 1:1.1.

5. A lubricating oil for metal surfaces capable of preventing corrosion thereof in the presence of moisture and air comprising a mineral oil containing between 0.01 and 0.5 per cent of a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and a primary fatty amine containing from 8 to 18 carbon atoms, said product having a pH between 5.5 and 7.5 and containing the said acid phosphate and amine chemically combined together in molar ratios between 1:1 and 1:1.1.

6. A method of preparing an oily composition, useful as a rust preventive lubricant, which comprises admixing with a mineral oil at least one primary fatty amine containing 8 to 18 carbon atoms, dissolving in said mixture an equimolecular quantity of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and maintaining the oil solution of reactants at a temperature between 80° and 185° F. until the reaction is substantially complete and then adjusting the pH of the reaction mixture to within the range 5.5 to 7.5 by the further addition of approximately 0.1 mole of said amine.

7. The method of claim 6 wherein said primary fatty amine is cocoamine.

8. A method of preparing lubricant compositions, capable of preventing corrosion of steel and other metal surfaces in the presence of moisture and air, which comprises dissolving in mineral oil at least one primary fatty amine containing 8 to 18 carbon atoms, gradually adding an equimolecular quantity of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate to the oil solution of said amine, at such a rate as to control the vigorous exothermic reaction and maintaining the reaction mixture below 185° F., agitating the oil solution of said reactants at such temperatures until the reaction is substantially complete, and then adjusting the pH of the reaction product to within the range 5.5 to 7.5 by the further addition of approximately 0.1 mole of said amine.

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