

UNITED STATES PATENT OFFICE

2,371,852

LUBRICANT COMPOSITIONS AND METHODS
OF MAKING THE SAMEHerschel G. Smith, Wallingford, and Troy L.
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PennsylvaniaNo Drawing. Application November 25, 1941,
Serial No. 420,439

8 Claims. (Cl. 252—51)

This invention relates to improvements in lubricant 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 rusting and other types of corrosion, in addition to affording lubrication.

Simple mineral oil films afford only a limited degree of protection to metal surfaces, from rust and other types of corrosion, especially 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 in the case of electric motors, where surfaces of steel and copper are subject to the action of air and moisture. 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 good lubricating properties, adapted to protect steel from rusting while being of itself free from tendencies to corrode copper and other metallic surfaces, 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 mineral oil composition including, as a rust inhibitor, the substantially neutral product obtained by reacting isoamyl octyl acid phosphate with di-cyclohexyl amine, in approximately equimolecular proportions, under such conditions 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 copper, steel and other metals, 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.

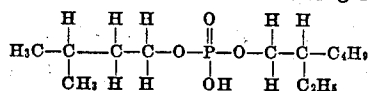
In general, various improved lubricants, such as household lubricants, machine oils, gun oils, turbine oils, slushing oils, and the like are prepared, by selecting a suitable lubricating oil or base and dissolving the required amount of the above described reaction product in the oil.

The invention finds special utility in preparing relatively light oils of the so-called household type, for lubricating light mechanism such as electric motors, guns, etc., for example in conjunction with highly refined lubricating oils, of Saybolt Universal Viscosity about 60 to 150 at 100° F., oils of 100 viscosity being especially suitable.

Usually from 0.1 to 1.0 per cent of the inhibitor is sufficient to impart to lubricating oils adequate rust-inhibiting properties. More concentrated oily solutions or oil mixtures of the inhibitor can be prepared, as a sort of stock solution which can be diluted with a plain lubricating oil to form a rust preventive lubricant.

The reaction products we employ are relatively stable compositions under ordinary conditions. At room temperatures they are heavy, viscous, oily, liquids. They are relatively non-volatile. They are insoluble in water and very resistant to hydrolysis, being in fact quite water repellent. On the other hand, they are moderately soluble in oils, both mineral and fatty oils, the solubility varying somewhat with the particular oil. For instance light paraffinic oils such as employed in making household lubricants, etc. dissolve approximately 0.50 per cent by weight of these reaction products, forming stable solutions. Naphthenic type mineral oils dissolve somewhat larger amounts.

The acid phosphate ester employed as one reactant can be readily prepared by known methods. Any commercial acid ester 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 other reactant, di-cyclohexyl amine is likewise a well known chemical compound, commercially available as a substantially pure material; though it is not necessary that a "C. P." amine be used. One of the commercial grades advantageous for the present purposes has the following properties:

Bolling point	°F.	493 (256° C.)
Melting point	°F.	32 (0° C.)
Sp. gr., 77°/77° F. (25/25° C.)		0.9104
Flash	°F.	212 (100° C.)
Fire	°F.	320 (160° C.)

The reaction between di-cyclohexyl amine and

the acid phosphate ester is exothermic. Temperature is controlled by heating or cooling as required.

The following example illustrates one advantageous method of preparing the rust inhibitor:

Example I.—Reaction is carried out in an iron kettle equipped with means for heating and cooling and for agitating the mixture. Into the kettle are introduced 181 pounds of commercial di-cyclohexyl amine, and 281 pounds of commercial isoamyl octyl acid phosphate are gradually added with stirring. The reaction is vigorous and quite exothermic, and the acid phosphate is added at such a gradual rate as to facilitate maintaining the reaction temperature below about 180° F. The mixture may be cooled if required to maintain it below that temperature. The reaction temperature is best maintained between 140 and 200° F. during the larger portion of the reaction. After all of the acid phosphate has been added, the mixture is ordinarily warmed to facilitate completion of the reaction. At this time the reaction mixture usually has a pH of 3 to 4 and the final adjustment and control of the pH value is then effected. In doing so we add 18 pounds of the amine and the mixture is further heated until it has a pH of approximately 7.2.

The rust inhibitor so obtained is a heavy viscous, oily liquid when cooled to room temperature. Similar viscous, oily rust inhibitors can be readily obtained having other pH values within the range of 5.5 to 7.5, by controlled adjustment of the pH during the last stage of the reaction.

The product of this example is sufficiently soluble in mineral oils for making our improved oil compositions. As the amine from which it is prepared is also soluble in mineral oils, we sometimes prepare the oily rust inhibitor in situ in mineral oil. In such embodiments of this invention, the di-cyclohexyl amine is first dissolved in the mineral oil and then the acid phosphate ester added, the mixture being stirred and maintained at the desired temperatures until the reaction is complete and the mixture adjusted to the proper pH value; the added mineral oil serving as a diluent, facilitating control of the reaction. The concentrates or oil solutions of neutral reaction products so obtained are useful addition agents to various types of lubricants. The preparation of such concentrates 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 means for heating and cooling and agitation. The initial temperature of the oil was 80° F. To this oil were added 181 pounds of di-cyclohexyl amine, which was thoroughly mixed with the oil by mechanical agitation and the final temperature of this mixture was 82° F. To the oil-amine mixture 281 pounds of commercial isoamyl octyl acid phosphate were added over a period of two hours, during which time the temperature of the reaction mixture rose to 188° F. After stirring for one hour, the pH of the mixture was 3.7. In order to increase this value to the desired range, nine pounds of di-cyclohexyl amine were added to the mixture and stirred, and the resultant mixture had a pH of 6.2. To secure a final adjustment, nine additional pounds of di-cyclohexyl amine were added to the mixture which after stirring for one hour, and cooling to room temperature, exhibited a pH of 7.4.

The oily mixture prepared in this Example II can be regarded as a sort of concentrated stock

solution, which can be stored indefinitely and incorporated in lubricating oils as desired to prepare commercial anti-rust oils, etc.

Example III.—A household-type lubricating oil was prepared by dissolving 0.05 per cent by weight of di-cyclohexyl amine isoamyl octyl phosphate, prepared as in Example I. Properties of the new oil and the base oil are tabulated below.

	Inhibited oil	Base oil
Gravity, °API.....	28.9	28.9
Viscosity, SUV:		
100° F.....	101.4	100.7
210° F.....	38.7	38.6
Flash, OC, °F.....	335	335
Fire, OC, °F.....	350	385
Pour, °F.....	-40	-45
Color, NPA.....	1.25	1.25
Carbon residue, per cent.....	0.02	Traco
Neutralization No.....	0.06	0.03
Special corrosion test No. 1:		
Steel strip.....	Passes	Fails
Copper strip.....	Passes	Fails

It is sometimes desirable to incorporate oiliness agents and extreme-pressure agents in rust-preventive oils; agents such as sperm oil and castor oils which have been processed to render them miscible with mineral oils. According to the present invention, a concentrate can be prepared, including the new rust inhibitor together with oiliness agents, which concentrate can be added to a plain mineral oil in quantity sufficient to impart the required rust preventive and oiliness properties.

Example IV.—In preparing such a concentrate, 60 per cent by weight of sperm oil, 20 per cent of mineral-oil-miscible-castor oil and 20 per cent of di-cyclohexylamine isoamyl-octyl phosphate are blended together in a suitable vessel, forming a fluid material which can be stored indefinitely. This mixture is readily soluble in oil and requires no special blending procedure to secure complete solution. It has the following properties:

Gravity, ° A. P. I.....	27.0
Sp. gr.: 60°/60° F. (15.5°/15.5° C.).....	0.8927
Viscosity, SUV:	
100° F. (38° C.).....	150
Color, N. P. A.....	3.75
Neutralization No.....	0.12
pH value.....	7.5

The mineral-oil-miscible castor oil and the sperm oil used in this example had properties as follows:

	Oil-miscible castor oil	Sperm oil
Gravity, °API.....	16.7	
Sp. gr. 60°/60° F. (15.5°/15.5° C.).....	0.9548	0.878-0.884
Viscosity, SUV:		
100° F. (38° C.).....	1,328	95-110
210° F. (99° C.).....	142.9	
Flash, OC, °F.....	485 (252° C.)	Min. 490 (254° C.)
Fire, OC, °F.....	600 (316° C.)	
Pour, °F.....	-35 (-37° C.)	Max. 60 (15.5° C.)
Color, NPA.....	2.25	Not darker than 3.0
Carbon residue, percent.....	0.48	
Neutralization No.....	3.20	Max. 2.0
Oleic acid equivalent, percent.....		Max. 1.0
Iodine No. (modified Hanus).....	103.8	75-90
Saponification No.....	190.4	120-140

Example V.—A so-called household oil was prepared by dissolving the composition of Example IV, in a light, highly-refined paraffinic mineral oil, in such proportions that the product contained 0.1 per cent of the new inhibitor, 0.3 per cent of sperm oil and 0.1 per cent of the castor

oil. Properties of the product as compared with those of the oil alone are tabulated below.

	Inhibited oil	Uninhibited base oil
Gravity, °API.....	33.5.....	33.5.....
Viscosity, SUV:		
100° F. (38° C.).....	104.9.....	105.6.....
210° F. (99° C.).....	39.7.....	40.0.....
Flash, OC, °F.....	375 (191° C.).....	370 (188° C.).....
Fire, OC, °F.....	430 (221° C.).....	430 (221° C.).....
Pour, °F.....	0 (-18° C.).....	0 (-18° C.).....
Color, Saybolt.....	+13.....	+16.....
Carbon residue, per cent.....	0.01.....	0.01.....
Neutralization No.....	0.20.....	0.02.....
Special corrosion test No. 1:		
Steel strip.....	Passes.....	Fails.....
Copper strip.....	do.....	Do.....
Special corrosion test No. 2:		
Steel strip.....	do.....	Do.....
Copper strip.....	do.....	Do.....
Special corrosion test No. 3:		
Steel strip.....	do.....	Do.....
Copper strip.....	do.....	Do.....
Evaporation loss, copper dish, per cent:		
212° F. (100° C.), 5 g., 48 hr.—		
Appearance of cup.....	Fair.....	Good.....
Sludge.....	Nil.....	Nil.....
Falex wear test:		
500 lb. jaw load, 15 min.—		
Wear: No. of Teeth.....	14.....	Fails.....
Slight oxidation No.....	8.....	5.....
Oxidation test, S. H. Kress Co.:		
Copper strip test, appearance.....	Medium stain.....	Light stain.....
Oxidized oil—		
Color, NPA.....	5.0.....	1.0.....
Neutralization No.....	0.20.....	0.01.....
Sludge, per cent.....	Nil.....	Nil.....

1 One tooth wear is equivalent to 0.0000218" wear on the test shaft

Example VI.—A turbine oil was prepared by dissolving 0.1 per cent of di-cyclohexyl amine isoamyl octyl phosphate, and 0.1 per cent of a phosphate of phenol-olefin condensation product in an oil of turbine grade. The properties of the oil alone and of the new product, are tabulated below.

	Inhibited oil				Uninhibited base oil			
Gravity, °API.....	30.4.....				30.7.....			
Viscosity, SUV:								
100° F. (38° C.).....	490.....				492.....			
210° F. (99° C.).....	65.8.....				65.8.....			
Viscosity index.....	108.....				108.....			
Flash, OC, °F.....	445 (229° C.).....				495 (252° C.).....			
Fire, OC, °F.....	500 (260° C.).....				510 (266° C.).....			
Pour, °F.....	0 (-18° C.).....				-5 (-21° C.).....			
Color, NPA.....	2.5.....				2.5.....			
Carbon residue, per cent.....	0.15.....				0.15.....			
Corrosion test (see below):								
Duration of test, hours.....	3	3	3	3	3	3	3	3
Oil temperature, °F.....	212	212	212	212	212	212	212	212
Air rate, cc./hr.....	2,000	2,000	36	36	2,000	2,000	36	36
Quantity of oil, cc.....	36	36	10	10	36	36	10	10
Water added, per cent:								
Distilled.....	10	10	10	10	10	10	10	10
Sea.....								
Test strip:								
Steel—								
Wt. change, mg.....	Nil	Nil	Nil	-0.1	+0.3	+1.3	-2.4	+1.6
Appearance.....	Good	Good	Good	Good	Poor	Poor	Stain	Stain
Copper—								
Wt. change, mg.....	-0.4	-0.6	Good	Good	+0.2	Poor	+0.5	+0.4
Appearance.....	Good	Good	Good	Good	Good	Poor	Fair	Fair
Neutralization No.....	0.08.....				0.06.....			
Emulsion test, 150° F.:								
Method 320.12, gov't—								
Distilled water.....	40-40-0 (7)				40-40-0 (34)			
1% salt solution.....	40-40-0 (7)				39-39-2 (60)			
N caustic soda solution.....	40-40-0 (6)				39-39-2 (60)			

The tests referred to in the foregoing examples are described in detail below. They are drastic tests of the rust preventive properties of oil compositions. In the tests a strip of steel or other metal is subjected to attack by moisture and air under extremely severe conditions.

Test No. 1.—Thirty-six cc. of the oil to be tested and 4 cc. of water are put in a 1" by 6" Pyrex test tube, and a polished copper or steel strip is immersed in the liquids. To mix the oil and

water, 2000 cc. of air per hour are bubbled through the mixture, from a point near the bottom. 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. 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 our di-cyclohexyl amine 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 this test, as the lower part of the strip is completely immersed in water, the only way for it to be wet by the oil is for the oil to creep down against water pressure. Unless an oil film is capable of spreading on the surface and displacing water therefrom, that is unless the surface is preferentially wetted by the oil, rusting immediately begins at the level where the oil and the water meet.

Test No. 2.—In this test 180 cc. of the oil to be tested and 20 cc. of water are placed in a 400 cc. beaker, and a polished steel strip is immersed in the oil-water mixture; 2000 cc. of humidified air per hour are passed through the mixture and the apparatus is maintained at 122° F. as in Test No. 1. The water level is maintained by daily additions of water, and at the end of twelve days the water layer is removed by syphon and fresh water is added. The water removed is analyzed to determine whether the inhibitor is

being extracted or leached from the oil solution. Fresh strips are added when the water is changed, so as to present a fresh surface to the partially leached oil. The test specimens are usually steel, copper, tin, and zinc, although other special metals may be used. This cycle is continued for 72 days, unless the test specimen becomes too corroded, making further testing impracticable.

Test No. 3.—The apparatus outlined in Test No. 1 is employed and the testing conditions are

identical except that water containing sodium chloride in the concentration equivalent to that of the total salt content of sea water is added instead of distilled water. This is a much more severe test and is conducted also for twelve days, the water level being maintained in the same manner as for Test No. 1.

An inhibitor which permits an oil to pass all three of these tests is considered an excellent inhibitor, as it is exposed to not only the leaching action of the water, but also to oxidation, and if rusting is prevented under these conditions, there is good assurance that the inhibitor will be capable of preventing, or at least retarding, rusting under even extremely severe service conditions.

The foregoing specific examples are merely illustrative of certain good embodiments of the invention. As stated, the new inhibitor can be incorporated, with beneficial results, in a wide variety of lubricating oils.

This 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. This effect is aggravated by the presence in the crankcase and oil therein 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 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 value 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 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 amine (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 dicyclohexyl amine, 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 petroleum lubricant is a light mineral oil having a Saybolt Universal viscosity between 60 and 150 at 100° F.

3. The composition of claim 1 wherein said petroleum lubricant contains from 0.01 to 1.0 per cent of said substantially neutral reaction 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 1.0 per cent of a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and dicyclohexyl amine, said product having a pH between 5.5 and 7.5 and containing 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 of viscosity between 60 and 150 seconds S. U. V. at 100° F. and containing between 0.01 and 1.0 per cent of a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and dicyclohexyl amine, 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 composition capable of being mixed with lubricating oil to improve its rust-preventive lubricating properties, comprising a blend of mineral oil and a substantially neutral addition product of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and dicyclohexyl amine together with an oil-miscible castor oil and sperm oil, said substantially neutral product having a pH between 5.5 and 7.5 and containing the said acid phos-

phate and amine chemically combined together in molar ratios between 1:1 and 1:1.1.

7. A method of preparing an oily composition, useful as rust preventive lubricant, which comprises dissolving dicyclohexyl amine in a mineral oil, admixing an equimolecular quantity of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate with the oil solution of said amine and maintaining the oil solution of reactants at a temperature between 80 and 200° F. 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.

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 dicyclohexyl amine in a mineral oil, 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 maintain the reaction mixture between 80 and 200° 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 of 5.5 to 7.5 by the further addition of approximately 0.1 mole of said amine.

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