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ANTI-CORROSION TURBINE OIL

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This invention relates to lubricating oils designed for use in steam turbines but adapted for use in other applications. More particularly, it relates to lubricating oils designed for use in marine turbines where corrosion by salt water is encountered. A specific form of the invention relates to lubricating oils designed to meet the rigid requirements of the U. S. Navy for marine turbine use. Broadly, the invention relates to mineral oils containing furfuryl amine salts of alkyl acid phosphates and, in a specific embodiment, it relates to mineral oils containing alkyl acid phosphate salts of mixtures of furfuryl amine and certain aliphatic amines.

Oils designed for the lubrication of stream turbines, especially those in marine use where exposure to salt water may occur through leaks or otherwise should meet several requirements including: (1) Relative freedom from emulsification with salt water as well as distilled water, (2) ability to protect the parts of the turbine from corrosion which may be caused by the steam, the steam condensate, or sea water, and (3) relative freedom from deterioration due to oxidation during continued use. In addition, it is highly desirable that the various additives used to provide or increase the above properties should not form any precipitate in the oil during storage. Although such precipitate may be small and of such nature as not to affect the utility of the oil, the presence of even a slight haze or "floc" in the oil reduces confidence in the oil on the part of the purchaser and/or operating personnel, in some instances to the point where the oil is not acceptable.

To assure purchase of turbine oils meeting its requirements in regard to the above characteristics the U. S. Navy has adopted rigid specifications as set forth in the Navy Department Specification pamphlet 14–O–15 dated August 15, 1945, and amendment thereto dated March 1, 1948, which requires oils, for approval, to pass specified emulsion, corrosion, oxidation tests as well as other requirements including freedom from precipitation of any constituents during storage. Since the corrosion problem is one of the most important, the Navy objects to oils which show any corrosion to the test specimen in the corrosion test, either on that part of the specimen immersed in the oil or on the portion of the test specimen above the oil. This is to assure protection to the parts of the turbine which are not continuously flooded with oil as well as those which are.

The corrosion test referred to is that specified in paragraphs E–5 and F–3C of the aforementioned pamphlet 14–O–15. Briefly, this corrosion test provides that a polished cylindrical steel specimen shall show no corrosion when partially immersed for 48 hours in a bath composed of 300 ml. of the oil and 30 ml. of synthetic sea water maintained at 140° F.

Another important test specified by the Navy specifications is the emulsion test. Briefly, in this test 40 ml. of the oil and 40 ml. of distilled water are stirred together at 1500 R. P. M. in a 100 ml. graduate at 130° F. for 5 minutes after which the oil must separate satisfactorily from the water in 30 minutes. The test is repeated using 1% NaCl solution instead of distilled water.

To supply anti-corrosion properties to lubricating oils it has been proposed to add alkyl acid phosphates in small quantities to the oil. While such oils exhibit marked anti-corrosion properties as compared to straight mineral oils, they fail to give good results in the Navy corrosion test, primarily due to corrosion of the test specimen above the oil level. This failure indicates that such oils may not give adequate protection in marine use, or in other applications where severe corrosion conditions are encountered.

It has been proposed by some to add various amines to the alkyl acid phosphate compounded oil sufficient to more or less neutralize the acidity of the acid phosphate. While this procedure has given more or less success, depending upon the amine used, the respective action of each of the proposed amines varies unpredictably, some amines giving little or no improvement in anticorrosion properties, some increasing the emulsion characteristics of the oil to a non-permissible extent, and some being incompatible with oxidation inhibitors normally used in the oil. Additionally many of the amines form with the alkyl acid phosphates (or with other constituents of the oil) small amounts of by-products of unknown composition which precipitate or form a haze in the oil upon storage.

In its broadest aspects, the present invention contemplates a mineral lubricating oil containing alkyl acid phosphates the acidity of which is wholly or partially neutralized by furfuryl amine. Such oils give adequate protection against corrosion, as indicated by no corrosion of the test specimen in the Navy test, either above or below the oil level. They have satisfactory demulsification characteristics and are compatible with oxidation inhibitors commonly employed. Though in some cases, especially when mono alkyl acid phosphates are present, a haze appears in the oil during storage, such haze is insufficient to affect the properties of the oil during actual use.

In a preferred embodiment of the invention, the acidity of the alkyl acid phosphate is neutralized by a mixture of furfuryl amine and a primary or secondary aliphatic amine of from 3 to 7 carbon atoms. Oils so prepared have all the advantages of those prepared with furfuryl amine alone, and additionally are generally free from any precipitate or haze formation during storage.

The neutralization of the phosphate by the amine should be carried out in situ in the oil to be used (or in a portion thereof) since, if carried out separately, difficulty will be experienced in effecting solution of the resulting product by the oil. The product resulting from the neutralization, either partial or complete, may be considered an addition salt of the amine and phosphate. However, it is uncertain how closely the amine is bound to the acid phosphate. Suffice it to say that the amine reacts with the acid phosphate with the liberation of heat. In the case of the mixed amines, in the preferred form of the invention, the product may be a mixture of addition salts or, when mono alkyl acid phosphates are present the product may contain addition salts of two amines.

The base oil used for the invention may be any refined mineral oil of otherwise suitable properties. For a turbine oil, for example, the base oil may be a 50 V. I. solvent refined hydrocarbon oil having a Saybolt viscosity at 130° F. of 185–205 seconds and having suitable anti-emulsion characteristics.

To the base oil (or a portion thereof) is added a desired amount of an acid alkyl phosphate having from 8 to 16 carbon atoms per alkyl group and furfuryl amine in an amount at least half that required for complete neutralization of the alkyl acid phosphate. By complete neutralization it is meant that one equivalent of amino nitrogen is present for each equivalent of acidic hydrogen

in the alkyl phosphate. Though the reaction may occur at ordinary temperatures, it is greatly facilitated by moderate increase in temperature such as, for example, 140° to 160° F. Such temperatures substantially reduce the viscosity of the oil and thereby facilitate contact of the reactants.

The acidic hydrogen equivalent of the alkyl acid phosphate may readily be determined by an electrometric titration of a sample of the acid alkyl phosphate with aqueous KOH solution to a pH of about 9. From the amount of KOH used the theoretical amount of amine required for complete neutralization may be readily calculated.

The invention contemplates the use of any alkyl acid phosphate, or mixtures of alkyl acid phosphates, having from 8 to 16 carbon atoms per alkyl group. Thus, n-octyl acid phosphate, n-decyl acid phosphate, n-dodecyl acid phosphate and the like are suitable. Mainly for commercial reasons, the preferred alkyl acid phosphate is "Lorol" acid phosphate, which is a mixture of phosphoric esters of "Lorol alcohol." The term "Lorol alcohol" is used in the trade to denote a mixture of primary normal aliphatic alcohols of 8 to 12 carbon atoms which are obtained by fractionation of the alcohols resulting from the reduction of cocoanut and/or palm kernel oils. "Lorol" acid phosphate mixtures are readily obtainable on the market and for this reason are preferred to the purified esters of greater scarcity and higher price. One "Lorol" acid phosphate type is sold under the trade name "Ortholeum 162" and is understood to be mainly a mixture of the mono and di acid phosphates of "Lorol alcohol."

The amount of the acid alkyl phosphate and furfuryl amine to be used may vary depending upon the degree of rust-inhibition required. Definite rust-inhibiting effect is obtained with as little as 0.005% by weight of alkyl acid phosphate. However, for satisfactorily meeting the Navy specifications for a turbine oil, at least 0.01%, and preferably at least 0.015%, should be used. Greater amounts may be used if desired up to the limit of solubility of the reaction product in the oil. The amount of the furfuryl amine may vary between about 50% to 150% of that theoretically required for complete neutralization of the acidity of the phosphate. Either the phosphate or the amine may be added to the oil first followed by the other. A convenient method of preparation is to prepare in advance a concentrate of the phosphate in one portion of the oil and a concentrate of the furfuryl amine in a second portion of the oil. The two concentrates can then be readily added in any desired amounts to the main body of oil and the desired reaction effected.

In the preferred form of the invention the acidity of the alkyl acid phosphate is neutralized by a mixture of furfuryl amine and a normal primary or normal secondary aliphatic amine having from 3 to 7 carbon atoms per alkyl group. For proper rust protection, the furfuryl amine should be present in an amount sufficient to neutralize at least half of the acidity of the phosphate and, for complete freedom from precipitate or haze formation in storage, the ratio of the furfuryl amine to aliphatic amine should be between 1:1 and 3:1 on a molar basis. The total amine present should not be in excess of 150% of that required for theoretically complete neutralization of the acidity of the phosphate.

In preparing the oil containing the reaction product of alkyl acid phosphate and mixture of furfuryl amine and aliphatic amine, it is important that the two amines be mixed before reacting with the alkyl acid phosphate. It is therefore convenient to add the two amines to the oil, thoroughly mix the same, and then add the alkyl acid phosphate, using heat as desired. However, it is desirable to keep the temperature below about 175° F. to avoid volatilization of the aliphatic amine prior to completion of the reaction. Alternately, a concentrate of the two amines may be made up in a portion of the oil and a concentrate of the phosphate in a second portion of the oil. The two concentrates may then be added to the remainder of the oil in proper proportions to effect the desired reaction. Should the phosphate be contacted with either amine prior to the other, difficulty may be experienced with haze formation in the finished oil on extended storage.

EXAMPLE I

A base oil having the following properties:

Gravity, °API	29.3
Flash, Cl. O. C., °F	470
Pour point, °F	15
Saybolt viscosity @ 100° F	410
Saybolt viscosity @ 130° F	187
Saybolt viscosity @ 210° F	58.5
Viscosity index	96
Color, ASTM	1½+
Emulsion, F. S. #320.13:	
Distilled water, cc. Web, after 30 min	1
Salt water, cc. Web, after 30 min	1
Carbon residue	0.03
Neutralization No., mg. KOH/g	0.01
Sulfur, per cent	0.10
Aniline point, °F	230

was heated to 160° F. and 0.015% by weight of Ortholeum 162 was added. After thorough mixing and cooling of the oil to 140° F., 0.00852% by weight (stoichiometric amount for complete neutralization) of furfuryl amine was added and stirred for 15 minutes. After cooling to room temperature, the oil was tested and found to pass the Navy specifications for corrosion and emulsion. However, after 3 days' storage in sunlight a slight precipitate appeared in the oil.

EXAMPLE II

The procedure of Example I was repeated using n-octyl acid phosphate instead of Ortholeum 162. Tests on the finished oil were similar to those obtained in Example I.

EXAMPLE III

The procedure of Example I was repeated using 0.00426% by weight of furfuryl amine. Tests on the finished oil were similar to those obtained in Example I.

EXAMPLE IV

A base oil having the same properties as that used in Example I was heated to 150° F. To the heated oil was added 0.00426% by weight of furfuryl amine and, after stirring for 3 minutes, 0.00383% by weight n-amylamine (i. e. equal molar proportions of the two amines). After stirring for 5 minutes, 0.015% Ortholeum 162 was added and the blend stirred for 30 minutes. After cooling, the oil was tested and passed the Navy corrosion and emulsion tests. No precipitate formed in the oil even after storage for 90 days in sunlight.

EXAMPLE V

The procedure of Example IV was followed except that, prior to cooling, 0.250% by weight of phenylalphanaphthyl amine, an anti-oxidant, was thoroughly mixed into the oil blend. The oil passed the Navy corrosion, emulsion, and oxidation tests. No precipitate formed during 90 days' storage in sunlight.

In the accompanying Table 1 are shown results obtained incorporating into a base oil of characteristics similar to that used in Example I the reaction product of Ortholeum 162 with various proportions of furfuryl amine, and also the reaction product of octyl acid phosphate with furfuryl amine. The table shows that good anti-corrosion properties are obtained providing the furfuryl amine is present in quantity sufficient to theoretically neutralize at least 50% of the acidity of the alkyl phosphate. The oils tested, however, did form a haze

in storage sufficient to be objectionable to some customers, including the U. S. Navy, but insufficient materially to affect the properties of the oil.

Table 1

Additives, Wt. Percent:				
Ortholeum 162	0.015	0.015	0.015	
n-Octyl Acid Phosphate				0.015
Furfuryl Amine	0.0019	0.0043	0.0085	0.0085
Tests (Navy Spec. 14-O-15):				
Corrosion—ASTM D665-47T—				
Rust at Liquid Phase	None	None	None	None
Rust at Vapor Phase	Fail	None	None	None
Rust at Interface	Fail	None	None	None
Emulsion—F. S. #320.13—				
Distilled Water	Pass	Pass	Pass	Pass
Salt Water	Pass	Pass	Pass	Pass
Precipitate Formation—				
Days in Sunlight to produce haze	3	3	3	3

Accompanying Table 2 shows results obtained by using a mixture of furfuryl amine and primary aliphatic amines according to the preferred form of the invention. The table clearly shows the advantages in lack of haze formation produced by the mixed amines. The table also indicates the necessity of the furfuryl amine being present in amount sufficient to neutralize at least 50% of the acidity of the alkyl acid phosphate.

Table 2

Additives, Wt. Percent:					
Ortholeum 162	0.015	0.015	0.015	0.015	
n-Octyl Acid Phosphate					0.015
Furfuryl Amine	0.0019	0.0043	0.0064	0.0043	0.0043
n-Butyl Amine		0.0032			
n-Amyl Amine	0.0575		0.0019		0.0038
n-Hexyl Amine				0.0044	
Tests (Navy Spec. 14-O-15):					
Corrosion—ASTM D665-47T—					
Rust at Liquid Phase	None	None	None	None	None
Rust at Vapor Phase	Fail	None	None	None	None
Rust at Interface	Fail	None	None	None	None
Emulsion—F. S. #320.13—					
Distilled Water	Pass	Pass	Pass	Pass	Pass
Salt Water	Pass	Pass	Pass	Pass	Pass
Precipitate Formation—					
Days in Sunlight to produce Haze	90+	90+	90+	90+	90+

In accompanying Table 3 are shown the results obtained by use of a mixture of furfuryl amine and secondary butyl amine in accordance with a specific embodiment of the preferred form of the invention. The results so obtained are contrasted with those obtained by use of a mixture of furfuryl amine and a tertiary aliphatic amine. Also in Table 3 are shown the use of the invention in conjunction with two well known oxidation inhibitors (2, 6, ditertiary butyl para cresol and phenyl-alpha-naphthyl amine) to produce oils meeting all the requirements of the U. S. Navy for turbine oils.

Table 4 illustrates the variety and unpredictability of results obtained by using the reaction product of alkyl acid phosphate and various amines in attempting to produce an anti-corrosion oil of suitable properties.

Table 3

Additives, Wt. Percent:				
Ortholeum 162	0.015	0.015	0.015	0.015
Furfuryl Amine	0.0043	0.0043	0.0043	0.0043
Di-n-butylamine	0.0057			
Tri-n-butylamine		0.0081		
n-Amyl Amine			0.0038	0.0038
2,6,Ditertiary butyl para cresol			0.250	
Phinyl-a-naphthyl Amine				0.250
Tests (Navy Spec. 14-O-15):				
Corrosion—ASTM-D665-47T—				
Rust at Liquid Phase	None	None	None	None
Rust at Vapor Phase	None	Fail	None	None
Rust at Interface	None	Fail	None	None
Emulsion—F. S. #320.13—				
Distilled Water	Pass		Pass	Pass
Salt Water	Pass		Pass	Pass
Oxidation—ASTM-D943-47T—				
Days for "break"			42	49
Precipitate Formation—				
Days in Sunlight to produce Haze	90+	7	90+	90+

Table 4

Amine Used	Navy Corrosion Test	Navy Emulsion Test	Precipitate Formation
n-Butylamine	(*)	Pass	Fail
Dodecylamine	(*)	Fail	Fail
Hexadecylamine	(*)	Fail	Pass
Di-octadecylamine	(*)	Pass	Fail
Di-2-Ethyl Hexylamine	Pass	Pass	Pass
Tri-n-butyl Amine	(*)	Pass	Fail
Tri-n-amylamine	(*)	Pass	Fail
Cyclohexylamine	Pass	Pass	Fail
Di-cyclohexylamine	(**)	Pass	Pass
Aniline	(*)	Pass	Fail

* Rust above oil level.
** Rust below oil level.

The oil used in each of the tests in Table 4 was similar to that used in Example I. The amount of alkyl acid phosphate (Ortholeum 162) used in each case was 0.015 weight percent of the oil and the amount of each amine was the calculated amount theoretically required to neutralize the acid phosphate.

Although, in the practice of the invention the mono or di alkyl phosphoric acid esters of any of the several aliphatic alcohols from octyl to hexadecyl alcohol may be used, mixtures of these are generally more readily available commercially. Such mixtures are intended to be included within the scope of the term "alkyl acid phosphate" as used in the claims and the word "phosphate" is intended to include a single phosphate or a plurality of the same unless otherwise specifically indicated.

I claim:

1. A hydrocarbon lubricating oil containing in solution as an essential rust-inhibiting component the product resulting from the admixing of at least 0.005% by weight of alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group and furfuryl amine in quantity from 50% to 150% of the amount theoretically required to neutralize the alkyl acid phosphate.

2. An oil according to claim 1 in which the hydrocarbon oil is of suitable grade for the lubrication of steam turbines and the quantity of alkyl acid phosphate is at least 0.01% by weight.

3. An oil according to claim 1 in which the alkyl acid phosphate is a mixture of phosphoric acid-esters of fatty alcohols of 8 to 12 carbon atoms derived from the group consisting of cocoanut and palm oils.

4. A hydrocarbon lubricating oil containing in solution as an essential rust-inhibiting component the product resulting from the admixing of at least 0.005% by weight of alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group, furfuryl amine in quantity at least about 50% of the amount theoretically required to neutralize said phosphate, and an amine selected from the group consisting of primary and secondary normal aliphatic amines having 3 to 7 carbon atoms per alkyl group, the molal ratio of the aliphatic amine to the furfuryl amine being between about 1:1 and 1:3 and the total of the furfuryl and aliphatic amines being not over about 150% of the amount theoretically required to neutralize said phosphate.

5. An oil according to claim 4 wherein the aliphatic amine is n-butyl amine.

6. An oil according to claim 4 wherein the aliphatic amine is n-amyl amine.

7. An oil according to claim 4 wherein the aliphatic amine is n-hexyl amine.

8. An oil according to claim 4 wherein the aliphatic amine is di-n-butylamine.

9. An oil according to claim 4 in which the total of the furfuryl amine and the aliphatic amine is about 100% of the amount theoretically required to neutralize the alkyl acid phosphate.

10. An oil according to claim 4 in which the alkyl acid phosphate has from 8 to 12 carbon atoms in the alkyl group.

11. An oil according to claim 4 in which the hydrocarbon oil is of suitable grade for the lubrication of steam turbines and the quantity of alkyl acid phosphate is at least about 0.015% by weight.

12. An oil according to claim 4 which has been prepared by mixing the furfuryl amine and aliphatic amine prior to admixture with the alkyl acid phosphate.

13. The method of preparing a hydrocarbon oil containing addition salts of alkyl acid phosphate with furfuryl and aliphatic amines without haze formation, which comprises: forming in at least a portion of the hydrocarbon oil a homogeneous solution of furfuryl amine and per each 3 moles of furfuryl amine, 1 to 3 moles of an amine selected from the group consisting of primary and secondary normal aliphatic amines having 3 to 7 carbon atoms per alkyl group, and then mixing with said solution any remaining hydrocarbon oil and alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group, the quantity of said phosphate being at least about two-thirds the theoretical amount required to react with the total of the two said amines and not over about twice the theoretical amount required to react with the furfuryl amine, and the total amount of hydrocarbon oil being sufficient to dissolve the resulting products but not more than 20,000 times by weight the amount of said phosphate.

14. The method of claim 13 wherein the mixing of phosphate and the remaining hydrocarbon oil with the said solution is at a temperature between about 140° F. and 175° F.

15. A hydrocarbon lubricating oil containing in solution as an essential rust-inhibiting component the product resulting from the admixing of at least 0.005% by weight of alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group and an amine base composed of at least 50 molal percent furfuryl amine with any remainder being an amine selected from the group consisting of primary and secondary normal aliphatic amines having 3 to 7 carbon atoms per alkyl group, the quantity of said base being not over about 150% of the amount theoretically required to neutralize said phosphate and the quantity of furfuryl amine in said base being at least about 50% of the amount theoretically required to neutralize said phosphate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,413,852	Turner	Jan. 7, 1947
2,442,581	Bishop	June 1, 1948
2,515,520	Leath	July 18, 1950