

## UNITED STATES PATENT OFFICE

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## COMPOUNDED LUBRICATING OIL

Samuel Clyde Vaughn, Berkeley, Calif., assignor  
to Tide Water Associated Oil Company, San  
Francisco, Calif., a corporation of Delaware

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This invention relates to lubricants especially adapted to the lubrication of steam turbines and, in particular, steam turbines employed in naval and other marine use where severe conditions conducive to rusting are encountered. Though especially designed for use in steam turbines, the lubricants of the invention may advantageously be employed for general lubrication, and are particularly valuable for use in installations where rusting conditions are encountered such as, for example, in internal combustion engines, air compressors, and the like.

It is an object of the invention to provide a lubricating oil for steam turbines which will give enhanced protection against rusting under operating conditions where rusting is normally encountered. It is also an object of the invention to provide a steam turbine oil meeting the requirements of the U. S. Navy specifications mentioned herein. Briefly, these purposes are accomplished in accordance with the invention by incorporating in a suitable base oil a minor but effective amount of the reaction product of an alkyl acid phosphate having 8 to 16 carbon atoms per alkyl group and amino bicyclohexyl. By use of the particular amine, amino bicyclohexyl, various advantages are obtained over turbine oils compounded with reaction products of alkyl phosphates and other amines, especially when commercial grades of alkyl phosphates are used and also in cases where oxidation inhibitors are incorporated into the oil in addition to the rust-inhibitor.

In the lubrication of modern steam turbines the requirements of the lubricants employed are most exactly since the lubricant comes in contact with condensed steam and, at times, even with sea water due to leaks in the condensing and cooling systems. The lubricant must separate successfully from the water without the formation of troublesome emulsions and must be able substantially to protect the metal surfaces of the turbines from rust even under these severe conditions. The rust protection is needed not only by those parts continually wetted by the oil, but also by those parts of the system which are not continually flooded by the oil. The lubricant must not foam to any substantial extent. Also, for commercial reasons, the lubricant should be entirely homogeneous and free from suspended matter and compatible with other additives such as oxidation inhibitors.

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In order to insure proper performance from oils supplied for marine steam turbines, the U. S. Navy has adopted rigid specifications set forth in the Navy Department Specification pamphlet 14-0-15 dated August 15, 1945. Among the important tests of these specifications is the test for "Corrosion (in pressure of salt water)" described therein in paragraphs E-5 and F-3C. In brief, 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 oil and 30 ml. of synthetic sea water maintained at 140° F. This test is recognized by the Navy as a means of indicating the degree of protection against rust afforded by a lubricant under test.

Another important test provided by the above mentioned Navy specifications is the emulsion test. Briefly, in this test 40 ml. of the oil under test and 40 ml. of distilled water are stirred together @ 1500 R. P. M. in a 100 ml. graduate @ 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.

Paragraph E-4 of the above Navy pamphlet requires that any additive agents used must remain uniformly distributed in the oil, i. e. there shall be no separation of a solid phase from the oil.

Many rust-inhibiting lubricants have been proposed for use in steam turbines. A large proportion of these are composed of well refined mineral oil to which has been added small quantities of alkyl phosphate esters. Improved results are claimed by many when acid alkyl phosphates are used and the acid radical is neutralized with a slight excess of an organic amine, for which purpose various amines have been suggested. In general, these lubricants have given more or less satisfactory results in steam turbines. However, most of them fail to meet the rigid Navy specifications for one or more of the following reasons:

(a) When tested by the severe Navy corrosion test rusting occurs on that portion of the steel specimen not immersed in the oil bath, or at the surface of the oil, indicating that the oil is somewhat deficient in the protection afforded to those parts of the turbine not continually wetted by the oil.

(b) The particular amine used to neutralize the acid alkyl phosphate, or the resulting compound,

is conducive to the formation of emulsions with either salt water or distilled water, and the compounded oil fails to meet the Navy emulsion requirements as indicated by the emulsion test mentioned above.

(c) A light flocculent precipitate or "floc" appears in the oil within a few days after its preparation. Although this floc may not be of any special disadvantage in the actual operation of the turbine, it greatly affects customer acceptance of the oil and is unacceptable by many, including the Navy. This floc phenomenon occurs with many of the amines proposed especially when mono-alkyl acid phosphates are used or with commercial di-alkyl phosphates which invariably contain significant amounts of mono-alkyl phosphates. Floc also appears in some otherwise satisfactory oils upon the addition thereto of an oxidation inhibitor, particularly when the oxidation inhibitor is an aromatic primary amine such as, for example, paraphenylene diamine, toluene diamine, diamino triphenyl methane, alkoxy anilines, and the like. Since it is desirable for a turbine oil to contain an oxidation inhibitor as well as a rust inhibitor, and since these aromatic amines are otherwise excellent oxidation inhibitors, it is highly important to choose a rust inhibitor which not only is free from floc formation when used alone but is also free from floc formation when used in conjunction with oxidation inhibitors, either compounded therewith originally or added later (for example, by the customer or distributor).

The present invention provides an inhibitor for hydrocarbon oil having enhanced rust-inhibiting properties with freedom from substantial emulsion forming tendency and of complete compatibility with the oil and with conventional oxidation inhibitors. When blended in proper proportions with an otherwise suitable base oil, the inhibitor provides a turbine oil meeting the severe requirements of the U. S. Navy specifications.

The inhibitor of the invention is the reaction product of an amino bicyclohexyl with an alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group. Of the amino bicyclohexyls the ortho and meta amino bicyclohexyls are preferred. Mainly for commercial reasons, the preferred alkyl 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 more 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."

Though for the reasons stated above "Lorol" acid phosphates are preferred, other alkyl acid phosphates containing from 8 to 16 carbon atoms per alkyl group are satisfactory. The di-alkyl phosphates are preferred, although the commercial grade containing significant amounts of mono-alkyl phosphates are entirely suitable. Generally organic amines tend to form with mono-alkyl phosphates small amounts of reaction products of unknown composition which are oil-insoluble and thus produce undesirable pre-

cipitates when used in mineral oils. However, with the amino bicyclohexyl of the present invention this tendency is not exhibited, thereby permitting the use of commercial grades of di-alkyl phosphates without the formation of objectionable floc.

Although the reaction product of the present invention may be prepared by mixing the alkyl acid phosphate selected with amino bicyclohexyl in stoichiometric proportions and the resulting product added to the base oil, it is convenient to add the ingredients to at least a portion of the base oil and permit the reaction to occur in the oil. A certain amount of heat, say up to about 175° F., will assist in the ready formation of the reaction product, taking care not to heat the uncombined alkyl phosphate to a temperature where decomposition of the same is initiated.

The proper proportions of amino bicyclohexyl to 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 amount of the amino bicyclohexyl to neutralize the acid radicals of the phosphate may be readily calculated. It is desirable to have a slight excess of amine present; however, good results have been obtained with from 25% deficiency up to 50% excess of amine.

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.

Into the base oil is incorporated a small but effective amount of the above described reaction product. For some anti-rust uses as little as 0.01% by weight of the reaction product may be used. However, for satisfactorily meeting the Navy specifications for a turbine oil, at least 0.02%, and preferably at least 0.03%, by weight should be used. The inhibitor has been found to be satisfactory in amounts up to 0.15% by weight and is believed to be satisfactory in even greater amounts although the additional cost may not be justified by any additional effectiveness.

The reaction product of the invention appears to be soluble in mineral oil in practically all proportions, and it is within the broad scope of the invention to prepare the reaction product, or a concentrate thereof in mineral oil, for subsequent use as a compounding agent for any desired oil. As stated prior the reaction product is compatible with oxidation inhibitors, even with aromatic primary amine oxidation inhibitors which frequently cause floc formation in oils containing amine salts of alkyl phosphate esters. Accordingly, it is also within the scope of the invention, broadly speaking, to include in the concentrate (or in the finished oil) desired amounts of an oxidation inhibitor.

#### Example I

A solvent refined base oil having the following properties:

Gravity, ° API	25.7
Pour point, ° F	-30
Flash point, ° F	400
Viscosity:	
@ 100° F., S. U.	447
@ 130° F., S. U.	188
@ 210° F., S. U.	55

Neutralization No.-----	0.06
Color, ASTM-----	2--
U. S. Gov't emulsion test @ 130° F. distilled water (minutes for separation)-----	10
1% NaCl (minutes for separation)-----	10
Carbon residue, per cent.-----	0.10
Sulfur, per cent.-----	0.31

was heated to 250° F. Into the heated oil was stirred 0.015% by weight of ortho amino bicyclohexyl. This primary amine is also called ortho-aminodicyclohexyl or 2-cyclohexyl-cyclohexyl amine. The resulting mixture was cooled to 175° F. after which there was added 0.015% by weight of Ortholeum 162 (stoichiometric amount). The reaction mixture was then stirred vigorously for 2 hours and allowed to stand for 16 hours. The resulting oil passed the Navy corrosion test and emulsion tests. No insoluble precipitate or floc occurred in the oil even after several months' storage.

#### Example II

Oil prepared as in Example I was heated to 150° F. and 0.25% by weight of an oxidation inhibitor (para phenetidine) was added with stirring. The resulting oil again passed the Navy corrosion test and emulsion tests and showed no precipitate or floc after several months' storage. This oil showed excellent oxidation stability when tested by various laboratory methods.

#### Example III

Oil prepared as in Example I was heated to 150° F. and 0.25% by weight of an oxidation inhibitor (2,6-ditertiarybutyl-4-methylphenol) was added with stirring. The resulting oil again passed the Navy corrosion test and emulsion tests and showed no precipitate or floc after several months' storage. This oil showed excellent oxidation stability when tested by various laboratory methods.

To further illustrate the superior properties of turbine oils compounded with the rust inhibitor of the present invention, the following table is given showing comparative tests with the same base oil compounded with approximately 0.03% of the reaction products of Ortholeum 162 with various representative amines. The table shows results with and without an oxidation inhibitor (para phenetidine).

Amine Used	Navy Sea Water Corrosion Test	Navy Emulsion Test	Precipitate Formation
Without Oxidation Inhibitor:			
N-Butylamine-----	(1)-----	Pass-----	Fail.
Dodecylamine-----	(1)-----	Fail-----	Do.
Hexadecylamine-----	(1)-----	do-----	Pass.
Bi-octadecylamine-----	(1)-----	Pass-----	Fail.
Tri-amine-----	(1)-----	do-----	Do.
Di 2-Ethyl Hexylamine-----	Pass-----	do-----	Pass.
Cyclohexylamine-----	do-----	do-----	Fail.
Di-cyclohexylamine-----	(2)-----	do-----	Pass.
Paraphenetidine-----	(1)-----	do-----	Fail.
Aniline-----	(1)-----	do-----	Do.
Amino bicyclohexyl-----	Pass-----	do-----	Pass.
With 0.25% Oxidation Inhibitor:			
N-butylamine-----	do-----	do-----	Fail.
Dodecylamine-----	do-----	Fail-----	Do.
Hexadecylamine-----	do-----	do-----	Do.
Di-octadecylamine-----	do-----	Pass-----	Do.
Tri-amine-----	do-----	do-----	Do.
Di 2-Ethyl Hexylamine-----	do-----	do-----	Do.
Cyclohexylamine-----	do-----	do-----	Do.
Di-cyclohexylamine-----	do-----	do-----	Do.
Paraphenetidine-----	do-----	do-----	Do.
Aniline-----	(1)-----	do-----	Do.
Amino bicyclohexyl-----	Pass-----	Pass-----	Pass.

<sup>1</sup> Rust above oil level.

<sup>2</sup> Rust below oil level.

From the table it is apparent that, of the amines tested, only the amino bicyclohexyl gave satisfactory results under all conditions.

Although, in the practice of the invention the mono and di-alkylphosphoric acid esters 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 a rust-inhibiting quantity of the addition product of an amino bicyclohexyl and alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group.

2. An oil according to claim 1 in which the addition product is present in a quantity from about 0.01% by weight up to 0.15%.

3. An oil according to claim 1 in which the alkyl acid phosphate contains substantial quantities of monoalkyl phosphate.

4. 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 coconut and palm oils.

5. An oil according to claim 1 in which the amino bicyclohexyl is ortho amino bicyclohexyl.

6. An oil according to claim 1 in which the amino bicyclohexyl is meta amino bicyclohexyl.

7. An oil according to claim 1 in which the hydrocarbon oil is of suitable grade for the lubrication of steam turbines and the addition product is present in a quantity between about 0.2% and about 0.15% by weight.

8. An oil according to claim 1 which contains in addition an oxidation inhibitor for the oil.

9. An oil according to claim 1 which contains in addition an aromatic primary amine oxidation inhibitor.

10. A concentrate suitable for addition to a hydrocarbon oil to impart rust-inhibiting properties thereto which consists essentially of a hydrocarbon oil containing from 0.15% by weight up to the limit of solubility of the addition product of amino bicyclohexyl and alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group.

11. A concentrate for addition to a hydrocarbon oil to impart rust-inhibiting and anti-oxidation properties thereto consisting essentially of a hydrocarbon oil containing upwards of about 0.25% by weight of an oxidation inhibitor and from about 0.15% by weight up to the limit of solubility of the addition product of amino bicyclohexyl and alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group.

12. A hydrocarbon lubricating oil containing a rust-inhibiting quantity of the reaction product produced by mixing, below the decomposition temperature of the reactants and above the temperature at which no addition product is formed, alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group and an amino bicyclohexyl, the latter being present in an amount between 75% and 150% of the stoichiometric quantity.

13. A hydrocarbon lubricating oil into which have been mixed, below the decomposition temperature of the additives and above the tempera-

ture at which no addition product is formed, alkyl acid phosphate having from 8 to 16 carbon atoms per molecule and an amount of amino bicyclohexyl from 75% to 150% of that required to neutralize the acid radicals of said phosphate, the total weight of said phosphate and said amino bicyclohexyl being between .01% and .15% of the weight of the hydrocarbon oil.

SAMUEL CLYDE VAUGHN. 10

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