Patented Oct. 20, 1953

2,656,375

UNITED STATES PATENT OFFICE

2,656,375

AMINO BICYCLOHEXYL-ALKYL ACID PHOSPHATE REACTION PRODUCT

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

No Drawing. Application September 6, 1951, Serial No. 245,429

5 Claims. (Cl. 260—461)

1

This invention relates to an amino bicyclohexyl reaction product and the means for manufacturing the same. More particularly it relates to the product formed by the reaction between an alkyl acid phosphate and amino bicyclohexyl, and to processes for its manufacture.

The reaction product described herein is useful as a surface active agent, an oiliness agent, a mild extreme pressure agent, a rust and corrosion inhibitor, and the like. It is especially valuable as a corrosion inhibitor for lubricating oils, particularly for use in connection with the lubrication of steam turbines and other marine gear where severe conditions conducive to rusting are normally encountered. It is also useful in various other lubricants, especially where rusting conditions are encountered such as, for example, in internal combustion engines, air compressors, and so forth. The product has various advantages over the reaction products of other amines and alkyl phosphates.

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 product of the present 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. This primary amine is sometimes called cyclohexyl-cyclohexylamine, the ortho isomer being designated as 2-cyclohexyl-cyclohexylamine and the meta isomer as 3-cyclohexyl-cyclohexylamine. 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."

2

Although 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 precipitates 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 precipitate or "floc."

The reaction product of amino bicyclohexyl may be manufactured either as an oil-free product, as an oil concentrate, or in situ with a base oil. It may be considered as an addition salt resulting from the neutralization of the acidity of the alkyl acid phosphate by the basicity of the amine. Since the alkyl acid phosphate comprises mono and di alkyl acid phosphates and the alkyl groups vary from C_8 to C_{12} in chain length, the reaction product cannot be represented by any one clear-cut structural formula. However it is a well defined clear reddish yellow viscous oil which shows no indication of crystallizing on standing and readily forms oil concentrates such as 5% and 50% solutions.

Substantially pure amino bicyclohexyl, such as is available commercially, may be used to form the reaction product. This material is advantageously preheated above 212° F., preferably in the range of 250° F. to 270° F., prior to contacting with the alkyl acid phosphate in order to prevent the formation of a floc which might otherwise occur. A general process for manufacturing the reaction product comprises contacting predetermined quantities of amino bicyclohexyl with alkyl acid phosphate at a temperature within the range of 100° to 200° F. with vigorous agitation for a period of several hours. The reaction normally proceeds rapidly with the evolution of heat, and a clear reddish yellow product results.

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 required to neutralize the acid radicals of the phosphate may be readily calculated. It is de-

sirable to have a slight excess of amine present; however, good results have been obtained with from 25% deficiency up to 50% excess of amine.

Although the reaction product of the 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.

Example I

About 250 grams of a mixture of the mono and di alkyl acid phosphates comprising an approximately equal ratio of mono and di alkyl acid phosphate and of C_8—C_{12} alkyl chain length with C_{10} predominant was placed in a reaction vessel and heated to 130° F. While stirring vigorously, 250 grams of ortho amino bicyclohexyl, preheated to 265° F. and cooled to room temperature, was added and the mixture thoroughly agitated for two hours. During this time the temperature rose to 190° F. A clear reddish yellow viscous oil reaction product resulted therefrom.

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. 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. It is also compatible with pour depressants, viscosity index improvers and anti-foam agents. 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 II

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	188
@ 210	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, percent	0.10
Sulfur, percent	0.31

was heated to 250° F. Into the heated oil was stirred 0.015% by weight of ortho amino bicyclohexyl. 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, resulting in an oil containing the reaction product of the invention.

To illustrate the superior utility of the reaction product when used in turbine oils, the following discussion is presented.

In the lubrication of modern steam turbines the requirements of the lubricants employed are most exacting 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.

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 the presence 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 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.

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 emul-

sions 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).

By the use of the reaction product of the present invention, turbine oils may be prepared which overcome the above disadvantages of other additives and satisfactorily meet the Navy specifications.

In the preparation of such a turbine oil the base oil may be any refined mineral oil of otherwise suitable properties. 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.

Example III

Oil prepared as in Example II was tested and found to pass the Navy corrosion test and emulsion tests. No insoluble precipitate or floc occurred in the oil even after several months storage.

Example IV

Oil prepared as in Example II 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.

Example V

Oil prepared as in Example II 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.

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.
Di-octadecylamine	(1)	Pass	Fail.
Tri-amylamine	(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-amylamine	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.
Amino bicyclohexyl	Pass	Pass	Pass.

[1] Rust above oil level.
[2] Rust below oil level.

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

The reaction product of the present invention is an extremely useful and marketable commodity, particularly when in the form of an oil concentrate which is readily adaptable for quantity shipment and is easily blended into important commercial products whereby quality and utility is greatly enhanced.

Although in the practice of the invention the mono and di-phosphoric 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.

This application is a continuation-in-part of my copending application Serial Number 130,345, filed November 30, 1949, now Patent No. 2,605,226.

I claim:

1. As a new chemical compound, suitable for use as a rust inhibiting additive for mineral oils, the addition product of amino bicyclohexyl and alkyl acid phosphate containing from 8 to 16 carbon atoms in each alkyl group.

2. The compound of claim 1 wherein the amino bicyclohexyl is ortho amino bicyclohexyl.

3. The compound of claim 1 wherein the amino bicyclohexyl is meta amino bicyclohexyl.

4. The compound of claim 1 wherein the alkyl acid phosphate is a mixture of phosphoric acid-esters of fatty alcohols of 8 to 12 carbon atoms derived from cocoanut and palm oils.

5. A process for the manufacture of the addition product of amino bicyclohexyl and alkyl acid phosphate which comprises: heating amino bicyclohexyl to a temperature between 212° and 270° F., then cooling and subsequently reacting said amine with alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group while maintaining the reaction temperature between 100° and 200° F.

SAMUEL CLYDE VAUGHN.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,285,854	Downing	June 9, 1942
2,371,853	Smith	Mar. 20, 1945
2,413,852	Turner	Jan. 7, 1947
2,516,914	Revukas	Aug. 1, 1950
2,574,955	Bishop	Nov. 13, 1951