United States Patent Office 3,819,647
Patented June 25, 1974

3,819,647

WATER-SOLUBLE SALTS OF IMIDAZOLINES WITH PHOSPHORIC ACID ESTERS OF (A) ETHOXYLATED LONG CHAIN ALCOHOLS AND (B) ETHOXYLATED ALKYL PHENOLS

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No Drawing. Continuation-in-part of abandoned application Ser. No. 864,883, Oct. 8, 1969. This application Feb. 28, 1972, Ser. No. 230,031
Int. Cl. C07d 49/34
U.S. Cl. 260—309.6 6 Claims

ABSTRACT OF THE DISCLOSURE

Imidazoline salts of phosphoric acid mono- and diesters of (a) ethoxylated long chain monohydric alkanols and (b) ethoxylated alkyl monohydric phenols, said salts being water-soluble and causing viscosity building in aqueous systems.

This application is a continuation-in-part of copending application Ser. No. 864,883, filed Oct. 8, 1969, now abandoned.

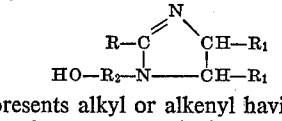
This invention relates to novel imidazoline salts of certain phosphate esters. More particularly this invention relates to novel water-soluble imidazoline salts of phosphated ethoxylated monohydric alkanols and alkyl monohydric phenols suitable for preparing aqueous hydraulic fluids, synthetic lubricants and the like.

The production and marketing of composition containing phosphate esters of various hydroxylic organic compounds has been carried on for a number of years and such compositions have been used as wetting agents, dispersants, emulsifiers, detergents, lubricants, corrosion inhibitors and the like. Various phosphate esters have been prepared utilizing a wide range of aliphatic and alkyl aryl hydroxylic organic compounds such as long chain aliphatic alcohols and ethylene oxide adducts or ethers of long chain aliphatic alcohols and alkylphenols. Illustrative disclosures are found in U.S. Pats. Nos. 2,052,029; 2,656,372; 2,701,258; 3,004,056; 3,042,697; 3,033,889 and 3,088,917.

Amine phosphate ester salts, including certain imidazoline phosphates, are known and have been disclosed, for example, in U.S. Pats. Nos. 3,010,903; 3,088,910; 3,166,249; 3,169,923; 3,203,895; 3,297,098 and 3,310,489. Heretofore known imidazoline salts of phosphate esters, notably as shown in U.S. Pat. No. 3,088,910 are oil-soluble materials.

This invention is concerned with novel and highly useful water-soluble salts of imidazolines with phosphoric acid esters selected from the group consisting of monoesters, diesters and mixtures of monoesters and diesters of (a) ethylene oxide adducts of monohydric alkanols containing from 8 to 18 carbon atoms or (b) ethylene oxide adducts of mono- and/or dialkyl mono-hydric phenols in which the alkyl radical or radicals contain from 4 to 18 carbon atoms, said ethoxylated alkanols or alkyl phenols containing from about 2 to about 40 mols of ethylene oxide per mol of alkanol or alkyl phenol. This invention also involves the production of aqueous compositions containing said imidazoline salts having effective lubricity, viscosity and viscosity stability properties.

The imidazolines suitable for preparing the imidazoline salts of the phosphate esters of the present invention are represented by the formula



where R represents alkyl or alkenyl having from 8 to 22 carbon atoms, R_1 represents hydrogen and lower alkyl

having from 1 to 6, preferably 1 to 2, carbon atoms, and R_2 is a member of the group consisting of alkylene having from 1 to 8 carbon atoms and lower alkyl substituents thereof, said lower alkyl having from 1 to 6 carbon atoms, and a radical of the structure

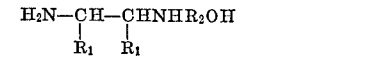
$$—CHR_1—CHR_1(NH—CHR_1—CHR_1)_x$$

wherein x is an integer from 1 to 5, preferably from 1 to 2.

The aforesaid imidazolines are readily prepared by condensing, under conditions of heating and stirring, a long chain aliphatic monocarboxylic or fatty acid (or a source thereof such as amides or esters of said acids) with a hydroxyalkyl alkylene polyamine, such as aminoethylethanolamine. The mol ratio of the acid to the polyamine is variable but generally walls within the range of 1 mol of the acid to 1 to about 2 mols of the polyamine, and the temperature at which the condensation reaction is carried out is generally in excess of 100° C., usually in the range of about 120° C. to about 250 or 300° C., and the reaction time is several hours, usually within the range of about 4 ot 12 hours, depending upon the particular reactants employed and the particular condensation temperature employed; or, where the reaction is carried out under less than atmospheric pressure, the reaction temperature may be somewhat reduced. Usually, the condensation temperature or temperature of heating and the duration of the heating are so correlated as to cause splitting out of water in excess of 1.5 mols for each mol of free acid and in excess of 0.5 mol for each mol of combined acid involved. Such imidazolines are described, for example, in U.S. Pat. No. 2,267,965.

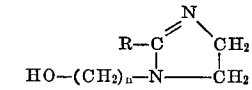
The long chain aliphatic monocarboxylic or fatty acids used in producing the imidazolines include saturated as well as ethylenically unsaturated naturally occurring and synthetic acids containing from 8 to 22, particularly 12 to 18, carbon atoms and encompass such acids as lauric acid, myristic acid, palmitic acid, oleic acid, stearic acid and commercial mixtures of various of such acids as are derived from animal, fish and vegetable oils and fats such as coconut oil, cottonseed oil, corn oil, tallow, babassu oil, palm kernel nut oil, soya oil, linseed oil, castor oil, olive oil, and also such monocarboxylic acid mixtures as are present in tall oil or refined tall oil and the like. In place of free acids, the amides or esters thereof can be employed, including the glyceride esters such as the foregoing oils and fats, as well as the monohydric alcohol esters such as the methyl esters of the foregoing acids.

The hydroxyalkyl polyamines, notably the hydroxy lower alkyl, lower alkylene polyamines which are used to produce the imidazolines have the general formula



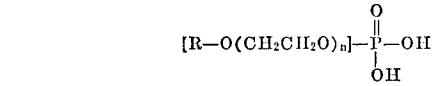
wherein R_1 and R_2 are as previously described herein and can likewise be selected from large numbers of known examples thereof, including aminoethylethanolamine or beta-hydroxyethyl ethylenediamine, hydroxyethyl diethylenetriamine, hydroxyethyl triethylenetetraamine, hydroxypropyl propylene diamine and other hydroxyalkyl alkylene polyamines of the 1,2 series, that is, wherein at least one amino group and one imino group are attached to adjacent carbon atoms.

The particularly preferred imidazolines for use in accordance with the present invention are represented by the formula

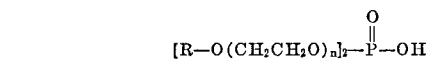


where R is C_8 to C_{22}, advantageously C_{12} to C_{18}, alkyl or alkenyl, and *n* is an integer from 1 to 5, advantageously 2. Of special utility are said imidazolines which are prepared by condensing oleic acid or tall oil fatty acids with aminoethylethanolamine.

The phosphoric acid esters which are neutralized with the aforementioned imidazolines to produce the novel water-soluble salts of the present invention are the monoesters of the formula:



and diesters of the formula:



R being the alkyl portion of the monohydric alkanol or the alkaryl portion of the alkyl monohydric phenol as the case may be, and *n* is an integer from 2 to 40. Mixtures of the aforesaid monoesters and diesters are also suitable for use in the present invention.

The phosphoric acid esters useful in preparing the novel water-soluble salts of the present invention are preferably prepared by reacting 1 mol of P_2O_5 with from 2 to 4.5 mols of the ethylene oxide adducts of the aforesaid alkanols or alkyl phenols at a temperature in the range of up to about 100° C., most advantageously in the range of about 50 to 65° C. as is disclosed, for example, in U.S. Pat. 3,004,056.

The linear and branched chain monohydric alkanols which may be subsequently ethoxylated and phosphorylated to form suitable phosphates generally comprise linear alkanols containing 8 to 18 carbon atoms and C_{10} to C_{20} branched chain alkanols.

Illustrative of such linear and branched chain monohydric alkanols are n-octyl alcohol, n-nonyl alcohol, n-decyl alcohol, n-dodecyl alcohol, n-tridecyl alcohol, n-tetradecyl alcohol, n-pentadecyl alcohol, n-hexadecyl alcohol, oleyl alcohol, n-stearyl alcohol, Oxo alcohols such as Oxo-hexadecyl alcohol and Oxo-pentadecyl alcohol (and other as shown in U.S. Pat. No. 2,965,678) 2-ethyl octanol, and branched chain dodecanols, tetradecanols, hexadecanols and octadecanols. Of special usefulness are the phosphoric acid esters of the 3 to 12 mol ethylene oxide adducts of C_{10} to C_{14} linear alkanols and mixtures of two or more of said alcohols.

The mono- and diesters of phosphoric acid with ethylene oxide adducts of alkyl monohydric phenols which may be employed in forming the novel water-soluble salts of the present invention are well known in the art. Such alkylphenols include mono- and dialkylphenols in which the alkyl radicals contain from 4 to 18 carbon atoms. Especially suitable and preferred are mono- and dialkylphenols wherein the alkyl substituent contains from 8 to 12 carbon atoms, such as nonylphenol, dinonylphenol and dodecylphenol. The mol ratio of ethylene oxide is variable within wide limits and generally about 2 to 40 mols of ethylene oxide per mol of alkylphenol or dialkyl phenol can be used. Preferred are those adducts in which there are about 6 to 18 mols of ethylene oxide per mol of mono- or dialkylphenol.

The novel water-soluble imidazoline salts of the present invention are readily prepared by simply admixing a suitable imidazoline and phosphoric acid ester at temperatures between about room temperature and about 100° C., or higher, and preferably in the area of about 70 to 75° C. In most cases, the imidazoline and the said phosphates will be liquid and the novel salt will be recovered in the liquid state. The imidazoline and phosphoric acid mono- or diester, or mixture of mono- and diester, are combined in approximately stoichiometric proportions, sufficient imidazoline being added to substantially neutralize the free acid groups present in the phosphate ester.

The aforesaid water-soluble imidazoline-phosphate ester salts lend themselves to a wide variety of practical applications. Of special note are the properties exhibited by an aqueous solution containing the novel compositions of the present invention. In aqueous solutions the imidazoline phosphates cause viscosity building and the system simultaneously shows viscosity stability and superior lubricity properties. Because of these properties, aqueous solutions of the novel imidazoline-phosphate salts may be employed as substitutes for hydrocarbons in numerous applications such as hydraulic fluids, transmission fluids, industrial fluids and as aqueous based synthetic lubricants such as cutting oils, rolling oils and drawing compounds in metal working procedures such as machining, grinding, stamping and the like, said aqueous lubricants containing from about 0.25% to 10%, or more, of the novel imidazoline salts.

Excellent non-inflammable hydraulic fluids have been prepared employing from about 2% to 20%, and preferably 5% to 10% by weight imidazoline phosphate in water and characterized by good lubricity and viscosity stability properties. Such fluids offer obvious advantages since conventional hydrocarbon fluids are flammable and emulsions used for this purpose have a tendency to break and become flammable under extreme conditions which cause the separation of phases.

The imidazoline phosphates or aqueous solutions containing the imidazoline phosphates of the present invention may also be employed, for example, as viscosity improving agents in liquid detergent compositions, as additives for other types of aqueous based synthetic lubricants, as emulsifiers, dispersants wetting agents, and as additives to surface active compositions.

The novel imidazoline phosphates and novel aqueous solutions containing same may also be used in metal cleaning compositions, dry cleaning compositions, froth flotation agents, additives to water or brine used in oil well secondary recovery techniques, in plasticizers and modifiers for synthetic resins, for incorporation into adhesives, paints and coatings, as solvents and as cleansing compositions, as additives in cosmetic preparations and gels, and as antistatic agents.

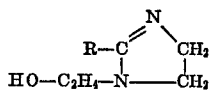
Various other materials may be added to the novel aqueous imidazoline phosphate compositions of the present invention, depending upon the particular purpose for which they will be employed. For example, water miscible solvents such as glycerol, ethylene glycol, butyl carbitol and ethylene glycol monobutyl ether may be added to reduce viscosity to a desired level; hydrotropes or solubilizers such as lower alkyl benzene sulfonates to compatibilize other materials; lubricating fluid additives such as oxiation inhibitors, corrosion and rust inhibitors exemplified by polyalkylene polyamides and the calcium and sodium sulfonates, antiwear additives and foam inhibitors; metal deactivating agents; agents to aid lubricity and to serve as bodying agents such as the sulfurized fatty acids, etc.

Other potential additives include the various anionic, nonionic and cationic surface active agents such as the alkyl sulfates, alkyl aryl sulfonates, polyoxyethylene alcohols and alkyl phenols and their phosphate and sulfate esters, fatty acids, fatty amines and amine oxides, fatty mono- and di-alkanolamides, quaternary ammonium compounds. Also includible are the alkaline builder salts such as trisodium phosphate, sodium tripolyphosphate, tetrapotassium pyrophosphate and buffering agents such as sodium carbonate, sodium bicarbonate, sodium sulfate, sodium metasilicate and the like, as well as special purpose additives such as dyes, bleaches, optical brighteners and antiredeposition agents.

The invention is further illustrated by the following examples which are not to be considered as limitative of its scope. All percentages reported are by weight.

EXAMPLE 1

A phosphate ester is prepared by reacting 3 mols of the 14 mol ethylene oxide adduct of dinonyl phenol with 1 mol of P_2O_5 (phosphorous pentoxide). The reaction is carried out under anhydrous conditions and at a temperature between about 50° C. and 95° C. and with slow addition of P_2O_5 so that the reaction temperature does not exceed 95° C. After all the P_2O_5 is added the mixture is held at reaction temperature for an additional half hour and an unreacted P_2O_5 is removed by filtration. The products so produced is an approximately equimolar mixture of mono- and diester. This phosphate ester is neutralized with a stoichiometric quantity of an imidazoline of the formula



where R is the aliphatic radical of oleic acid. The viscosity properties of various solutions of this imidazoline phosphate are listed below:

STORMER VISCOSITY (23° C.)

	Kinetic units
Water	30
150 SUS paraffin oil	53
1% (in water) imidazoline salt	36
5% (in water) imidazoline salt	53
10% (in water) imidazoline salt	112

EXAMPLE 2

The viscosity stability of aqueous solutions of the imidazoline salt of Example 1 was measured with a Raytheon Sonic Oscillator. The viscosity before and after 56.6 minutes of shear simulated by the Sonic Oscillator are listed below:

	5% aqueous solution	10% aqueous solution
Initial viscosity, SUS	48.2	281.5
Final viscosity, SUS	55.9	300.0
Percent change	+16	+6.5

EXAMPLE 3

Aqueous solutions of the imidazoline salt of Example 1 were subjected to the Falex Load Test Method to demonstrate lubricity and load carrying characteristics. Briefly, the test employs a Faville Le Vally lubricant tester equipped with an automatic loading device, load gauge, torque indicating gauge, brass shear pins, steel journals and steel V bearing blocks. The lubricant is placed in the machine and torque readings are taken at 350 lb. increments until failure occurs or the maximum load of 4500 lbs. is reached. Failure is indicated either by sudden shearing of the brass locking pins or wear occurring at such a rate that the loading ratchet is not able to maintain the load and the load actually decreases. The results are summarized in the following table. Data for 150 SUS paraffin oil was included for purposes of comparison.

FALEX WEAR TEST DATA

Composition:	Extreme pressure load failure at—
0.25% imidazoline salt	3000 lbs.
10% imidazoline salt	4250 lbs.
150 SUS paraffin oil	500 lbs.

Conditions:
Temperature, 150° F.
Time, 2 mins. each at 250, 500 and 750 lbs. and 15 mins. at 1000 lbs.

EXAMPLE 4

Four ball wear data for the listed concentrations of aqueous solutions of the imidazoline salt described in Example 1 are listed below. The values are well within the 0.8 mm. maximum wear scar specified by the Bureau of Mines for fire resistant hydraulic fluids.

FOUR BALL WEAR DATA

Composition:	Wear scar diameter (mm.)
5% imidazoline salt	0.64
10% imidazoline salt	0.14

Conditions:
Speed: 600 r.p.m.
Time: 60 minutes.
Temperature: 167° F.
Load: 40 kg.
Steel balls: 52/100.

EXAMPLE 5

A phosphoric acid mono-ester of a 12 mol ethylene oxide adduct of nonylphenol is neutralized with a stoichiometric quantity of imidazoline prepared by reacting 1 mol of lauric acid with 1.1 mols of aminoethylethanolamine.

EXAMPLE 6

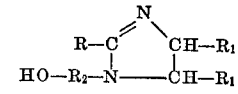
A phosphoric acid diester of a 10 mol ethylene oxide adduct of dodecyl alcohol is neutralized with a stiochiometric quantity of an imidazoline prepared by reacting 1 mol of tall oil fatty acids with 1.15 mols of aminoethylethanolamine.

EXAMPLE 7

A phosphoric acid ester (mixture of approximately equimolar quantities of mono- and diester of a 15 mol ethylene oxide adduct of Oxo-hexadecyl alcohol) is neutralized with a stoichiometric quantity of an imidazoline prepared by reacting 1 mol of oleic acid with 1.5 mols of aminoethylethanolamine. An aqueous solution containing about 10% by weight of this novel imidazoline salt is prepared and exhibits excellent lubricity and viscosity stability properties and is particularly suitable for use as a noninflammable hydraulic fluid.

What is claimed is:

1. A water-soluble salt of (a) an imidazoline having the formula



in which R represents alkyl or alkenyl having from 8 to 22 carbon atoms, R_1 represents hydrogen and lower alkyl having from 1 to 6 carbon atoms, and R_2 is a member of the group consisting of alkylene having from 1 to 8 carbon atoms and lower alkyl substituents thereof, said lower alkyl having from 1 to 6 carbon atoms, and a radical of the structure

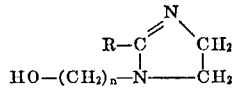
$$—CHR_1—CHR_1(NH—CHR_1—CHR_1)_x$$

wherein x is an integer from 1 to 5, with (b) a phosphoric acid ester of a member of the group consisting of monoesters, diesters and mixtures of monoesters and diesters of ethylene oxide adducts of (i) monohydric alkanols having from 8 to 18 carbon atoms and (ii) mono- and dialkyl monohydric phenols in which the alkyl radical or radicals have from 4 to 18 carbon atoms, said ethylene oxide adducts containing from about 2 to 40 mols of ethylene oxide per mol of alkanol or alkyl phenol, said imidazoline being present in an amount to substantially neutralized the free acid groups in said phosphoric acid ester.

2. A water-soluble salt according to claim **1**, said imidazoline being the condensation product of a fatty acid having from 8 to 22 carbon atoms with a hydroxy lower

alkyl lower alkylene polyamine of the group consisting of aminoethylethanolamine, hydroxyethyl diethylene triamine, hydroxyethyl triethylene tetraamine and hydroxypropyl propylene diamine.

3. A water-soluble salt in accordance with claim 1 wherein the imidazoline corresponds to the formula

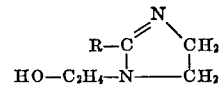


wherein R represents an alkyl or alkenyl having from 8 to 22 carbon atoms and *n* is an integer from 1 to 5.

4. A water-soluble salt according to claim 3 wherein R has from 12 to 18 carbon atoms and *n* is 2.

5. A water-soluble salt according to claim 4 wherein said phosphoric acid ester is that of a member of the group of ethoxylated mono- and dialkyl monohydric phenols in which the alkyl radical or radicals have from 8 to 12 carbon atoms, and in which said ethoxylated alkylphenol contains from 10 to 18 mols of ethylene oxide per mol of alkylphenol.

6. A water-soluble salt of an imidazoline of the formula:



wherein R is the aliphatic radical of oleic acid, with the phosphoric acid ester of ethoxylated dinonyl phenol, said ethoxylated dinonyl phenol containing 10 to 18 mols of ethylene oxide per mol of dinonyl phenol.

References Cited

UNITED STATES PATENTS

Re. 23,227	5/1950	Blair et al.	260—309.6
3,422,166	1/1969	Davis	260—924
3,484,505	12/1969	Cyba	260—925
3,711,403	1/1973	Redmore	260—309.6

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U.S. Cl. X.R.

252—32.5; 260—584 R, 950, 951