

UNITED STATES PATENT OFFICE

2,387,537

FATTY AMINE SALTS OF ALKYL
PHOSPHORIC ACIDS

Herschel G. Smith, Wallingford, and Troy L. Cantrell, Lansdowne, Pa., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

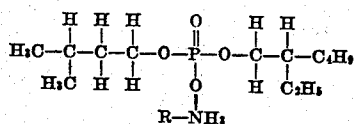
No Drawing. Application March 19, 1945,
Serial No. 583,650

9 Claims. (Cl. 260-461)

This invention relates to fatty amine salts of alkyl phosphoric acids and it comprises oil-soluble, substantially neutral addition products of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and a primary fatty amine containing from 8 to 18 carbon atoms, said neutral addition products being useful as rust preventive compounds or rust inhibitors; and it further comprises methods of making said neutral addition products wherein the said acid phosphate and primary fatty amines are chemically combined together in approximately equimolecular ratios to produce substantially neutral addition products having a pH between 5.5 and 7.5, said addition products or amine salts being readily soluble in and miscible with hydrocarbons such as volatile hydrocarbon solvents, mineral oils, waxes and the like; all as more fully hereinafter described and claimed.

This application is a continuation-in-part of our prior copending application Serial No. 420,438, filed November 25, 1941, which became U. S. Patent No. 2,371,851 on March 20, 1945. In that application, we have described and claimed improved anti-rust petroleum lubricants and mineral oil compositions containing minor amounts of the substantially neutral addition products of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate and primary fatty amines containing 8 to 18 carbon atoms, as a rust inhibitor or rust preventive compound. The present application is directed to such rust inhibitors or rust preventive compounds, per se.

That is, the present invention relates to new oil-soluble, substantially neutral primary fatty amine salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid. Generically, these fatty amine salts may be represented by the following formula:



wherein R represents an alkyl group containing from 8 to 18 carbon atoms. As shown by the above generic formula, these fatty amine salts are addition products of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate di-ester and primary fatty amines containing from 8 to 18 carbon atoms.

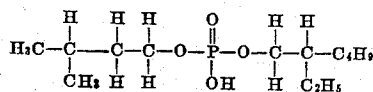
As a class, these fatty amine salts are relatively non-volatile, even at elevated temperatures. Most of them are oily, viscous liquids at room temperatures. Others are soft, waxy solids

which melt to oily liquids at slightly elevated temperatures. All of them are insoluble in water and aqueous liquids, and are resistant to hydrolysis. Indeed, these oily and waxy amine salts are quite water-repellent. Also, they are relatively stable compounds. For instance, they can be heated to elevated temperatures as stated ante, and this is frequently done in incorporating them in waxes, petrolatums, and mineral oils. However, if heated to excessive temperatures, say 260° F. or above, for long periods, they become converted into corresponding amide compounds, water being split off at such higher temperatures.

Further, our new fatty amine salts are readily soluble in oils, both mineral oils and fatty oils. Of course, their solubility varies somewhat with the particular oil and amine salt, but is quite high in general. Further, in addition to being readily soluble in mineral oils, they are readily miscible with other hydrocarbons, such as petrolatums, waxes and volatile hydrocarbon liquids, and coating compositions containing the same; they being readily soluble in hydrocarbon liquids, particularly volatile hydrocarbon solvents. When incorporated in hydrocarbons, such as mineral oils and the like, they impart marked anti-rust qualities thereto, as shown in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851. In other words, as described and illustrated in that application, our new primary fatty amine salts are excellent rust preventive compounds or rust inhibitors.

Further, as described in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851, our rust inhibitors or neutral addition products can be readily prepared by reacting 3-methyl-butyl, 2-ethyl-hexyl acid phosphate with the primary fatty amine in approximately equimolecular ratios; the reaction being so controlled as to produce substantially neutral addition products having a pH value within the range of 5.5 to 7.5 (as measured with a quinhydrone-calomel electrode assembly).

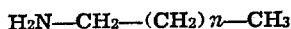
The above acid phosphate ester is a di-ester of ortho phosphoric acid and has the following formula:



This compound is also known as 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid.

The primary fatty amines employed to react

with the acid phosphate ester may be represented by the following generic formula:



wherein n is a number between 8 and 16. This generic class includes the following members:

Mono-capryl amine, $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{NH}_2$
 Mono-lauryl amine, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{NH}_2$
 Mono-myristyl amine, $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{NH}_2$
 Mono-palmityl amine, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{NH}_2$
 Mono-stearyl amine, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{NH}_2$

We may prepare our rust inhibitors by reacting the acid phosphate ester with some particular one of these amines, but more usually mixtures of amines of this group are employed, as they afford a somewhat better product than if only one amine is used. One commercially available mixture which we ordinarily employ is so-called "coco amine," made in known ways by conversion of coconut oil fatty acids into the corresponding amines. Coco amine contains a major amount of mon-lauryl amine (the C_{12} amine) with minor amounts of its adjacent homologues. The commercial "coco amine" has an average molecular weight of 210, and this value is taken as a commercial weight in reacting this commercial amine with the said acid phosphate ester.

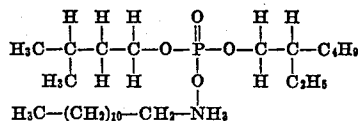
Generically, these primary fatty amines readily react with 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid; the reaction being quite exothermic, as shown in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851. As there stated, in making our rust inhibitors from these reagents, the reaction temperature is carefully controlled. Usually, the reaction temperature is held between 140° and 200° F.; the reaction mixture being externally cooled if necessary.

The following examples illustrate certain advantageous embodiments of this invention:

Example I.—Into a suitable vessel, equipped with means for heating, cooling and agitating the charge, there were charged 281 pounds of 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid, and then 185 pounds of dodecyl amine were gradually added; the said amine being added at such a rate as to maintain the temperature of the reaction mixture below 180° F. and thus avoid splitting out water from the addition product so obtained. After the exothermic reaction had subsided, a further 18 pounds of dodecyl amine were added and the reaction mixture stirred until the reaction was completed.

The amine salt or addition product so obtained was an oily, viscous liquid at room temperature. It had a light amber red color and a pleasant odor. It was readily soluble in liquid hydrocarbons such as mineral oils, volatile hydrocarbon solvents and the like. Also, it was readily miscible with petrolatum, waxes and like hydrocarbons.

This dodecyl amine salt is an addition product having the following formula:



That is, the above compound is an addition salt of mono-lauryl amine and 3-methyl-butyl, 2-ethyl-hexyl acid phosphate di-ester.

In the above example, in lieu of mono-lauryl

amine (primary dodecyl amine), other primary fatty amines may be employed to form similar oil-soluble neutral amine salts. For instance, mono-capryl amine, mono-stearyl amine, and the other primary fatty amines mentioned ante may be employed. As shown in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851, all of these amine salts or addition products are excellent rust inhibitors.

Further, in the practice of this invention, mixtures of such primary amines may be employed in forming our rust inhibitors. Indeed, sometimes commercial mixtures of these primary fatty amines are reacted with the said acid phosphate di-esters to produce mixtures of these amine salts or rust inhibitors, they being advantageous for the present purposes. The preparation of one such advantageous rust inhibitor or rust preventive compound is illustrated in the following example.

Example II.—Into a suitable vessel, equipped with heating and cooling coils and means for mechanical agitation, are added 210 pounds of coco amine, and 281 pounds of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate are slowly added so as to keep the temperature of the reaction below 180° F., whereby to avoid splitting out of of water from the addition product so formed. After the addition of the acid phosphate, a further 20 pounds of coco amine were added and the mixture stirred until the reaction was completed; about one hour being required. The addition products so obtained were substantially neutral amine salts; the pH value thereof being approximately 7.2.

Further, the product obtained in Example II was an oily, viscous liquid at room temperature. It had a light amber red color and a pleasant odor. It was readily soluble in mineral oils and light hydrocarbons, but practically insoluble in water.

As the addition products obtained in the foregoing examples are substantially insoluble in water, the following procedure was used in measuring the pH of these amine salts and oils containing them. A sample thereof was dissolved in normal butanol containing a small amount of water and adjusted exactly to pH 7.0; the butanol dissolved the water-insoluble amine salt and served as a blending agent for the water, but not appreciably altering the pH value thereof. Then, the pH of the sample was measured by electrometric or colorimetric procedures; the results obtained by either procedure being within the experimental error of such procedures. That is, the pH is measured as described in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851.

Further, as described in the application, the rust inhibitors so prepared may be incorporated in mineral oils to impart marked anti-rust qualities thereto; usually from 0.1 to 25% by weight on the oil being employed. That is, our rust inhibitors are readily soluble in mineral oils. In fact, they may be formed in situ in the mineral oil, as described in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851; both the amine and acid phosphate di-ester being themselves readily soluble in the oils. Thus, in the practice of the present invention, mineral oils may be employed in Examples I and II ante as a solvent and diluent. Likewise, other hydrocarbons may be also employed as a diluent in such methods, advantageously a volatile hydrocarbon solvent, such

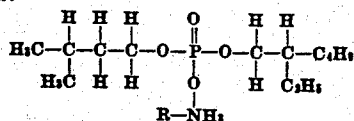
as solvent naphtha, Stoddard solvent, and the like. The solutions in volatile solvent so obtained are useful in forming protective coatings on metals; the evaporation of the solvent coating the metal with a water-resistant film of these rust inhibitors. In this way, metals can be effectively protected against rust and corrosion even when subjected to drastic conditions.

Likewise, our new amine salts or rust inhibitors are also soluble in other hydrocarbons, such as waxes, petrolatum, and the like. Thus, they can be readily incorporated in various coating compositions such as heavy mineral oils, greases, petrolatum, petrolatum jellies, and waxes, as stated in our prior application Serial No. 420,438, now U. S. Patent No. 2,371,851; they being soluble in and compatible with such compositions. When incorporated therein, even in small amounts, they impart marked anti-rust qualities to such compositions.

Thus, a wide range of improved protective coating compositions may be prepared with the aid of our new rust inhibitors. Further, as stated ante, they are useful, per se, as rust preventive compounds.

What we claim is:

1. As new compositions of matter, useful as rust preventive compounds and for other purposes, the oil-soluble addition salts having the following formula:



wherein R represents an alkyl group containing 8 to 18 carbon atoms, said amine salt being a substantially neutral compound soluble in mineral oils and miscible with hydrocarbons.

2. The composition of claim 1 wherein said addition salt is the primary dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.

3. The composition of claim 1 wherein said addition salt is the cocoamine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.

4. As new compositions of matter, the oil-soluble addition salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid and primary fatty amines containing 8 to 18 carbon atoms, said amine salts being substantially neutral compounds soluble in mineral oils and miscible with hydrocarbons.

5. As an improvement in the manufacture of oil-soluble rust preventive compounds, the improved process which comprises reacting 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid and a primary fatty amine containing 8 to 18 carbon atoms, in substantially equimolecular proportions, while maintaining the reaction temperature below 200° F., to produce substantially neutral addition products thereof.

6. The process of claim 5 wherein the reaction is effected at temperature between 140° and 200° F.

7. The process of claim 5 wherein the said reaction is effected in the presence of a liquid hydrocarbon solvent, said solvent serving as a diluent to facilitate control of the reaction and the reaction temperature.

8. As an improvement in the manufacture of oil-soluble, rust preventive compounds, the improved process which comprises reacting a primary fatty amine containing 8 to 18 carbon atoms with 3-methyl-butyl, 2-ethyl-hexyl acid phosphate at temperatures between 140 and 200° F., the said amine and acid phosphate ester being reacted and combined in substantially equimolecular proportions to form substantially neutral addition products thereof.

9. The process of claim 8 wherein said reaction is effected in the presence of a volatile liquid hydrocarbon solvent.

HERSCHEL G. SMITH.
TROY L. CANTRELL.