

UNITED STATES PATENT OFFICE

2,383,502

ACID TRIPHOSPHATES AS BUILDERS FOR
ALKYL SULPHATES AND OTHER SOAPLESS
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Ohio, a corporation of OhioNo Drawing. Application February 6, 1941,
Serial No. 377,714

10 Claims. (Cl. 252—138)

This invention relates to builders for detergents and especially for those synthetic anionic surface active compounds which are suitable as washing agents in aqueous solution and which consist of balanced water-soluble and oil-soluble groups in chemical combination. These builders consist essentially of certain acid salts of triphosphoric acid, $H_5P_3O_{10}$.

In the present specification the term "builder" is employed to mean a substance used with or in a detergent to aid in cleansing. Also, the term "anionic" as applied to synthetic detergents is intended to designate that class of synthetic detergents which ionize in water to give negatively charged particles or anions containing the fat soluble group and any unqualified reference in the specification and claims to "synthetic detergents" is to be considered as being limited thereto.

It is an object of this invention to improve the sudsing and detergent properties of the above described synthetic detergents.

A further object is to provide a compound which will improve the sudsing and detergent properties of the above described synthetic detergents.

Other objects will be apparent from the following description.

Compositions have already been provided for improving the sudsing and detergent action of ordinary soap. These compositions owe their effectiveness partly to their ability to combine with the constituents present in natural hard water to form precipitates with them or to form substantially non-dissociated complex ions, thus avoiding the loss of a certain amount of soap which would otherwise be consumed in precipitating these constituents. It should be borne in mind that in general ordinary soap will not produce a noticeable lather or exert useful detergent effects in hard water until the hardness or soap precipitating constituents have first been rendered inactive. In this respect the detergents for which the builders of the present invention have been provided are different from soap since in all cases these detergents are inherently resistant toward the ingredients imparting hardness to the water.

I have found that certain water-soluble acid salts of triphosphoric acid, $H_5P_3O_{10}$, are particularly adapted as builders for synthetic detergents of the class above described.

Normal water-soluble salts of triphosphoric acid such as the sodium salt, $Na_5P_3O_{10}$, have been suggested for use in combination with detergents, but as far as I am aware no one has proposed the use of the acid salts of triphosphoric acid and it has not been known that these acid salts are definitely superior to other salts of triphosphoric acid such as the normal salts in aiding

the cleansing power of anionic synthetic detergents which possess stability in neutral and dilute acid solution. By so transforming the normal triphosphate to an acid compound, it becomes no longer suitable as a builder for soap because it is too acid and will result in the formation of undesirable acid soap when used therewith. I am not aware of the exact reason for this surprising action of the acid triphosphates toward anionic synthetic detergents but I am certain that the action is not due to the acid condition of the compound because other phosphates in acid condition do not possess the advantageous properties of the acid triphosphates. For example, it has been suggested to employ acid pyrophosphates as builders for soap. These compounds are not builders for synthetic detergents herein concerned even when made as acid as the triphosphates of the present invention.

According to the present invention any water-soluble acid triphosphate salt having a general average formula of $M_xH_{5-x}P_3O_{10}$ wherein M is an alkali metal and x is any value between 5 and 3 is suitable for use and will exhibit a building action superior to the normal completely neutralized salt. Thus the salts coming within the scope of my invention are those salts having compositions between but not including that of the completely neutralized normal salt $M_5P_3O_{10}$ and the acid salt $M_3H_2P_3O_{10}$ wherein M represents an alkali metal.

In the following description of my invention I shall refer to sodium acid triphosphates as illustrative of compounds coming within the scope of the present invention. However, it is to be understood that other alkali metal salts, such as the potassium salt, may be substituted therefor. In fact any water-soluble acid triphosphates, such as any ammonium acid triphosphate, having the characteristics of the alkali metal acid triphosphates may be employed in the practice of my invention, and in the specification and claims reference to "alkali metal" salts is intended to include such water-soluble acid triphosphates.

In the preparation of the detergent builders of the present invention, I find it convenient to treat a completely neutralized salt such as $Na_5P_3O_{10}$ with suitable small quantities of an acid substance such as sulphuric acid, hydrochloric acid, phosphoric acid, acetic acid, etc., as well as acid salts such as sodium acid sulphate, sodium dihydrogen phosphate and disodium dihydrogen pyrophosphate and similar acid reacting materials. Even organic substituted oxy acids of phosphorus and sulphur such as unneutralized alkyl sulphuric acid may be employed to obtain the desired acidity. Thus the unneutralized detergents herein contemplated may be employed as the acid substance.

The amount of acid material added is preferably controlled by pH measurement made on a dilute aqueous solution containing for example from 0.1% to 1.0%, of the salt. For example, a 0.5 per cent solution of $\text{Na}_3\text{P}_3\text{O}_{10}$ at 25 to 35° C. will have a pH value of 9½ to 10. By adding to this salt an equimolar amount of $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$, a salt mixture having the average formula



will result. The pH value of a 0.5 per cent solution of this salt will be about 7.

In accordance with the present invention improvement in builder efficiency will be noted as the pH value of the salt solution is reduced, becoming quite marked by the time the pH value reaches 7. Further reduction in pH value will result in further marked improvement in builder efficiency, and salts having pH values as low as 5 will be outstanding in this respect. While further reduction in the pH value even to 4 does not result in an adverse effect, I prefer to use triphosphate salts which have pH values not substantially lower than 5 because at the lower pH values the triphosphate salts lack the desired degree of stability; they lack desirable buffering power and certain of the synthetic detergents herein contemplated also lack stability under such highly acid conditions. Accordingly the optimum range of pH value for the builders of the present invention is from about 5 to about 7 as measured in dilute (e. g. 0.5 per cent) aqueous solution at 25 to 35° C., but of course slightly higher pH values under 9.5 may be employed to advantage. The acidity factor will not be changed appreciably by the alkali metal portion of a molecule and consequently alkali metal salts other than the sodium salt may be employed as above stated.

The following example will illustrate the nature of my invention, it being understood that the limitations and conditions expressed therein are given by way of illustration only and are not to be considered as defining the scope of the invention in any way.

My invention may be practiced as follows. One part of normal sodium triphosphate is combined with 1 part of trisodium dihydrogen triphosphate to give a mixture which in 0.5% aqueous solution will have a pH value of about 7. To 3 parts of the mixture of acid triphosphate is added sufficient commercial sodium alkyl sulfate (45% active ingredient) prepared from the higher alcohols obtained by the hydrogenation of coconut oil so that the resulting composition possesses triphosphate and active alkyl sulphate in the ratio of 3:7. This mixture may then be employed as a detergent in washing operations with highly satisfactory results, superior to those obtained by the use of the sodium alkyl sulphate alone.

Instead of using the trisodium dihydrogen triphosphate to effect acidification, sulphuric acid or other acid substance as above described may be employed.

Comparative detergency tests under controlled standardized conditions in hard water containing salts chemically equivalent to 21 grains CaCO_3 per U. S. gallon have shown that a mixture of 7 parts sodium alkyl sulphate from coconut oil alcohols (active ingredient basis) with 3 parts triphosphate acidified with sulphuric acid so as to have a pH value of about 7 in 0.5% solution as builder is superior in detergent power to the sodium alkyl sulphate alone, the sodium alkyl sulphate acidified to a pH value of about 7, or to a mixture of unacidified normal sodium triphos-

phate and the sodium alkyl sulphate in the ratio of 3:7 (active ingredient basis).

For example, a series of such controlled tests have shown that a 0.1 per cent aqueous solution (active ingredient basis) of the detergent containing the acidified builder of the present invention will wash to the same degree of whiteness as a 0.4 per cent aqueous solution (active ingredient basis) of the alkyl sulphate alone or mixed with unacidified triphosphate in the same ratio, and to a higher degree of whiteness than a 0.4 per cent aqueous solution of alkyl sulphate (active ingredient basis) acidified to a pH of about 7. Also when the detergent of the present invention was tested at 0.4 percent (active ingredient basis) concentration superior washing powder over the other detergent mixtures was observed.

I have illustrated the superior washing power of a mixture of acid triphosphate and synthetic detergent in the ratio of 3:7, but other ratios of course may be employed. For example, benefit will result if the ratio of acid triphosphate to synthetic detergent is in the range from 1:20 to 3:2. However, the advantage is especially outstanding when the ratio is in the range from 1:5 to 1:1, all ratios, of course, being expressed on an active ingredient basis.

Instead of the sodium alkyl sulphate detergent used in the above example water-soluble salts of other alkyl sulphuric acids suitable for use in washing operations and having eight to eighteen carbon atoms in the alkyl radical may be built with the acid triphosphates of the present invention with surprising beneficial results. Especially are my builders useful in assisting the cleansing action of water-soluble salts of those alkyl sulphuric acids having ten to fourteen carbon atoms in the alkyl radical and with these detergents the builder action is particularly outstanding. Thus the alkyl sulphates derived from the higher alcohols obtained from oils of the coconut oil type, of which coconut oil and palm kernel oil are typical examples, are markedly improved in their cleansing action by the addition of the acid triphosphates. These alkyl sulphates of course consist predominantly of lauryl and myristyl sulphates.

In addition to the alkyl sulphate detergents other sulphonated or sulphated anionic synthetic surface active compounds which are referred to generically herein and in the claims as "sulphonation products" and which are suitable as washing agents in aqueous solution are improved by the addition of acid triphosphates of this invention. For example, beneficial results will be noted when the builders are employed with detergents of the Igepon type such as the water-soluble salts of the higher fatty acid monoesters of lower molecular weight hydroxy alkyl sulphonic acids (oleic acid ester of the sodium salt of isethionic acid and lauric acid ester of 1,2 dihydroxy propane 3 sodium sulphonate) and of the higher fatty acid amides of methyl taurine (ammonium salt of oleic acid amide of methyl taurine). Likewise the use of my builders with water-soluble salts of the sulphated higher fatty acid monoglycerides (sodium salt of coconut oil monoglyceride sulphuric acid) the higher alcohol esters of sulphocarboxylic acids (sodium salt of lauryl sulphoacetic acid) and higher alkylated benzene sulphonic acids (potassium salt of kerosene benzene sulphonic acid) will be advantageous.

The invention, however, is not limited to the use of my builders with the above specific types

of anionic detergents. Any type of anionic synthetic surface active compound suitable for use as a washing agent may be employed without departing from the spirit of this invention.

My invention is not limited to any particular method of mixing the acid triphosphate salts with the anionic synthetic detergents. They may be incorporated in the detergent in any of the forms in which the detergents are manufactured. The builder may be mechanically mixed in, it may be crutched into the detergent in the form of a slurry, it may be dissolved in a solution of the detergent. While such ready-for-use mixtures may be manufactured and may be preferable for many purposes, it is likewise within the scope of my invention to add my builder to water prior to the adding of the detergent or vice versa, or to add both builder and detergent simultaneously but separately to the water. Specifically my invention resides in the presence in the detergent solution at the time of use of an anionic synthetic detergent and my builder of reduced alkalinity irrespective of the previous history of the builder. It is immaterial to the practice of my invention, furthermore, whether the alkalinity of my builder be reduced prior to or simultaneously with mixing with the detergent, or whether it be reduced prior to or simultaneously with solution in the wash water.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. As a new washing composition of improved washing efficiency, an anion active soapless synthetic surface active organic compound suitable as a washing agent in aqueous solution, in admixture with an alkali metal acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M represents an alkali metal and x has any value between 5 and 3, and having a pH value in dilute aqueous solution less than 9.5 but not less than 5.

2. As a new washing composition of improved washing efficiency, a synthetic detergent agent suitable as a washing agent in aqueous solution and selected from the group consisting of water-soluble salts of higher alkyl sulphuric acids, higher fatty acid esters of low molecular weight hydroxy alkyl sulphonic acids, higher fatty acid amides of methyl taurine, higher fatty acid monoglyceride sulphuric acids, the higher alcohol esters of sulphocarboxylic acids, and higher alkylated benzene sulphonic acids in admixture with an alkali metal acid triphosphate having a pH value less than that of $M_5P_3O_{10}$ but greater than that of $M_3H_2P_3O_{10}$ as measured in dilute aqueous solution wherein M is an alkali metal.

3. As a new washing composition of improved washing efficiency, a water-soluble salt of an alkyl sulphuric acid having eight to eighteen carbon atoms in the alkyl radical and suitable for use as a washing agent in aqueous solution, in admixture with an acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M is an alkali metal and x is any value between 5 and 3, and having a pH value in dilute aqueous solution less than 9.5 but not less than 5.

4. As a new washing composition of improved washing efficiency, a water-soluble salt of alkyl sulphuric acids derived from higher alcohols obtained from coconut oil and suitable for use as a washing agent in aqueous solution, in admixture

with an alkali metal acid triphosphate having a pH value in dilute aqueous solution from about 5 to higher than 7 but less than 9.5.

5. A washing composition of improved washing efficiency comprising essentially a water-soluble salt of an alkyl sulphuric acid derived from a higher alcohol containing from ten to fourteen carbon atoms and sodium acid triphosphate having the general average formula $Na_xH_{5-x}P_3O_{10}$ wherein x has any value between 5 and 3 and wherein the said acid triphosphate has a pH value from about 5 to about 7 in dilute aqueous solution.

6. As a new washing composition of improved washing efficiency, a mixture comprising essentially sodium lauryl sulphate and a sodium acid triphosphate having the general average formula $Na_xH_{5-x}P_3O_{10}$ wherein x is any value between 5 and 3, and having a pH value of about 7 in dilute aqueous solution.

7. As a new washing composition of improved washing efficiency, a water-soluble salt of an alkyl sulphuric acid having eight to eighteen carbon atoms in the alkyl radical and suitable for use as a washing agent in aqueous solution, in admixture with an alkali metal acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M is an alkali metal and x is any value between 5 and 3, and having a pH value in dilute aqueous solution less than 9.5 but not less than 5, said acid triphosphate and said water-soluble salt being in the ratio from 1:20 to 3:2.

8. As a new washing composition of improved washing efficiency, a water-soluble salt of a higher alcohol ester of a sulphocarboxylic acid and suitable for use as a washing agent in aqueous solution, in admixture with an alkali metal acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M is an alkali metal and x has any value between 5 and 3, and having a pH value in dilute aqueous solution less than 9.5 but not less than 5.

9. As a new washing composition of improved washing efficiency, a water-soluble salt of a higher fatty acid amide of methyl taurine and suitable for use as a washing agent in aqueous solution, in admixture with an alkali metal acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M is an alkali metal and x has any value between 5 and 3, and having a pH value in dilute aqueous solution less than 9.5 but not less than 5.

10. As a new washing composition of improved washing efficiency, a mixture of a synthetic detergent agent suitable for use as a washing agent in aqueous solution and selected from the group consisting of water soluble salts of higher alkyl sulphuric acids, higher fatty acid esters of low molecular weight hydroxy alkyl sulphonic acids, higher fatty acid amides of methyl taurine, higher fatty acid monoglyceride sulphuric acids, the higher alcohol esters of sulphocarboxylic acids, and higher alkylated benzene sulphonic acids, and a penta alkali metal triphosphate with a sufficient portion of an acid reacting material to give an alkali metal acid triphosphate having the general average formula $M_xH_{5-x}P_3O_{10}$ wherein M represents an alkali metal and x has any value between 5 and 3 and to reduce the alkalinity of said triphosphate to a pH value less than 9.5 but not less than 5 as measured in dilute aqueous solution.

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