

UNITED STATES PATENT OFFICE

2,651,829

SURFACE ACTIVE MEDIA

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9 Claims. (Cl. 28—72.3)

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Organic derivatives of phosphoric acids have frequently been described in literature. As free acids or as salts they are intended for use as auxiliary media such as foaming, wetting, and emulsifying agents, in the treatment of fibres, and in other cases they are used in conjunction with oils and film-forming substances as anti-rust agents. Particularly esters of phosphoric acids with substances having at least 8 carbon atoms are particularly described for this use. No essential difference is made in this connection between mono- and di-esters. Even tri-esters are included. A distinction is made between the usability of the free acids and that of the salts, insofar as in the treatment of textiles the neutral salts are preferred. No distinction is made between the corresponding derivatives of the different phosphoric acids.

These substances are frequently compared with surface-active sulphonates or soaps, and referred to as substitutes for the same. The limitation of the lipophilic radicals of these compounds therefore adheres strictly to the rules applicable to soaps, wetting, and emulsifying agents. In view of the properties claimed and of the interest of the industry in the products described, the introduction of these substances into practical use might have been expected, but this has not occurred.

The description given in literature of the properties, wherein sulphonates and soaps are indicated as comparable products, leads to the assumption that the statements made schematically accept the experience gained in the development of synthetic washing agents. However, the compounds mentioned in the literature often cannot be produced by the described process. If, on the other hand, the mentioned esters of phosphoric acid are produced in an unequivocal manner, substances are obtained having quite different properties from those described. Thus the alleged esters of orthophosphoric acid described in German patent specification No. 575,660 cannot be obtained in the manner described.

The sulpho acids referred to by way of comparison, irrespective as to whether these are genuine sulpho acids or sulphuric acid esters, are readily soluble in water, attack metals intensely, and form readily soluble alkali metal salts, and in many cases also readily soluble alkaline earth and heavy metal salts. On the other hand, solubility exists in the case of phosphoric acid esters only with the lowest members of the series, whereas for example phosphoric acid-mono-beta-naphthyl ester already dissolves with intense opalescence, and products of still higher molecular weight, for example phosphoric acid-alkylphenyl ester, i. e. one of the compounds having at least 8 carbon atoms also described in the

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aforesaid literature, when diluted with water, is very difficultly soluble and yields difficultly soluble alkali metal salts and practically insoluble alkaline earth metal and heavy metal salts.

The fatty acids or soaps likewise mentioned in literature by way of analogy also act differently from the aforementioned esters of phosphoric acid. In the case of fatty acids, as is well known, water-solubility only prevails with their low members, whereas the members of the series used for the production of soaps become increasingly insoluble in water and are incapable of absorbing water. On the other hand, the phosphoric acid esters in the form of the free acid and also the higher members thereof absorb a considerable amount of water to form jelly-like products, and may be converted into, and kept in, a state of dispersion in suitable manner even without the addition of emulsifiers, which is impossible in the case of fatty acids. The acid phosphoric acid esters can also emulsify oils, which the fatty acids only do in the form of their salts.

Therefore phosphoric acid esters and their salts should not be considered as equivalents of fatty acids and soaps. If in the literature phosphoric acid products are compared with soaps, fatty acids, and sulphonates, it may well be assumed that either the properties of the phosphoric acid esters were not correctly recognised, or that during the investigations phosphoric acid esters were not available and that other products were used to replace the phosphoric acid esters.

It is remarkable that even more recent patent literature, for example British patent specification No. 354,300 and the United States patent specifications No. 2,005,619 and No. 2,026,785 recite this faulty ideology. It is true that it is stated in the United States patent specification No. 2,005,619, line 14 et seq., that the organic derivatives of phosphoric acid hitherto described were restricted with regard to technical usability on account of their low solubility in water; but although this United States patent specification and United States patent specification No. 2,026,785 describe a number of new variations of organic derivatives of phosphoric acids, no new rule is given regarding the use of the products, either in respect of the method of application or as regards the purpose of use.

It has now been found that esters of orthophosphoric acid produced by the reaction of organic hydroxyl compounds with phosphorus oxychloride and a gentle saponification of the resulting chlorine containing intermediate product with water may be used with particular advantage if the hitherto customary methods of operation with sulphuric acid esters and their salts or with fatty acids and their salts are abandoned.

Whereas in the case of sulphuric acid the re-

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placement of a hydrogen atom by an organic radical even weakening the acid character in principle preserves it, the entry of one or two organic radicals into the molecule of the phosphoric acid deprives the latter of the character of a mineral acid. Compounds in which all three atoms of hydrogen of the phosphoric acid have been substituted by organic radicals have again different properties and are usable only to a limited extent for the purposes hereinafter described. The esters of phosphorous acid, hypophosphorous acid, and thiophosphoric acid, act quite differently. Their equalization in literature with the esters of orthophosphoric acid shows that the specific character of the mono- and di-esters of orthophosphoric acid was hitherto not recognised.

An example will illustrate the fundamentally different action of the organic derivatives of orthophosphoric acid in comparison with orthophosphoric acid itself and with sulphuric acid or a free sulpho acid. If powdered iron is introduced into dilute solutions of sulphuric acid or octodecylsulfo acid or orthophosphoric acid, a vigorous development of hydrogen sets in immediately; this, however, does not happen when using mono-octodecyl-phosphoric acid ester or a mono-alkyl (approximately C_{12}) - phenyl - phosphoric acid ester, although their solutions have an acid character. Even when free sulphuric acid or orthophosphoric acid is added to these solutions, the generation of hydrogen takes place only gradually. This shows clearly that the basis for this surprising action is not based only on lower acidity of the phosphoric acid esters, which have pH values of for example 1 to 2, but on the formation of surface layers. Although octodecylsulpho acid can be regarded as a surface-active substance, it cannot exert the surface protecting action of the phosphoric acid. The phosphoric acid esters therefore constitute substances with substantially different properties from those of soaps and sulphonates.

The mono- and di-esters of orthophosphoric acid and their acid salts form in the pH range of 1 to 7 with reactive materials compounds the nature of which cannot yet be properly defined chemically and physically, but they are of great value for use in technical processes. Thus for example wool fibres, skins intended for tanning, dirt-containing albumin, casein, and finally other compounds having a basic reaction, for example basic dyestuffs, and even cellulose absorb only small amounts of the phosphoric acid esters or their salts from a solution, but they then tenaciously retain these amounts. Thus new surface layers with different properties are produced.

According to the invention, mono-esters, di-esters, or mixtures of the two, and also their acid salts may be used. The mono-esters display a more strongly acid character and hence have greater affinity, due to the acid radical, to the material treated than the corresponding di-esters. By varying proportions of mono- and di-ester in the mixture, gradual differences may be attained between the two types. According to the invention, the mono-esters are preferred in aqueous treatment baths on account of their higher acidity.

Since in the case of textile processes, a reaction between the metal parts of the apparatus and the hitherto customary treatment agents frequently has an undesirable influence upon the quality of the products, for instance the influence of dye-

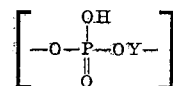
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ing, damage to the fibre by catalytic processes, and so on, the organic derivatives of phosphoric acid to be used according to the invention offer an entirely novel manner of avoiding such damages.

Due to the lower acidity of the organic derivatives of the orthophosphoric acid a decisive advantage results, for example, in the treatment of the skin and hair.

The use of the organic derivatives of orthophosphoric acid and their acid salts, for example with alkalis or organic bases, and if desired with the use of buffer substances, leads to decided improvement in this respect. On the one hand, the derivatives of phosphoric acid adhere sufficiently strongly—the di-esters less strongly than the mono-esters—to achieve a durable hold, but on the other hand their acid character is too weak to effect blocking of functionally important groups of proteins, such as is in the case of sulphonates. With the aid of phosphoric acid as functional group, substances acting in various directions can therefore be supplied, for example radicals having a highly fatty action—for instance when aliphatic compounds of high molecular weight for instance with 8 to 18 carbon atoms or known equivalents are selected—or else radicals having a lean action, for instance aliphatic or aromatic radicals of low molecular weight. By the substitution of these radicals with other physiologically and chemically active groups, such as halogen, OH radicals, CN, urea radical, and the like, any desired effects can be obtained.

The poly-condensed phosphoric acid esters obtainable when using polyhydric alcohols, and in which free hydroxyl groups have still remained on the phosphorus, and also their salts, can also be used according to the invention. Such compounds correspond to the general structural formula:



where Y represents a bifunctional organic hydroxyl compound and x a whole number greater than 2.

The washing capacity of the acid esters of orthophosphoric acid is "as such" rather poor, whereas the free acids are easily adsorbed. This and the fact that they are easily taken up by oils makes them readily emulsifiable and usable as auxiliary washing agents, for example for a pretreatment or for the admixture of small amounts to usual washing agents. In baths containing bleaching agents they prevent the catalytic action of metal residues or of the apparatus, which is particularly important when used together with synthetic washing agents. Their softening action reduces the mineralisation of the washed articles.

In cases in which the phosphoric acid esters, in spite of their insufficient solubility, are used for special reasons, for instance in the acid felt-ing or fulling of cloth, care must be taken to remove them after use by an after-treatment with solvents or washing agents or protective colloids. In other cases the affinity of the phosphoric acid esters is very welcome, if the newly formed layers are to remain on the treated objects. In this case no after-treatment is needed.

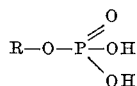
The acid orthophosphoric acid esters may also be used in the pure state, as lumps, powders, jellies, as emulsions, ointments, soaps, solutions

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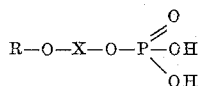
and also with inert carrier substances, for example Vaseline oil. Other components for example fats, waxes, oils, and organic solvents may be used simultaneously. In cases where due to inadequate solubility in water obnoxious precipitations occur, they may be eliminated by the addition of solvents of various types or of agents having a protective colloid action, for example soaps, sulphonates, ethylene oxide products, quaternarily surface-active substances, glue, vegetable mucilages, polyglycerine, urea, and so forth.

Those tertiary esters of the phosphoric acids in which the surface-active radicals have become water-swellable or water-soluble by the incorporation of hydrotropic groups in the molecule may also be mixed with mono- and/or di-esters of ortho-phosphoric acid. Such compounds exert an intense surface-active action and are therefore particularly suitable for being mixed with mono- and di-esters, alone or mixed with one another or with other auxiliary substances.

In carrying out the invention, use may be made of the following derivatives of the acids of phosphorus, for example, ortho-, pyro-, meta-, or polyphosphoric acids, with mono- or polyvalent hydroxyl compounds of a surface-active character, which carry for example saturated or unsaturated aliphatic radicals with a chain length of 6 and more atoms of carbon, aromatic, aliphatic-aromatic, alicyclic, or heterocyclic radicals. These radicals may be bound to the phosphoric acid direct or through other polyvalent hydroxyl compounds, for example sorbite, erythrite or glycerine, glycol, amino-alcohols, and their poly-ethers or mixed ethers, for example, oxyethylation products of the aforesaid polyhydric alcohols. These compounds correspond to the general structural formula:

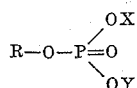


and



where R represents a lipophile radical, for example an aliphatic alcohol with more than 6 atoms of carbon and OX a hydrophile radical, for example a bi- or poly-functional alcohol or etherification products thereof. The surface-active radicals may also be bound like esters or amides to the aforesaid hydroxyl compounds in the form of the corresponding carboxylic acids. Substituents, for example amino groups, halogen, and the like, can also be incorporated in the surface-active radicals.

Depending on the basicity of the phosphoric acids (ortho-, pyro-, meta-, poly-phosphoric acids), one or more surface-active radicals may be incorporated in the phosphoric acid, while identical or different ester components may be used. Together with and instead of the surface-active radicals, as described above, radicals of a pronounced hydrophilic character, for example glycol, glycerine, polyglycol, sorbite, and the like, may be used as ester components. Mixed esters of this kind have the general structure:



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where R represents a lipophile radical and Y and X either lipophile or hydrophile mono- or polyvalent radicals. In compounds of this type which contain still nonesterified hydroxyl groups, these may be further esterified as desired.

The introduction of such polyvalent hydroxyl compounds into the molecule also permits multiple esterifications with the phosphoric acids.

Tertiary esters can be made increasingly water soluble by the increasing incorporation of hydrotropic radicals, for example those with accumulated OH groups, or with accumulated ether bonds, both as bridge links and as independent ester components. Such compounds have considerable emulsifying power. Esterification with more than one phosphoric acid radical in the molecule acts in the same sense when using polyhydric alcohols.

The invention will be illustrated by the following examples:

Example I

Raw wool, washed in a neutral or alkaline bath, is given as final treatment, a dip in an aqueous suspension of a mono-dodecylphenyl phosphoric acid ester, of which preferably 10 to 30 grams are added per litre. Oils and fats can be incorporated in the after-treatment solution in the usual way. Various advantages are obtained at the same time: the acid reaction of the phosphoric acid ester neutralises any alkali residues which may still be present and will be harmful to the durability of the wool when dry, and brings the wool within a very favourable pH range. The ester is distributed very uniformly over the fibre and permits perfect combing of the fibres with low waste. At the same time leather and metal parts of the spinning apparatus are protected against decomposition or rusting, which is not the case with synthetic emulsifiers on a sulphonate or ethylene oxide basis.

Example II

Wool dyed with indigo is known to bleach out very rapidly when exposed to light in the presence of iron-containing olein. This process can be considerably retarded if 2% of a phosphoric acid monoalkylphenyl ester is added to the oil.

Example III

Woollen piece goods, which may also contain considerable proportions of vegetable fibres, after preliminary cleaning or in the dirty state, have poured over them in the fulling mill a solution of 6 to 10% concentration of a phosphoric acid monocyclohexyl ester and are fulled in the usual way.

The slipping action produced by the product, in conjunction with the acid reaction, effects good felting of the cloth. The iron parts of the fulling mill, which are otherwise exposed to serious danger with an acid fulling bath, are not attacked, so that secondary effects, for example the action of iron on dyestuffs, do not occur. After the fulling, the material is neutralised and washed with the addition of the usual agents or alkalis. The feel of the material is remarkably soft and far better than when sulphuric acid is used. Surface-active organic sulpho acids cannot be used as they severely attack metal.

Example IV

To 80 parts by weight of spindle oil with a viscosity of 8° Engler are added 20 parts by weight of a mixture consisting of equal parts of a pri-

mary phosphoric acid ester of the eight-fold oxyethylated oleyl alcohol and the ten-fold oxyethylated dibutyl phenol. The mixture is brought into the form of a 5% aqueous emulsion with a pH value between 4 and 7 and used for the spinning of wool or wool containing fibre mixtures.

In consequence of the good lubricating and felting action, which is exerted with an acid reaction, the working times customary in alkaline fulling can be considerably reduced, which means the conservation of the material. The regulation of the degree of acidity can be effected by acetic acid, formic acid, but particularly with phosphoric acid, as desired. After completion of the fulling process, the material treated in this manner is washed clean with the addition of a little ammonia to the washing water.

Example V

50 parts of spindle oil or black oil are worked up with 50 parts of the mixture described in Example IV, to form a homogeneous preparation, and is converted with water into a 25% emulsion or colloidal solution. Rags or other waste material is impregnated therewith, torn up on the opener, and further worked up as in Example IV. It also serves the same purposes of use.

Example VI

Raw cloths have poured over them on the fulling machine an aqueous solution which contains per litre 20 grams of a mixture of the secondary orthophosphoric acid ester with an eight-fold oxyethylated octadecyl alcohol and a tertiary orthophosphoric acid ester of the same alcohol. By adding formic acid the pH value is adjusted to 3. With this solution the cloths are fulling in various ways, while in consequence of the auxiliary media greatly assisting felting the fulling time is considerably shortened. Resistance to tearing and abrasion is far superior to that of cloths fulling in alkaline baths.

Example VII

For the tearing of rags, a solution is used which contains per litre 20 grams of a neutral ester of orthophosphoric acid from 2 mols of oenol etherified with 4 ethylene oxide radicals, and 1 mol of triglycol. In order to increase the wetting action, soaps, alcohol sulphonates, oxyethylated fat derivatives of various composition, aryl or alkaryl sulphonates, fatty acid condensation products, and the like, may be added thereto.

The torn material produced by the addition of such substances can be spun and woven in the usual way, without adding further oil. In order to achieve the prescribed dimensions the material is fulling with a pH value of 3 to 4, which was obtained by the addition of free formic acid and the primary ester acid of orthophosphoric acid with dibutyl cresol to the fulling water, on the fulling machine. The cloths lose little fibrous material and more quickly attain the desired length and width than is possible by fulling in an alkaline bath.

Example VIII

For the purpose of greasing wool use is made of a 5% suspension consisting of the following mixture of substances: 20 grams per litre of a mixture of oleyl amine, which has been made water-soluble with 6 ethylene oxide groups, the acid primary ester of orthophosphoric acid with lorol as neutralising agent, 20 grams of mineral oil in emulsified form, 10 grams of a tertiary poly-

condensate from 3 mols of triglycol and 1 mol of orthophosphoric acid ester. The wool treated in this manner is distinguished by excellent resistance to heat. In particular, its functional economy is very favourable.

What I claim is:

1. In the processing of wool the step of fulling the wool with a surface active phosphoric acid ester in an aqueous medium, said phosphoric acid ester being selected from the group consisting of an ortho-phosphoric acid monoester, an ortho-phosphoric acid di-ester and a mixture of the said esters.

2. In the processing of wool according to claim 1, the use of an aqueous solution of between about 6-10 per cent of a phosphoric acid monocyclo-hexyl ester.

3. In the processing of wool according to claim 1, the use of an aqueous solution containing 25 grams of a phosphoric acid diphenyl ester per liter.

4. In the processing of wool according to claim 1, the use of a mixture consisting of equal parts of a primary phosphoric acid ester of the eight-fold oxyethylated oleyl alcohol and the ten-fold oxyethylated dibutyl phenol.

5. In the processing of wool according to claim 1, the use of the secondary orthophosphoric acid ester with an eight-fold oxyethylated octadecyl alcohol and a tertiary orthophosphoric acid ester of the same alcohol.

6. In the processing of wool according to claim 1, the use of a mixture of the acid primary ester of orthophosphoric acid, lauryl alcohol to act as a neutraliser, 20 grams of an emulsified mineral oil, 10 grams of a tertiary poly-condensate from 3 mols of triglycol and 1 mol of an orthophosphoric acid ester.

7. In the processing of wool the step of fulling the wool with a surface-active phosphoric acid ester in an aqueous medium, said phosphoric ester being selected from the group consisting of an ortho-phosphoric acid monoester, an ortho-phosphoric acid di-ester and a mixture of the said esters and being at least partially neutralised to a pH-value of 1-7.

8. A process according to claim 7, wherein said surface-active phosphoric acid ester is used in mixture with a neutral ortho-phosphoric acid ester having a hydrotropic group incorporated therein.

9. A process according to claim 1 wherein said surface active phosphoric acid ester is used in admixture with neutral ortho-phosphoric acid ester having a hydrotropic group incorporated therein.

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