

UNITED STATES PATENT OFFICE

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PHOSPHORIC ACID ESTERS

Benjamin E. Harris, Chicago, Ill.

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10 Claims. (Cl. 260—99.20)

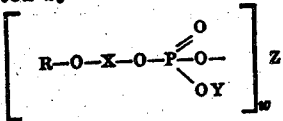
My invention relates to a new class of chemical substances. It relates more in particular to a class of chemical substances having the properties of interface modifiers when employed in a treating bath containing textile, leather or ores. The object of the invention is the provision of a new class of chemical substances.

Another object is the provision of a class of chemical substances adapted for use as interface modifiers.

Still another object is the provision of a treating bath employing the new interface modifiers of my invention.

The substances of my invention have many useful applications in the arts where frothing, wetting, penetrating, detergent, emulsifying, and other interface modifying functions are required. They are in general possessed of at least two groups, one having a hydrophile function and the other having a lipophile function in the molecule. The hydrophile function is performed primarily by a phosphate group; that is, a group containing phosphorus in the form of a phosphorus oxide acid radical, giving the molecule as a whole an affinity for aqueous materials. The lipophile group is any radical such as acyl or alkyl derived from a fatty acid or its corresponding alcohol and has a definite affinity for oils and fats. The hydrophile phosphate group is linked to the lipophile group by means of a polyhydroxy substance of a class consisting of sugars, sugar alcohols, glycols, glycerols, polyglycerols, polyhydroxycarboxylic acids, and polyglycols. In general, an ester linkage joins the polyhydroxy substance and the phosphate group. The linkage between the polyhydroxy substance and the lipophile group may be either an ester or ether linkage.

Many of the compounds of my invention may be represented by the formula



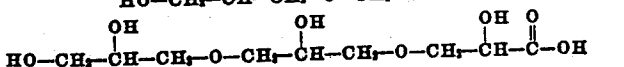
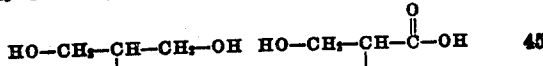
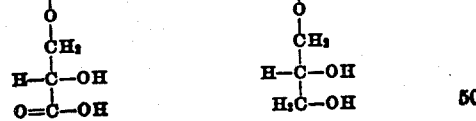
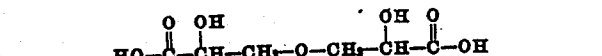
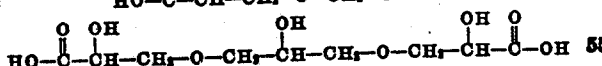
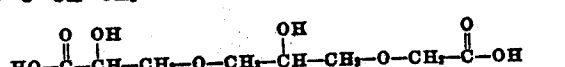
wherein "R" is a lipophile group, "X" is the residue of a polyhydroxy substance, "Y" and "Z" are cations, and "w" is a small whole number.

More specifically, the compounds of my invention may be defined as phosphoric acid esters of polyhydroxy substances wherein at least one hydroxy group of the polyhydroxy substance has its hydrogen substituted by a lipophile group.

Preferably, for use in foods, the compounds are devoid of groupings wherein nitrogen is linked directly to carbon belonging to radicals in esterified form, as, for example, in choline groups, but by this expression I do not mean to exclude compounds with inorganic ammonium nitrogen and compounds of nitrogen linked to carbon belonging to cationic, i. e., salt-forming radicals which are not in esterified form. Whenever the term "non-nitrogenous" is hereinafter employed, it will be understood to have this significance.

The lipophile group may include any fatty acid group having at least four carbon atoms such as the fatty acid radicals of the following acids: caproic acid, capric, caprylic, valeric, butyric, abietic, hydroxystearic, benzoic, benzoylbenzoic, naphthoic, toluic, palmitic acid, stearic, lauric, melissic, oleic, myristic, ricinoleic, linoleic acid or mixed fatty acids derived from animal or vegetable fats and fish oils such as lard, coconut oil, corn oil, cottonseed oil, partially or completely hydrogenated vegetable oils such as cottonseed oil, corn oil, sesame oil and fatty acids of various waxes such as beeswax and carnauba wax; or the lipophile group may be an alkyl radical derived from an alcohol corresponding to any of the preceding acids, such as octanol, cetyl alcohol, lauryl alcohol, etc.

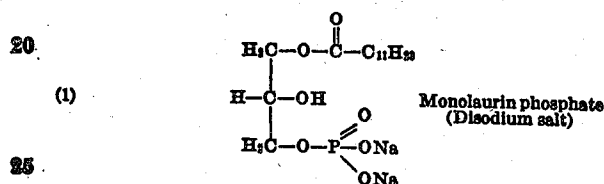
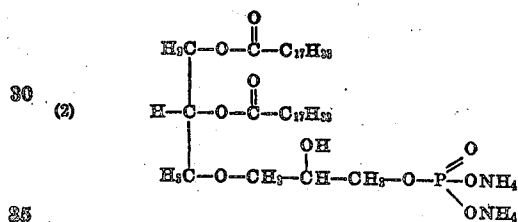
Specific examples of polyhydroxy substances, the residues of which may serve as linkages between the lipophile groups and the hydrophile phosphate groups are as follows: mucic acid, tartaric acid, saccharic acid, gluconic acid, glucuronic acid, gulonic acid, mannonic acid, trihydroxyglutaric acid, glyceric acid, and the like, as well as carboxylic oxidation products of polyglycerols which may be represented by the formulae:



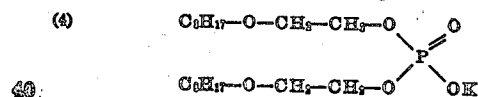
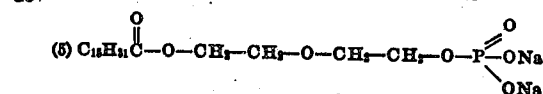
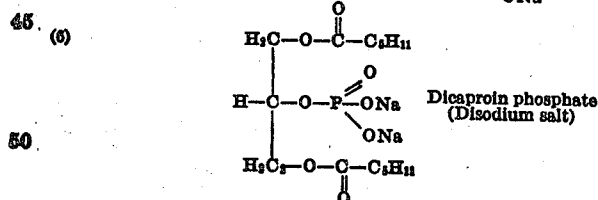
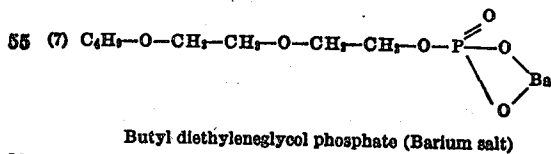
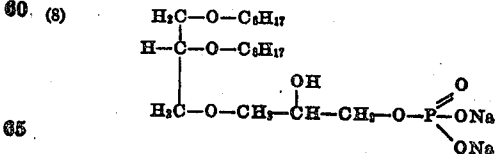
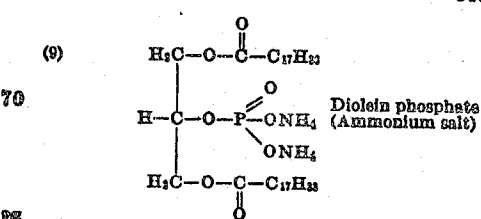
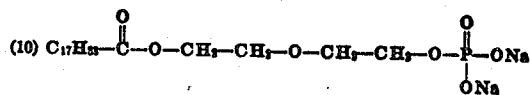
and sugars such as: xylose, galactose, fructose, 60

maltose, sorbitol, glucose, dulcitol, arabitol and other sugar alcohols such as hexahydric alcohols derived from sugars, and other substances having free hydroxy groups. The above polyglycerols and their oxidation products are produced by polymerizing glycerine, preferably by heating with about 1% of alkali at temperatures from 250° C. to 260° C. for about three hours in the presence of an inert gas. This reaction mixture will give a mixture of various polyglycerols, the size of the molecules depending upon the time of polymerization. The mixtures of polyglycerols are then oxidized with mild oxidizing agents to convert at least one of the primary hydroxy groups to a carboxylic group.

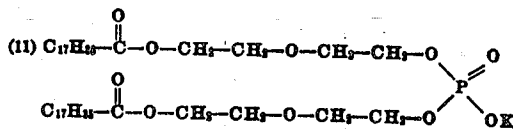
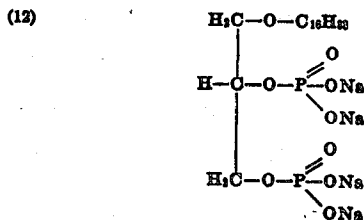
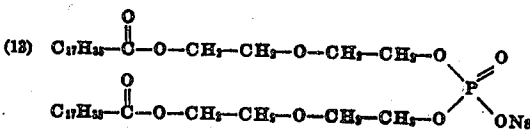
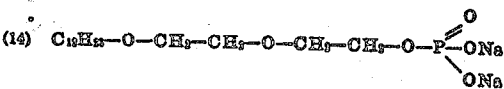
Examples of substances of my invention may be represented as follows:



(3) Cetyl sorbitol phosphate

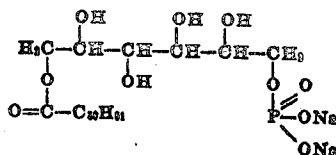
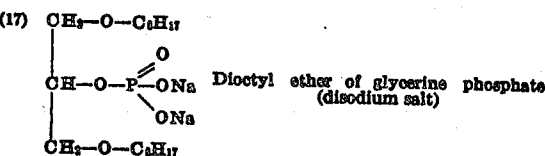
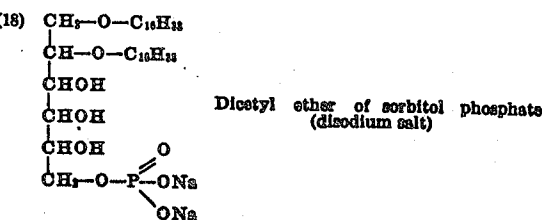
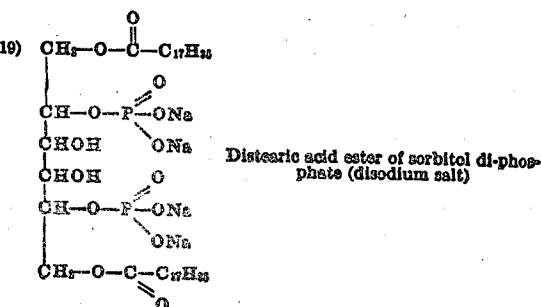


Stearic acid ester of diethylene glycol disodium orthophosphate



(15) Sorbitol stearate monophosphate (ammonium salt)

(16) Sorbitol malic acid monophosphate (sodium salt):



of such a series, the differences may be only very slight, becoming more appreciable the further removed any two selected members of the series are from each other.

- 5 While the illustrative examples listed hereinabove represent principally single substances, it must be understood that the invention is by no means limited to single substances. Indeed, in practice, it is frequently more convenient to prepare a mixture of the substances of my invention and to use such a mixture. For example, I may
10 prepare a mixture of diglycerides by any convenient method, such as described hereinbelow and then introduce into each member of this mixture of diglycerides a phosphate radical by a convenient method.

Example.—Preparation of mixture of diglyceride phosphates from corn oil.

- Heat a mixture of 880 parts of corn oil and 50
20 parts of glycerol in an inert atmosphere with stirring to 220° C. Add 0.88 part of flake caustic soda. Raise the temperature to 250° C., continue stirring and heat at 250° C. or thereabout for two hours. Cool to room temperature in an inert at-
25 mosphere. This product is essentially a mixture of diglycerides.

- To 200 parts of the above product dissolved in 600 parts of isopropyl ether (free of alcohol and water) add 50 parts of phosphorus pentoxide and
30 heat under reflux with stirring for three hours to 60° C., taking care to keep the reaction mixture out of contact with atmospheric moisture.

Now free this reaction production of ether, preferably by distillation.

- 35 The residue is a somewhat sirupy, oily material which may be used as such, or it may be neutralized with gaseous ammonia or aqueous ammonia or other alkaline agents. Also, the product may be washed by salting it out with brine several
40 times, purified, or otherwise treated if desired. It consists in the main of a mixture of diglyceride phosphates, the significant, predominant constituent of which is represented by No. 9 in the list of examples hereinabove.

- 46 In place of corn oil in the above, I can use cottonseed oil, peanut oil, sesame oil, sunflower oil, neat's-foot oil, coconut oils, hydrogenated oils, lard, tallow, etc., cod oil and other common tri-
glycerides.

- 50 If, on the other hand, it is desired to prepare a single substantially pure substance analogous to the above, it is only necessary to treat diolein with phosphorus pentoxide as described above.

- This procedure, for introducing phosphate radicals, described directly above, I have also successfully used in the preparation of materials represented by Nos. 1, 2, 5, 6, 8, 10, 12, 14, 15 and 16
55 in the list of examples shown hereinabove, as well as others. It is, of course, obviously within the skill of any qualified chemist to compute molal or multiples of molal proportions of the reactants with respect to each other.

- It is evident that I may prepare the ethers or the esters of the polyhydroxy substances in any desired or known ways and subsequently esterify
65 one or more of the remaining hydroxy groups of the polyhydroxy substance to introduce therein the phosphoric acid radical or, alternatively, I may first esterify the polyhydroxy substance with
70 a phosphorus containing derivative to form a phosphoric acid ester and I may then esterify or etherify one or more of the remaining hydroxy groups of the polyhydroxy substance by esterifying or etherifying procedures well known in the
75 art.

The polyhydroxy substances which are the linking substances between the lipophile group or groups and the hydrophile phosphate group may be conveniently considered as falling into two groups. The first of these groups includes compounds containing less than four esterifiable hydroxy groups and is exemplified by glycerine, glycol and polyglycols. The second group contains those substances which have more than three esterifiable hydroxy groups, examples of which are the sugars and sugar alcohols, the polyglycerols such as di- and tri-glycerol, etc. It will be understood that my compounds may have one or more lipophile radicals and one or more hydrophile phosphate radicals attached to the polyhydroxy substance. Thus for example, I may have the mono-phosphate of the di-oleic acid ester of sucrose, or the di-phosphate of the di-oleic acid ester of sucrose. Similarly, I may have the di-stearic or other fatty acid ester of di- or tri-glycerol mono- or di-phosphate. In a similar way, as described above, instead of the acyl derivatives of the polyhydroxy substances I produce the corresponding alkyl derivatives.

As I have described above, my compounds may contain either ester or ether linkages. Any known methods of etherifying polyhydroxy substances may be employed. The following examples are illustrative:

Example.—Sodium octylate



is treated with a 25% molal excess of glycerine alpha bromhydrin. The mixture is heated under-reflux with exclusion of moisture and with stirring until the anticipated amount of sodium bromide has formed. The sodium bromide is filtered out of the hot reaction mixture and the product, namely, glycerol alpha octyl ether, is separated from the excess mono bromhydrin by fractional distillation under reduced pressure. The ether is treated with phosphorus pentoxide to form the phosphate ester, by the general procedure described in the examples listed hereinabove.

Example.—Potassium cetylate



is reacted with excess ethylene glycol chlorhydrin by the procedure described in the above example to form the glycol mono octyl ether. This is then treated with P_2O_5 to form a phosphoric acid ester of cetyl glycol ether. This may be neutralized with ammonia or some other alkaline or potentially alkaline material to give salts of the cetyl glycol ether phosphate.

In the neutralization of the phosphate group or groups, considerable latitude and modification may be employed. While the phosphate group may be left unneutralized, I find that, in general, the products are more suited to the purpose for which they are intended if they are treated with a suitable inorganic or organic anti-acid agent. Examples of inorganic and organic anti-acid agents which may be used satisfactorily are bicarbonates of the alkali metals, potassium hydroxide, potassium carbonate, metallic sodium, sodium hydroxide, sodium oxide, sodium carbonate, ammonium hydroxide, ammonia gas, and other anti-acid materials of the alkali earth group, sodium stearate, calcium stearate, aliphatic and aromatic amines, alkylolamines, such as mono-, di- and tri-ethanolamine and mixtures thereof, and also other anti-acid materials in which case the hydrogen of the phosphate group

or groups is replaced by a cation such as sodium, potassium, ammonium, calcium, magnesium, aluminum, zinc, amines, alkylolamines, etc. It will be understood that by the term "cation", as used throughout the specification and claims, is meant such elements as are mentioned herein and, in general, atoms or radicals which are regarded as bearing a positive charge.

The products above described may be added in suitable proportions to a treating bath containing an aqueous medium, with or without an additional substance, such as for example alkalis, mordants, dyes, color discharging reagents, H_2O_2 , color reducing agents, oils, sulphonated oils, mordanting salts, fabrics and other reagents or substances used in treating baths, and the treating bath so formed can be employed with satisfaction in all of the arts in which interface modification is desired. For example, dyeing, bleaching, scouring, leather stuffing, and otherwise treating fabrics, fibers and other materials in a treating bath of this character is productive of good results. Also in the stuffing of leather, dyeing, and otherwise treating furs, and in many other arts, a treating bath employing the materials of my invention may be used. In flotation of ores it may be used in connection with other reagents to modify the interface between the finely divided ore and the aqueous medium.

While I have described several methods for the preparation of the materials of my invention, it must be understood that the scope of the invented class of substances is by no means limited by these methods. Other convenient methods may be used. This also applies, and particularly so, to supplementary procedures of purification or isolation which lie strictly within the province of skill of any qualified chemist whose procedures in each instance must be governed by the properties of the materials concerned, and by the degree or the character of the purity desired.

Wherever the prefix "poly" is employed, it will be understood to mean more than one.

The term "residue", as used throughout the specification and claims, is employed in its originally understood chemical significance. For example, where one of the hydroxyl groups of glycerine is esterified with a fatty acid or etherified with an alcohol and another of the hydroxyl groups of the glycerine is esterified with a phosphoric acid, that which remains of the glycerine molecule, for example



is the "residue" of the polyhydroxy substance, in this case glycerine.

This application is a continuation-in-part of my application, Serial No. 705,825, filed January 8, 1934.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A phosphoric acid ester of a polyhydroxy substance having not less than four esterifiable hydroxy groups but not including hexahydric alcohols, the hydrogen of at least one of said hydroxy groups being replaced by a lipophile radical having at least four carbon atoms.

2. The product of claim 1 wherein said ester is at least partially neutralized.

3. The product of claim 1 wherein the lipophile radical is an acyl radical.

4. A polyphosphoric acid ester of a polyhydroxy substance having not less than four esterifiable hydroxy groups, the hydrogen of at least one of said hydroxy groups being replaced by a lipophile radical having at least four carbon atoms.

5. The product of claim 4 wherein said ester is at least partially neutralized.

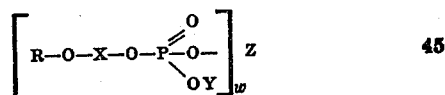
6. The product of claim 4 wherein the lipophile radical is an acyl radical.

7. The product of claim 4 wherein the polyhydroxy substance is a sugar.

8. A phosphoric acid ester of a polyglycerol, the hydrogen of at least one hydroxy group of the polyglycerol being replaced by a lipophile radical having at least four carbon atoms.

9. The product of claim 8 wherein the lipophile radical is an acyl radical.

10. An ester of phosphoric acid with lipophile and hydrophile groups, said ester being represented by the formula



wherein R, the lipophile portion of the molecule, has at least four carbon atoms, X is the residue of a polyhydroxy substance having not less than four esterifiable hydroxy groups but not including hexahydric alcohols, Y and Z represent cations, and w is an integer.

BENJAMIN R. HARRIS.