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SURFACE ACTIVE COMPOSITIONS

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This invention relates to the production of surface active compositions, and more particularly to an improved process for preparing surface active compositions containing mixtures of primary and secondary phosphate esters of hydroxylic organic compounds.

Hydroxylic organic compounds have been previously esterified with a number of different phosphating agents including phosphoric acid, P_2O_5, PCl_3, and $POCl_3$ and the like. While such processes have in some instances produced surface active compounds or compositions, they have been commonly subject to a number of procedural disadvantages and/or have failed to produce a surface active product having optimum properties for certain end uses. Thus, the use of $POCl_3$ as the phosphating agent yields products containing bound chlorine atoms, and in addition requires careful manipulation to remove the HCl produced during the reaction. Further, the HCl raises problems of corrosion. The use of phosphoric acid or solutions of P_2O_5 in phosphoric acid as phosphating agent generally yields inconsistent mixtures of different types of esters, including esters of pyrophosphoric acid, phosphoric acid, primary, secondary and tertiary phosphates, and the like. When P_2O_5 has been employed, considerably greater molar ratios of the hydroxy compounds were regarded as necessary to bring the solid P_2O_5 into solution.

In the copending application of Leslie G. Nunn and Stanley H. Hesse, Serial No. 852,188, filed November 12, 1959, a process is disclosed for producing phosphate esters of hydroxylic organic compounds, which process is directed towards eliminating the above mentioned disadvantages.

Said process broadly comprises reacting one mole of P_2O_5 with 2 to 4.5 moles of a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom under substantially anhydrous conditions and at a temperature below about 110° C. This process does not require the use of an excess of the hydroxylic organic compound (in this instance the defined nonionic surface active agent), in order to bring the P_2O_5 into solution. Substantially no tertiary phosphate ester is formed by this process and little or no P_2O_5 remains in the composition. Depending upon the particular ratio of P_2O_5 to the nonionic surface active agent employed, and the nature of such nonionic, the product may in some instances contain some unreacted nonionic surface active agent which for certain uses is actually advantageous.

For similar reasons, the proportions of secondary phosphate ester:primary phosphate ester:free nonionic in the products of this invention will in general fall within the range of about 20 to 45% secondary ester:30 to 80% primary ester:0 to 40% nonionic, by weight.

While the process disclosed in said application is highly effective, it has been found that the products thus produced are somewhat colored and that such products tend to become discolored or to darken on storage. Uncolored or light colored products are required in many uses for surface active agents and many formulators of such compositions, particularly liquid detergent compositions, have rigid color specification for the components of such formulations which require substantially colorless raw materials.

It is an object of this invention to provide a process for producing phosphate esters of nonionic surface active agents which will result in lighter colored or substantially colorless products. Another object of this invention is to improve the process disclosed in said copending application whereby lighter colored or substantially colorless products are formed. Still another object of this invention is the provision of such a process which will result in phosphate ester products having improved stability to discoloration or darkening on storage. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by my discovery that lighter colored or substantially colorless products are obtained when the phosphation reaction disclosed in said copending application is carried out in the presence of a small or catalytic amount of a phosphorus-containing compound selected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid. More particularly, my invention includes a process comprising reacting one mole of P_2O_5 with 2 to 4.5 moles of a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom, under substantially anhydrous conditions and at a temperature below about 110° C. in the presence of a small amount of one or a mixture of the aforementioned hypophosphorous or phosphorous acid compounds.

By the use of such compounds in the described phosphation reaction, it has been found that an unexpected and substantial improvement in the (absence of) color of the products and the resistance of such products to discoloration in storage is obtained. Products resulting from the use of the present invention generally have VCS (varnish color scale, Gardner scale, standards of 1933) values of at least one less than products of the same process carried out in the absence of the hypophosphorous or phosphorous acid compound. Products having a VCS color of about 1 or less are thus made possible, as compared with VCS colors of from about 2 to 7 or more for products produced without the aid of the present invention. Further, the products of this invention have been found to resist discoloration or darkening even after storage for three to six months.

Since this invention is applicable for the improvement of the inventive process disclosed in said copending application, the entire subject matter of said copending application is incorporated herein by reference thereto. Stated otherwise, said application fully discloses nonionic surface active agents employed as reactants in the phosphation reaction, the conditions of reaction, the manner of carrying out the reaction, and the products thus produced, all of which are employed in the present process.

Briefly stated, the nonionic surface active agents employed as reactants in the present invention are well known in the art and are disclosed along with suitable methods for their preparation in numerous patents and other publications. In general, they may be obtained by condensing a polyglycol ether containing the required number of alkenoxy groups or an alkylene oxide such as propylene oxide, butylene oxide, or preferably ethylene oxide, with an organic compound containing at least 6 carbon atoms and a reactive hydrogen atom. As such compounds containing a reactive hydrogen atom there may be mentioned alcohols, phenols, thiols, primary and secondary amines, and carboxylic and sulfonic acids, and their amides. The amount of alkylene oxide or equiv-

alent condensed with the reactive chain, will depend primarily upon the particular compound with which it is condensed. As a convenient rule of thumb, an amount of alkylene oxide or equivalent should be employed which will result in a condensation product containing about 20 to 85% by weight of combined alkylene oxide. However, the optimum amount of alkylene oxide for attainment of the desired hydrophobic-hydrophilic balance may be readily determined in any particular case by preliminary test and routine experimentation.

In general, the nonionic surface active agents having the molecular configuration of a condensation product of at least one mole of an alkylene oxide, preferably ethylene oxide, with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom are preferably polyoxyalkylene derivatives of alkylated and polyalkylated phenols, multi-branched chain primary aliphatic alcohols having the molecular configuration of an alcohol produced by the Oxo process from a polyolefin of at least 7 carbon atoms, and straight chain aliphatic alcohols of at least 10 carbon atoms. Examples of these derivatives and other suitable nonionic surface active agents which may be phosphated in accordance with the present invention are included below. In this list, "E.O." means "ethylene oxide" and the number preceding same refers to the number of moles thereof reacted with one mole of the given reactive hydrogen-containing compound.

Nonylphenol+9–11 E.O.
Nonylphenol+2 E.O.
Dinonylphenol+7 E.O.
Dodecylphenol+18 E.O.
Castor oil+20 E.O.
Tall oil+18 E.O.
Oleyl alcohol+20 E.O.
Lauryl alcohol+4 E.O.
Lauryl alcohol+15 E.O.
Hexadecyl alcohol+12 E.O.
Hexadecyl alcohol+20 E.O.
Octadecyl alcohol+20 E.O.
Oxo tridecyl alcohol:
(From tetrapropylene)+7 E.O.
(From tetrapropylene)+10 E.O.
(From tetrapropylene)+15 E.O.
Dodecyl mercaptan+9 E.O.
Soya bean oil amine+10 E.O.
Rosin amine+32 E.O.
Coconut fatty acid amine+7 E.O.
Cocoa fatty acid+10 E.O.
Dodecylbenzene sulfonamide+10 E.O.
Decyl sulfonamide+6 E.O.
Oleic acid+5 E.O.
Polypropylene glycol (30 oxypropylene units)+10 E.O.

In carrying out the phosphation reaction in accordance with this invention, the P_2O_5 is preferably added gradually, with vigorous agitation, to the nonionic surface active agent in liquid form. If the latter agent is a solid at room temperature, it should be heated to above its melting point. Addition of the nonionic surface active agent to the P_2O_5 is inadvisable since this has been found to result in the formation of tar and the like and to prevent the reaction from proceeding to completion. The reaction is exothermic and in some cases cooling is necessary to prevent the temperature from going above about 110° C. since this tends to produce discolored and darkened products. The reaction proceeds continuously during addition of the P_2O_5 and solution thereof in the nonionic surface active agent, and is substantially 90% complete or more by the time all of the P_2O_5 has been added. The few particles of solid P_2O_5 remaining in the reaction medium may be removed at this point if time is of the essence, but it is preferred in the interests of economy to allow the reaction to proceed for an additional period of time which may range from ½ to 5 hours or more at ambient temperatures up to about 110° C. until all of the P_2O_5 has dissolved indicating complete reaction between the reactants involved. Vigorous agitation during the reaction is highly desirable to facilitate and expedite completion of the reaction.

It is an advantageous feature of this invention that the P_2O_5 may be employed in dry, solid form as a granular powder or other finely divided or particulate form, for reaction with the above defined nonionic surface active agents. However, if desired, the P_2O_5 may first be dispersed in an inert organic diluent such as benzene, xylene, ether, pentane, or low and high boiling hydrocarbon fractions.

After completion of the reaction, the reaction mixture may be cooled and discharged. If carried out under rigid anhydrous conditions the product should consist of a mixture of the primary and secondary phosphate esters of the nonionic surface active agent combined, depending upon the proportions of reactants, in some instances with a small proportion of unreacted nonionic surface active agent. Any small amount of water present in the reaction mixture will result protanto in the formation of some phosphoric acid in the product. The degree of esterification in the product may be determined by potentiometric titration or by titration with alkali to methyl orange and then to phenolphthalein.

As referred to above, the essence of my invention resides in the addition to the reaction medium of a small amount of hypophosphorous or phosphorous acid compound. Generally, about 0.01 to 5% and preferably about 0.1 to 2% of such compound, based on the weight of the nonionic surface active agent being phosphated is sufficient to provide the desired improvements with respect to prevention of color degradation of the products and improvement in resistance of the products to color degradation in storage. Hypophosphorous acid and its alkali metal salts, e.g. sodium and potassium salts are generally preferred although any metal, alkaline earth metal, ammonium or amine salt of hypophosphorous acid or phosphorous acid may be employed, in addition to phosphorous acid per se. When hypophosphorous acid is employed, it is preferred to use a 30 to 50% aqueous solution thereof although aqueous solutions of this acid and other of the water soluble hypophosphorous and phosphorous acid compounds may be employed in the form of aqueous solutions ranging in concentration from less than 5 up to 70% or more. It should be borne in mind that the reaction should be carried out under substantially anhydrous conditions and accordingly the water introduced in such solutions should be held to a minimum.

The salts of hypophosphorous acid and phosphorous acid employed herein may be in their hydrated or dehydrated form. As examples of such salts, there may be mentioned aluminum, cadmium, sodium, potassium, lithium, calcium, strontium, barium, magnesium, ammonium, mono-, di-, and tri-methylamine, -ethylamine, -propylamine, -ethanolamine, and -propanolamine, pyridinyl, and morpholinyl phosphites and hypophosphites.

Esters of phosphorous acid may also be employed. These esters may be described as mono-, di-, and trialkyl, -aryl, and -cycloalkyl phosphites. It will be understood that mixed esters are included. As some specific examples of such esters in which the esterifying group generally contains from about 1 to 20 carbon atoms, there may be mentioned ethyl phosphite, lauryl phosphite, Oxo tridecyl phosphite (the esterifying alcohol having the molecular configuration of an alcohol produced from tetrapropylene or triisobutylene by the Oxo process), stearyl phosphite, phenyl phosphite, cyclohexyl phosphite, the corresponding di- and tri-substituted phosphites, ethyl phenyl phosphite, ethyl diphenyl phosphite, lauryl cyclohexyl phosphite, dipropyl phenyl phosphite, and the like.

In accordance with this invention, the hypophosphorous or phosphorous acid compound is preferably admixed with the non-ionic surface active agent prior to addition there-

to of the P_2O_5. If desired, however, such compound may be added simultaneously with the addition of the P_2O_5 or, if anhydrous, may be admixed with the P_2O_5 prior to its addition to the nonionic surface active agent. It will accordingly be understood that the hypophosphorous or phosphorous acid compound or mixture thereof may be added at the start of the reaction or continuously or intermittently as the reaction proceeds.

measurable by this method the highest being 18. Products prepared with the use of the additives referred to in the table sustained no change in color after 3 to 6 months' storage.

It will be understood that all parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

Ex.	Nonionic agent	Nonionic parts	P_2O_5 parts	Parts	Additive	VCS color
1	Nonylphenol+2 E.O. $C_9H_{19}C_6H_4(OC_2H_4)_2OH$	2,288	284	Control		2
2	do	2,288	284	3.4	Hypophosphorous acid (50%)	<1
3	Nonylphenol+4 E.O. $C_9H_{19}C_6H_4(OC_2H_4)_4OH$	2,355	213	Control		4
4	do	2,355	213	4.2	Hypophosphorous acid (50%)	<1
5	Nonylphenol+6 E.O. $C_9H_{19}C_6H_4(OC_2H_4)_6OH$	484	47.3	Control		4
6	do	484	47.3	1.0	Hypophosphorous acid (50%)	<1
7	do	484	47.3	0.5	Sodium hypophosphite	<1
8	do	484	47.3	2.0	Triphenyl phosphite	2
9	Nonylphenol+10 E.O. $C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$	1,821	108	Control		4
10	do	1,821	108	7.0	Hypophosphorous acid (30%)	<1
11	Nonylphenol+100 E.O. $C_9H_{19}C_6H_4(OC_2H_4)_{100}OH$	605	11.9	Control		2
12	do	605	11.9	1.2	Hypophosphorous acid (50%)	1
13	Dinonylphenol+7 E.O. $C_{18}H_{38}C_6H_3(OC_2H_4)_7OH$	327	23.6	Control		5
14	do	327	23.6	1.0	Hypophosphorous acid (30%)	<1
15	Dodecylphenol+6 E.O. $C_{12}H_{25}C_6H_4(OC_2H_4)_6OH$	1,052	94.4	Control		4
16	do	1,052	94.4	3.0	Hypophosphorous acid (50%)	<1
17	Oxo tridecyl alcohol [1]+3 E.O. $C_{13}H_{27}(OC_2H_4)_2OH$	166	23.7	Control		7
18	do	166	23.7	1.0	Hypophosphorous acid (50%)	2
19	do	166	23.7	1.0	Phosphorous acid	2
20	Lauryl alcohol+4 E.O. $C_{12}H_{25}(OC_2H_4)_4OH$	724	71	Control		7
21	do	724	71	1.3	Hypophosphorous acid (50%)	1

[1] From tetrapropylene by the Oxo process.

The products of this invention may be supplied in free unneutralized form, or in the form of the partially or completely neutralized salts containing as cations alkali metals, alkaline earth metals, metals, ammonium and organic amines. Use in the form of such salts is in some instances preferred or necessary, as for example when employed in alkaline surface active and other compositions. It is to be understood that such salts are to be regarded as the equivalent of the present products in their free form. As examples of suitable cations, there may be mentioned sodium, potassium, lithium, calcium, strontium, barium, magnesium, iron, tin, cadmium, aluminum, antimony chromium, manganese, mercury, nickel, silver, zinc, ammonium and aliphatic, alicyclic, aromatic, and heterocyclic organic amines such as the mono-, di-, and tri-methylamines, -ethylamines,-propylamines,-laurylamines, -stearylamines, -ethanolamines, propanolamines,- butanolamines, -hexanolamines,- cyclohexylamines, -phenylamines, pyridylamine, morpholinylamine, and the like.

The examples in the following table are only illustrative of the present invention and are not to be regarded as limitative. In each of these examples, the nonionic surface active agent is first charged to a reactor equipped with an agitator. If the charge is solid at room temperature, it is heated to melt the same. The additive referred to in the table is then added to and dissolved in the nonionic surface active agent with vigorous agitation. The solid granular P_2O_5 is then charged to the reactor with vigorous agitation over a period ranging from about 5 minutes to about 1 hour and usually about 15 minutes. After the initial exothermic reaction subsides, the reaction mixture is heated to 100° C. and held at this temperature for about 5 hours after which the mixture is cooled and discharged. A sample of the reaction mixture is titrated with alkali to methyl orange and then to phenolphthalein as a control on the esterification. The VCS color readings are measured in the prescribed manner. A reading of one is the lowest color reading

This invention has been disclosed with respect to certain preferred embodiments and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

I claim:

1. In a process comprising reacting 1 mole of P_2O_5 with 2 to 4.5 moles of a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide with one mole of a compound containing about 6 to 150 carbon atoms and a reactive hydrogen atom and selected from the group consisting of phenol, alkyl phenols, aliphatic alcohols, fatty acids, fatty amines, fatty amides, rosin amines, long chain sulfonamides, long chain-substituted aryl sulfonamides, and high molecular weight mercaptans under substantially anhydrous conditions and at a temperature below about 110° C. down to about room temperature, the improvement comprising carrying out the reaction in the presence of a small amount of a phosphorus-containing compound selected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid.

2. A process as defined in claim 1 wherein said reactive hydrogen-containing compound is an alkyl phenol of at least 10 carbon atoms.

3. A process as defined in claim 1 wherein said reactive hydrogen-containing compound is a multi-branched chain primary aliphatic alcohol having the molecular configuration of an alcohol produced by the Oxo process from a polyolefin of at least 7 carbon atoms.

4. A process as defined in claim 1 wherein said reactive hydrogen-containing compound is a straight chain aliphatic alcohol of at least 10 carbon atoms.

5. A process as defined in claim 1 wherein said phosphorus-containing compound is hypophosphorous acid.

6. A process as defined in claim 1 wherein said phosphorus-containing compound is sodium hypophosphite.

7. A process as defined in claim 1 wherein said phosphorus-containing compound is phosphorous acid.

8. A process as defined in claim 1 wherein said phosphorus-containing compound is triphenyl phosphite.

9. In a process comprising gradually adding with agitation one mole of dry, solid P_2O_5 to 2 to 4.5 moles of a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide with one mole of a compound containing about 6 to 150 carbon atoms and a reactive hydrogen atom and selected from the group consisting of phenol, alkyl phenols, aliphatic alcohols, fatty acids, fatty amines, fatty amides, rosin amines, long chain sulfonamides, long chain-substituted aryl sulfonamides, and high molecular weight mercaptans, and allowing the phosphation to proceed under substantially anhydrous conditions and at a temperature below about 110° C. down to about room temperature, the improvement comprising first dissolving in the nonionic surface active agent a small amount of a phosphorus-containing compound selected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid.

10. A process as defined in claim 9 wherein said reactive hydrogen-containing compound is an alkyl phenol of at least 10 carbon atoms.

11. A process as defined in claim 9 wherein said reactive hydrogen-containing compound is a multi-branched chain primary aliphatic alcohol having the molecular configuration of an alcohol produced by the Oxo process from a polyolefin of at least 7 carbon atoms.

12. A process as defined in claim 9 wherein said compound is a straight chain aliphatic alcohol of at least 10 carbon atoms.

13. A process as defined in claim 9 wherein said phosphorus-containing compound is hypophosphorous acid.

14. A process as defined in claim 9 wherein said phosphorus-containing compound is sodium hypophosphite.

15. A process as defined in claim 9 wherein said phosphorus-containing compound is phosphorous acid.

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