United States Patent

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[72] Inventor **Robert Ernst**
Los Angeles, Calif.

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[73] Assignee **Textilana Corporation**
Hawthorne, Calif.

[54] **SURFACE ACTIVE NONIONIC 2-HYDROXYALKYL 3-ALKOXY-2-HYDROXYALKYL PHOSPHATE ESTERS**
10 Claims, No Drawings

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[50] **Field of Search** 260/950, 951, 953, 978

[56] **References Cited**

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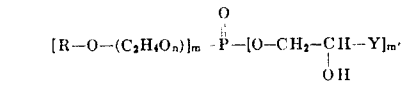
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Primary Examiner—Charles B. Parker
Assistant Examiner—Richard L. Raymond
Attorneys—Philip Subkow and Kendrick and Subkow

ABSTRACT: Surface active nonionic 2-hydroxyalkyl and 3-alkoxy-2-hydroxyalkyl phosphate esters having one or two higher alcohol or alkylphenol oxyethylate radicals, and conforming to the following general formula:



where R is a linear or branched alkyl group having eight to 18 carbon atoms, of which at least six are in an uninterrupted carbon-to-carbon chain, or an alkylphenyl group having eight to 15 carbon atoms in a linear or branched alkyl group, of which the alkyl substituent has at least four carbon atoms in an uninterrupted carbon-to-carbon chain, which may be branched but is Y is hydrogen or an alkyl group with an uninterrupted carbon chain of one to 16 carbon atoms, or a methoxyalkyl group $-CH_2-O-R'$, where R' is an alkyl radical having one to 18 carbon atoms; n is a number of two to 20; m is a number of one or two; m' is a number of one or two; and $m + m'$ equals 3. Such compounds being useful as detergents, drycleaning agents, wetting agents, emulsifiers and lubricants.

SURFACE ACTIVE NONIONIC 2-HYDROXYALKYL 3-ALKOXY-2-HYDROXYALKYL PHOSPHATE ESTERS

SUMMARY OF THE INVENTION

Anionic organic phosphates acid esters and their salts, derived from alkylene oxide adducts of higher alcohols or alkylphenols, have gained commercial importance as surfactants. These anionic phosphates show, however, a marked sensitivity to hard water, giving rise to inferior detergency and foaming properties. Stability of emulsions prepared with these surfactants will also be impaired in most cases when di or polyvalent metal ions are encountered.

I have discovered that I can convert these acid esters into nonionic surface active agents which are not sensitive to polyvalent cations by reacting the anionic organic phosphate esters described above with an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide, octylene oxide, etc., or glycidyl ethers of alcohols, to produce nonionic phosphate esters having one or two hydroxyalkyl substituents. Highly useful nonionic surfactants and lubricants are obtained from precursor anionic phosphate acid esters when these precursors are derived from higher alcohols having eight to 18 carbon atoms, or alkylphenols having eight to 15 carbon atoms in the alkyl chain or chains. The alkylene oxide adduct should preferably contain from two to 20 ethylene oxide radicals in a di or poly ethyleneglycol ether group, to provide the desired surface active properties of the nonionic hydroxyalkyl derivative.

DETAILED DESCRIPTION

In order to obtain the nonionic phosphate esters having the desirable properties set forth herein, I prefer to employ as precursors organic acid phosphates which conform substantially to the following generic formula:

$$[R-O-(C_2H_4O)_n]_m-\overset{\overset{O}{\|}}{P}-[OH]_{m'}$$

where R is a linear or branched chain alkyl group having eight to 18 carbon atoms in an uninterrupted carbon chain, or an alkylphenyl group having eight to 15 carbon atoms in a linear or branched but otherwise unsubstituted alkyl group; n is a number of at least two; m is a number of one or two; n' is a number of one or two; and $m+m'$ equals three.

The preparation of anionic organic phosphate acid esters has been described by Ulrich and Sauerwein, German Pat. No. 696,317 (1940). Compounds which, if suitable prepared by the process of my invention, are useful as precursors in the practice of my invention are listed also by Nunn and Hesse, U.S. Pat. No. 3,004,056 (1961), and by Mansfield, Canadian Pat. No. 716,029 (1965).

In a preferred practice, the mono and di orthophophoric acid esters employed in this invention are obtained by reaction of a suitable ethoxylate with phosphorus pentoxide. By so doing I am able to insure that the reaction products will contain a suitable low concentration of free phosphoric acid and that the precursor is suitable for the purposes of my invention.

I have discovered that the presence of free phosphoric acid (H_3PO_4) in the above-described acid phosphate esters promotes the formation of polyglycolethers and esters thereof. Such impurities and products of side reaction are undesirable, and their presence can be reduced to a substantial degree, as demonstrated in the examples, when using the mono or di or mixed mono and di orthophosphoric acid esters, free of phosphoric acid or with such free phosphoric acid suitably limited.

As a practical matter, and as a preferred embodiment of my invention, I desire to use anionic phosphate acid esters containing less than about 10 percent free phosphoric acid (H_3PO_4) and preferably less than about 5 percent.

I also prefer that the anionic phosphate acid esters employed as precursors in forming the nonionic phosphate esters of my invention shall contain less than about 10 percent of the nonionic oxyethylate employed in the esterification by which the precursor acid esters are formed.

Precursors containing impurities in amounts in excess of the percentages set forth above result in undesirable nonionic esters. Therefore, I prefer that the precursor be formed so that it shall be substantially free of phosphoric acid and of nonionic oxyethylate employed in the formation of the precursor.

The oxyethylates used as reactants in the process of my invention are chosen from the group having eight to 18 carbon atoms in an uninterrupted carbon chain, or from alkylphenols having one or two linear or branched chain alkyl substituents of eight to 16 carbon atoms, of which at least four carbon atoms are in an uninterrupted carbon chain. They may be produced from the higher alcohols derived from animal or vegetable fats and fatty acids by hydrogenolysis or sodium reduction. Examples are coconut fatty alcohols, tallow alcohols and fractions thereof. The alcohols may be derived from the Ziegler process, British Pat. No. 763,828 (1965), or from higher alpha olefins, obtained from thermal cracking of petroleum wax, or polymerization of ethylene or propylene, by reaction with carbon monoxide and hydrogen (hydroformylation), as, for instance, described in German Pat. No. 931,405 (1955). The secondary alcohols, derived for instance from chlorinated paraffins, are also desirable intermediates.

The preferred alkylphenols for production of the corresponding esters are the mono and di alkyl phenols, such as are derived, for instance, from diisobutylene, propylene trimer or tetramer, or higher olefins, by alkylation with phenol by conventional techniques.

I have found that the performance of these precursor compounds, in a number of applications illustrated below, can be greatly improved by conversion of the same to the corresponding hydroxyalkyl nonionic esters by reaction with oxirane compounds

The preparation of anionic organic phosphates has been disclosed in numerous papers and patents (see supra). Phosphoric acid, polyphosphoric acid, phosphorus pentoxide, and phosphorus oxychloride have been suggested as reagents.

I have found that it is preferable for the purpose of my invention that the above alcohols or alkylphenols be reacted with at least 2 moles of ethylene oxide, and more preferably with an amount sufficient to result in an oxyethylate containing from 2 to 20 oxyethylate radicals. The oxyethylation is described for instance, in U.S. Pat. No. 1,970,578(1934).

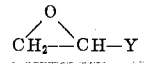
The phosphoric acid esters employed for this purpose should be as free as possible of unreacted phosphoric acid (H_3PO_4). Substantially complete conversion to the nonionic hydroxyalkyl phosphate ester is obtained at temperatures below 100° C. by employing an amount of alkylene oxide or oxirane compound greater than the stoichiometric amount calculated from the acid number of the anionic acid phosphate. Preferably, in order to achieve approximately 90 percent to 100 percent conversion to the desired nonionic surface active phosphate ester, an excess of about 20 to 50 mole percent should be employed.

Surfactants so obtained have superior detergency in laundering and drycleaning operations. These novel surface active agents exhibit a negative coefficient of solubility on heating in aqueous solution. This property is particularly desirable when employing such compounds in metal working operations to reduce friction, wear and corrosion, either by themselves or in combination with mineral or fatty oils.

In order to obtain the organic acid phosphate esters, having a low content of H_3PO_4 and unreacted nonionic starting material, I prefer to react the above enumerated nonionic oxyethylates with a 0.8–1.2 mole ratio of P_2O_5 for each 3 moles of the nonionic oxyethylate, based on its hydroxyl value. The molar ratio is adjusted to produce a mixture of mono- and di-acid esters, containing preferably below 10 percent unreacted nonionic starting product and preferably less than 5 percent

free H_3PO_4. In most cases, best results are obtained with the use of 1.0–1.1 mole of P_2O_5 for each 3 moles of nonionics, based upon hydroxy groups. Examples 1 to 9 employ such preparations.

The oxides preferred to be used in this 2-hydroxyalkyl esterification of the above-described acid phosphate esters conform to the following general structure:



where Y is hydrogen or an alkyl group with an uninterrupted carbon chain of one to 16 carbon atoms, or a methoxyalkyl group $-CH_2-O-R'$, where R' is an alkyl radical having one to 18 carbon atoms. Typical examples of such oxides are: ethylene oxide, propylene oxide, 1,2 butylene oxide, 1.2 octylene oxide, etc., and alkyl glycidyl ethers such as octyl glycidyl ether, lauryl glycidyl ether, tallow fatty glycidyl ether.

The higher 1,2 alkylene oxides may be prepared by epoxidation of alpha olefins with organic peracids, such as peracetic acid. Any other suitable process may be employed. The glycidyl ethers may be obtained, for instance, by the process given in U.S. Pat. No. 2,989,547 (1961).

The esterification of the phosphoric acid esters with the oxirane compounds, according to the process of my invention, is exothermic and takes place readily even at low temperatures, such as ambient room temperatures. In a prepared procedure, the mono-, di-, or mixed mono- and di-acid phosphate ester is charged into a suitable reaction vessel, such as a glass, glass lined, or stainless steel reactor, equipped for heating and cooling, and the oxirane compound added generally at such rate as to prevent loss of the oxirane compound by evaporation. This may be achieved by merely controlling the rate of addition, by external cooling, or both.

With oxides such as ethylene oxide and propylene oxide, the reaction is best carried out in a pressure vessel (autoclave) at moderate pressures, below about 4 atmospheres. Propylene oxide and other low boiling oxirane compounds such as butylene oxide can, however, also be handled at atmospheric pressures, by means of an efficient reflux condenser. The higher oxirane compounds an even be reacted in an open vessel.

Addition of the oxide is made while agitating the phosphoric acid ester. With oxides having a low flash point, addition is best made at ambient temperature, below the surface of the acidic reagent, and air should be excluded by evacuation and/or purging with an inert gas such as nitrogen. The use of inert gas will also assist in the production of light colored products. This is a most desirable feature, and it will be noted that the neutral hydroxyalkyl esters of this invention are characterized as extremely light colored or colorless products. Such colors are generally substantially lower than the color level of the acid phosphate ester starting material. The nonionic hydroxyalkyl phosphates are lower in viscosity and are therefore much easier to handle in preparation and use than their anionic precursors. Thus, acid esters which may be solid at room temperature will generally be low viscosity liquids when converted to the nonionic hydroxyalkyl esters.

These and other factors will be demonstrated in the examples below.

The reaction proceeds, it is believed, through opening of the oxirane ring, resulting substantially in the formation respectively of 2-hydroxylalkyl and 3-alkoxy-2-hydroxypropyl esters. As pointed out, a moderate excess over stoichiometric quantitied, calculated from the acid value of the acid ester, is generally desirable to achieve a conversion to the nonionic ester in high yields of, for instance, 90 percent or greater. Since the yield of the finished product, even following vacuum stripping, is about 100 percent based upon the reagents charged, the excess of oxide charged must, I conclude, react with the hydroxyl groups formed. There may, therefore, also be present a minor amount of diglycoletheresters.

EXAMPLE 1

To produce mono and di phosphoric acid ester of linear primary alkanol (C_{12}-C_{13}) polyoxyethylate of 6.5 moles ethylene oxide, a 3,000 ml., four-necked flask, equipped with a stainless steel stirring assembly, thermometer, inlet tube for nitrogen gas, and funnel, was charged with the following reagents:

Neodol 23–6.5, a nonionic linear primary alkanol (C_{12}–C_{13}) polyoxyethylate of 6.5 moles ethylene oxide, hydroxyl number 112.1, water content 0.05 percent; equivalent molecular weight 500.44; 3.0 moles	1,501.3 g.
Phosphorus pentoxide, 1.1 mole	156.2 g.

The phosphorus pentoxide was powdered into the above nonionic gradually over a period of 1 hour and 15 minutes at ambient temperature. The reaction mass was purged with nitrogen throughout the preparation.

The exotherm of the reaction raised the temperature from 24° C. to 40° C. The temperature on falling was then raised by means of an electrically heated mantle to 65° C. and held there for 3 hours. All P_2O_5 had gone into solution at this point, and the acid number was found to be 100.2 (Theory: 102.4).

The acid ester was cooled and filtered and gave the following analytical values:

Acid number	105.5
Free nonionics, chromotagraphically with Amberlite MB1 resin	8.2%
Free phosphoric acid (H_3PO_4)	0.13%
Color, Gardner Hellige, VCS	below 1
Appearance	viscous fluid

Amberlite MB–1 resin is a mixture of cation resin = $RSO3^-H^+$ and anion resin a = $RN(CH_3)_3{}^+{}_{OH}{}^-$, regenerated for use in deionization applications, sold by Mallinckrodt Chemical Works.

EXAMPLE 2

To produce mono and di phosphoric acid ester of linear primary alkanol (C_{12}-C_{15}) polyoxyethylate of 9 moles ethylene oxide, a reactor as described in example 1 was charged with:

Neodol 25–9, a nonionic linear primary alkanol (C_{12}–C_{5}) polyoxyethylate of 9 moles ethylene oxide, hydroxyl number 98.3; water content 0.11%; equivalent molecular weight 57.07; 3.0 moles	1,712.1 g.
P_2O_5, 1.1 mole	156.2 g.

The phosphorus pentoxide was added as in example 1. The resulting product, on heating for 2½ hours at 55°–61° C., cooling and filtering, gave the following analytical values:

Acid number	87.5
Free nonionics, chromatographically with Amberlite MB–1 resin	8.39%
Free H_3PO4	0.17%
Color, Hellige, VCS	2
Appearance	Pastry opaque semisolid

Neodol 23–6.5 and Neodol 25–9 are products sold by Shell Chemical Company.

EXAMPLE 3

To produce mono and di phosphoric acid ester of linear secondary alkanol (C -C_{15}) polyoxyethylate of 7 moles ethylene oxide, a reaction apparatus as described in example 1 was charged with:

Tergitol 15–S–7, linear secondary alkanol (C_{11}–C_{15}) polyoxyethylate of	

7 moles ethylene oxide, hydroxyl number 108.6; water content 0.2%; equivalent mol. wt. 516.4; 3.0 moles	1,549.2 g.
P_2O_5, 1.05 mole	149.1 g.

The phosphorus pentoxide was added as in example 1. The reaction mass was then brought to 65° C. and maintained there for 1 hour. The acid number was then found to be 94.4 (Theory: 99.5) and rose slightly thereafter.

On cooling and filtering, the following analytical values were obtained:

Acid number	99.0
Free nonionics, chromatographically with Amberlite MB-1 resin	6.13%
Free H_3PO_4	0.22%
Appearance	viscous liquid.

Tergitol 15-S-7 is a product sold by Union Carbide Corporation.

In the examples, the parenthetical matter (C_{12}-C_{13}), (C_{12}-C_{15}), and (C_{11}-C_{15}), where it relates to esters is intended to indicate mixtures of esters, and where it relates to ethers is intended to indicate a mixture of ethers, in which the indicated carbons of the individual compounds are within the indicated ranges.

EXAMPLE 4

To produce mono and di N-octyl diethyleneglycol ether acid phosphate, a reaction apparatus as shown in example 1, but having a capacity of 2,000 ml., was charged with:

Alfol 8 (commercial n-octanol), which has been reacted with 2 moles of ethylene oxide (n-octyl diethyleneglycol ether), hydroxyl number 258; equivalent molecular weight 217.44; 3.0 moles	652.3 g.
P_2O_5	156.2 g.

Proceeding as in example 1, the P_2O_5 was added over a period of 3 hours, at a temperature below 50° C. The reaction mass was then heated to 80° C. and held there for 3 hours. The following analytical values were found with this run:

Acid number	209.0
Free nonionics, chromatographically with Amberlite MB-1 resin	3.1%
Free H_3PO_4	3.27%
Color, Hellige VCS	1
Appearance	Viscous liquid.

Alfol 8 is a product sold by Continental Oil Company.

EXAMPLE 5

To produce mono and di phosphoric acid ester of n-octanol, 3 moles equivalent of normal octanol was O_{with} 1.04 mole of P_2O_5 at a maximum temperature of 70° C.

The product showed the following analytical values:

Acid number	309.0
Free alcohol, chromatographically with Amberlite MB-1 resin	1.10%
Free H_3PO_4	0.52%
Color, Hellige VCS	2
Appearance	Viscous liquid.

EXAMPLE 6

To produce mono and di phosphoric acid ester of nonylphenol polyoxyethylate of 9 moles ethylene oxide, 3 moles equivalent of nonylphenol polyoxyethylate of 9 moles of ethylene oxide, having a hydroxyl number of 92.6 and a water content of 0.5 percent, was reacted with 1.2 moles of P_2O_5 at a maximum temperature of 80° C., and showed the following analytical values:

Acid number	114.8
Free nonionics, chromatographically with Amberlite MB-1 resin	9.4%
Free H_3PO_4	0.87%
Mono ester	62.5%
Color, Hellige VCS	Below 1.
Appearance	Viscous liquid.

EXAMPLE 7

To produce mono and di phosphoric acid ester of nonylphenol polyoxyethylate of 6 moles ethylene oxide, 2.95 moles equivalent of nonylphenol polyoxyethylate of 6 moles ethylene oxide, having a hydroxyl number of 116 and a water content of 0.1 percent, were reacted with 1.0 mole of P_2O_5 at a maximum temperature of 80° C., and gave the following analytical results:

Acid number	104.1
Free nonionic, chromatographically with Amberlite MB-1 resin	8.12%
Free H_3PO_4	0.12%
Mono ester	37. %
Color, Hellige VCS	below 1

EXAMPLE 8

To produce the compound of example 1, by phosphation with polyphosphoric acid, a reaction apparatus as described in example 1 was charged with Neodol 23-6.5, hydroxyl value 112.1, equivalent mol. wt. 500.45, 2.0 moles...1000.9 g.

Polyphosphoric acid, 115% H_3PO_4 (84% P_2O_5 equivalent) This amount is equal to 1 mole P_2O_5.	169.0 g.

The polyphosphoric acid was added to the nonionic over a period of 1½hours. The temperature rose from 25° C. to 40° C. as a result of the exothermic reaction. The batch was then brought to 100° C. through application of heat and held there for 3 hours.

On cooling, this phosphoric acid ester gave the following analytical values:

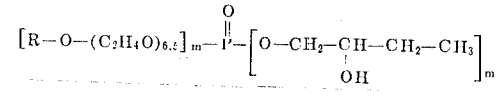
Acid number	183.3
Free nonionics, chromatographically with Amberlite MB-1 resin	27.9%
Free H_3PO_4	5.1%
Color, Hellige VCS	Below 1.
Appearance	Viscous liquid.

Comparing the process of example 1 with that of example 8, it will be seen that the unesterified nonionic impurity is more then three times as great as when using P_2O_5 and that the free phosphoric acid is about 40 times as great as when using the P_2O_5.

Examples 9 through 17 and 19 illustrate preferred embodiments for production of the nonionic phosphate esters of my invention.

EXAMPLE 9

Production of nonionic 2-hydroxybutyl ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{13}) polyoxyethylate



Where R is $C_{12}H_{25}$ and $C_{13}H_{27}$; m and m' are numbers of one or two; and $m+m'=3$.

A 2,000 mi. four-necked distilling flask, equipped with a vacuum tight stainless steel stirring assembly, thermometer, inlet tube for nitrogen gas, graduated addition funnel and ice/alcohol cooled reflux condenser, was charged with:

3.0 moles phosphoric acid ester of Example 1, acid number 105.5, equivalent mol. wt. 531.75	1,595.25 g.
moles 1,2 butylene oxide, mol. wt. 72.11	302.86 g.

Was charged into the addition funnel and added drop by drop to the acid ester, while continuously purging with nitrogen.

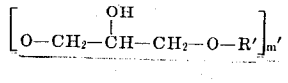
The addition of the oxide was completed in 1½ hours, with the rising from 26° C. to 55° C., due to the exotherm of the reaction. Only very mild reflux occurred, since the reaction is quite instantaneous. Mild external heat was applied by means of an electrically heated mantle, and the reaction mass was continuously stirred at 60° C. for 2 hours. A sample was then taken and analyzed for completion of reaction by determining the acid number. The acid number was found to be 3.1.

The condenser was now connected to a vacuum system and the internal pressure reduced to about 25 mm. hg., while agitating the resulting nonionic for an additional hour at 60° C. to remove traces of unreacted oxide. Upon cooling, the acid number was found to be 2.8, corresponding to a conversion to the triester of 96.8 percent based upon the calculated acid number of the reagents.

The product was a colorless, clear liquid and gave 99 percent transmittance at 425 mμ, using a Coleman Model 6D Junior spectrophotometer and a 25 mm. ×105 mm. cuvette. This nonionic phosphate ester dissolves readily in distilled and hard water to give solutions having excellent detergent properties and exhibiting good foaming and wetting properties as shown in the tables below

EXAMPLE 10

Production of nonionic 2-hydroxy-3alkoxy (C_8-C_{10}) ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{13}) polyoxyethylate. The structure is as shown in example 9, but the *m'* radical is:



Where R' is a mixture of n-octyl and n-decyl.

A 1000 ml. four-necked distilling flask, equipped as in example 9, was charged with:

0.7 moles phosphoric acid ester of example 1	372.3 g.
The addition funnel was charged with 0.98 moles	224.0 g.

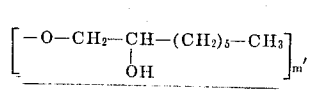
of n-octyl/n-decyl glycidyl ether containing minor percentages of n-hexyl and n-dodecyl fractions as follows: C_6=4%, C_8=57%, C_{10}=38%, C_{12}=1%, with an oxirane oxygen content of 7percent and an equivalent molecular weight based upon the oxirane value of 228.6.

The addition of the glycidyl ether was completed over a period of 1 hour and 20 minutes, and the temperature rose from 26° C. to 44° C. The reaction mass was then brought to 70° C. and held there for 2 hours. The acid number was then found to be 4.7. Continuing the reaction at this temperature level caused the acid number to fall further to 2.8, corresponding to a conversion to the nonionic phosphate of 95.7 percent. The nearly colorless, clear liquid compound gave 99½ percent transmittance at 425 mμ when tested as in example g.

This surfactant gave very good detergent properties in laundering and dry-cleaning evaluations.

EXAMPLE 11

Production of nonionic 2-hydroxyoctyl ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{15}) polyoxyethylate. The structure is as shown in example 9, where R is a saturated linear alkyl radical having 12–15 carbon atoms, *n* equals 9, and the *m'* radical has the structure:



and *m* and *m'* have the same value as in example 9.

The reaction apparatus shown in example 10 was charged with:

phosphoric acid ester of example 2, 0.5 mole	320.6 g.
1,2 Octylene oxide, oxirane oxygen 12.2%, 0.6 mole	78.7 g.

was charged into the addition funnel.

The octylene oxide had an iodine number of 0.3, a saponification number of 3, and a mol. wt. of 131.15, based upon the oxirane oxygen value, and was derived from Ziegler αoctene. The oxide was added over a period of 45 minutes at an initial temperature of 33° C., and the batch temperature rose to 49° C. The reaction was then heated for 2 hours at 70° C., and the acid number fell to 7.9. Heating for an additional period of 2½ hours did not alter the acid number. The conversion to the nonionic phosphate was of the order of about 89 percent.

An additional 0.05 mole, equal to 6.6 g. of 1,2 octylene oxide, was added to the reaction mass, previously cooled to 25° C. On further heating for 3 hours at 70° C., the acid number dropped to 3.8, corresponding to a conversion to the nonionic ester of 94.5 percent.

This surfactant had good solubility in aliphatic solvents such as kerosene, Stoddard Solvent and mineral oil, and was an excellent emulsifier for these petroleum products. This nonionic phosphate ester is capable of solubilizing water in Stoddard Solvent or similar drycleaning solvents, which is of great importance in the removal of water dispersible soil and in the reduction of static electrical charges from garments of synthetic hydrophobic fibers.

The preparation of a compound having analogous properties is shown in example 12.

EXAMPLE 12

Production of nonionic 3-alkoxy (C_8-C_{10})-2-hydroxypropyl ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{15}) polyoxyethylate. The structure is as shown in example 10. R and *n* are as shown in example 11.

The apparatus of example 10 was charged with:

phosphoric acid ester of example 2, 0.5 mole	320.6 g.
Octyl/decyl glycidyl ether (as in 100.6 mole	137.2 g.

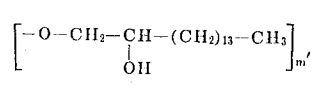
was added at a temperature of 45° C. over a period of about 1 hour. The temperature rose to 51° C. and was then increased further, by external heating, to 70° C. and held there for 2 hours. The acid number had dropped to 10.0 at this point and did not decrease upon prolonging the reaction time.

The addition of two increments of 0.05 mole each of the glycol ether brought the acid number to 4.14 and gave, therefore, a conversion of 92.9 percent to the nonionic ester.

The product was a pale, nearly colorless liquid, unlike the semisolid (pasty) acid ester from which it was derived. As in the case of example 11, **this surfactant possessed excellent emulsifying properties for a wide variety of petroleum solvents and oils, as well as chlorinated solvents, vegetable and animal oils. The product was a good drycleaning detergent and lubricant.**

EXAMPLE 13

Production of nonionic 2-hydroxyhexadecyl ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{15}) polyoxyethylate. The compound has the configuration shown in example 11, where the *m'* radical has the structure:



The apparatus of example 10 was charged with:

phosphoric acid ester of example 2, 0.5 mole	320.6 g.
1,2 Hexadecylene oxide, oxirane oxygen 6.1%, 0.6 mole	170.5 g.

was charged into the addition funnel. The hexadecylene oxide had an iodine number of 1.6 an a mol wt. of 262.3 based upon the oxirane oxygen value.

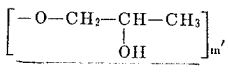
The oxide was added at an initial temperature of 33° C. over a period of 35 minutes. The temperature rose to 47½° C. The reaction mass was then heated to 70° C. and held there for 2½ hours. The acid number was then found to be 3.37, corresponding to a conversion to the nonionic ester of 94.1 percent.

This compound imparted softness to fabrics when used in detergent or drycleaning operations.

EXAMPLE 14

Production of nonionic 2-hydroxypropyl ester of mono and di acid phosphate of nonylphenol polyoxyethylate.

The structure conforms to that shown in example 9, where R is nonylphenyl, *n* is 6, and the *m'* radical is:



The apparatus of example 10 was charged with:

phosphoric acid ester of example 7, 1 mole	537.8 g.
Propylene oxide, mol. wt. 58.08, 1.3 mole	75.5 g.

was weighed into the addition funnel and added drop by drop at an initial temperature of 26° C. over a period of about 2 hours. The temperature roe to 48° C. on completion of the addition.

The batch was then heated to 60° C. following exhaustion of the exotherm, and was maintained there for 1 hour. The acid number had decreased to 15.0. An additional 0.2 mole, 11.6 g. of propylene oxide was gradually added to bring the acid number to a final value of 4.6, corresponding to 94.8 percent conversion to the nonionic phosphate eater.

The product was a nearly colorless liquid and gave 90 percent transmittance at 425 mμ as compared to a transmittance of 81 percent for the acid phosphate precursor.

It is to be noted that a reduction in color and viscosity from the level of the corresponding anionic species is a general and desirable feature of these novel nonionic phosphate esters. This surfactant exhibited outstanding detergency, as shown in the accompanying table.

EXAMPLE 15

Production of nonionic 2-hydroxybutyl ester of mono and di acid phosphate of nonylphenol polyoxyethylate. The structure is such as is shown in example 9, where R is nonylphenyl and the ethoxy integer "n" is nine.

The flask of the reaction apparatus described in example 10 was charged with:

phosphoric acid esther of example 6, 1.1 mole	537.6 g.
1,2 Butylene oxide, 1.43 mole	103.1 g.

was added drop by drop over a period of 1 hour and 40 minutes, with the temperature of the reaction mass rising from 25° C. to 60° C. The temperature fell on exhaustion of exotherm, and the batch was mildly heated to maintain the temperature at 60° C. After 3 hours at this temperature, the acid number had fallen to 17.0 (a conversion to the nonionic ester of 82.2 percent), and 0.3 mole, 21.6 g. of 1,6 butylene oxide was added to further improve the yield of the nonionic ester to a preferred range of 90 percent or above.

After additional stirring at 60° C, the acid number had dropped to 4.73, corresponding to a conversion to the nonionic ester of 94.9 percent.

The compound was a plate, straw colored liquid, giving 84 percent transmittance at 425 mμ as compared to 80 percent for the acid precursor This surface active agent was useful as a detergent, frothing and wetting agent.

EXAMPLE 16

Production of nonionic 3-alkoxy (C_8-C_{10})-2-hydroxypropyl ester of mono and di acid phosphate of linear secondary alkanol (C_{11}-C_{15}) polyoxyethylate. The compound conforms to the structural formula of example 9, where R is a linear secondary alkyl group having 11–15 carbon atoms and the oxyethylene group "*n*" is an integer of seven.

The apparatus and method of reaction were as shown in example 9, except for the use of a 1000 ml. flask. This was charged with:

phosphoric acid ester of example 3, 0.5 mole	283.3 g.
Octyl/decyl glycidyl ether (as in example 10), 0.65 mole	148.6 g.

was added gradually from an addition funnel over a period of 1¼ hour. The exotherm raised the temperature of the reaction mass from 26° C. to 46° C. On heating to 70° C., the acid number fell to 8.0.

Although this constitutes a yield of 87.6 percent nonionic phosphate ester, an additional 0.05 mole, 11.4 g. of the oxide was added and the reaction continued for 1 hour, whereupon the acid number dropped to 5.5, with a corresponding 9.13 percent yield of the nonionic ester.

The compound was a pale amber liquid, giving a 67 percent transmittance at 425 mμ, as compared to the much darker acid phosphate precursor, which gave a transmittance of only 15 percent. This surfactant gave good results in drycleaning detergent evaluations.

EXAMPLE 17

Production of nonionic 2-hydroxypropyl ester of mono and di acid phosphate of linear primary alkanol (C_{12}-C_{13}) polyoxyethylate.

The apparatus employed in the previous example was charged with:

phosphoric acid ester, example 8, 1.0 mole	306.0 g.
Propylene oxide, 1.4 mole	81.3 g.

was gradually added from the funnel. The reaction temperature was held below 35° C. through external cooling with ice/water. The addition of the oxide required about 1½ hours. The reaction mass was then heated to 60° C. for 2 hours.

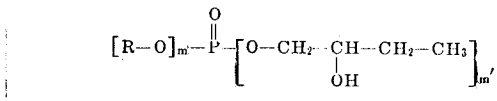
A sample taken showed less than 70 percent conversion to the nonionic ester, based upon the calculated acid value of the reagents. A further addition of 0.4 mole, 23.2 g. of propylene oxide brought the acid number to 25.7, corresponding to 81.2 percent conversion to the nonionic ester.

A second increment of 23.2 g. (0.4 mole) of propylene oxide resulted in a drop of acid value to 4.3, or a 96.6 percent conversion to the nonionic phosphate. At this point 2.2 moles of the oxide had been consumed, to bring the conversion to the nonionic ester to 90 percent or greater. This large excess of the alkylene oxide is believed to be necessary because of the higher concentration of free phosphoric acid in the precursor formed in the process of example 8, where polyphosphoric acid was used. This is a substantially higher excess than required with acid phosphates prepared by reaction with P_2O_5. The latter are therefore preferred. The oxide charged had combined nearly quantitatively with the resulting phosphate, since upon stripping at 80° C. and 28½ inches of vacuum for 1 hour the yield found was 97.7 percent of theory.

EXAMPLE 18

Production of nonionic 2 -hydroxybutyl ester of mono and di acid phosphate of n-octanol.

This compound conforms to the following formula:



where R is n-octyl, and *m* and *m'* have the values shown in example 9.

A 1,000 ml. flask equipped as in example 9 was charged with:

mono and di phosphoric acid ester of described 5, example 5, 2.0 moles (based on acid number	363.1 g.
1,2 Butylene oxide, 3.4 mole	245.1 g.

was added gradually at an initial temperature of 23° C. A top temperature of 40° C. was recorded during the additions. The batch was finally heated to 60° C. for 2 hours.

The resulting compound was a light, straw-colored liquid, having an acid number of 4.7, calculating as a 97.6 percent conversion to the nonionic phosphate ester.

The product proved to be insoluble in distilled or hard water.

The presence of diglycolether esters as a result of side reaction is also indicated by the infrared spectrum of a sample of example 18. In this example, no other ether group would be present in the structure. An infrared absorption band typical for the ether linkage occurred at 9 μ, typical for the C—O—C ether linkage. The presence of such minor amounts of side reaction product has not proved detrimental.

EXAMPLE 19

Production of nonionic 2-hydroxybutyl ester of mono and di acid phosphate of n-octyl diethyleneglycol ether.

The structural formula is that given in example 9, where R is n-octyl and the integer "n" is two.

The apparatus shown in the previous example was charged with:

mono and di phosphoric acid ester of n-octyl diethyleneglycol ether, described in example 4, 2.0 moles	536.8 g.
1,2 Butylene oxide, 3.0 moles	216.3 g.

was added over a period of 3 hours. The batch temperature rose from 24° C. to 36° C. through the exothermic reaction. On cooling and standing overnight, the acid number had dropped to 7.5. The reaction mass was heated under agitation to 60° C. for 3 hours the following day. This resulted in a final acid number of 4.9 and corresponded to a nonionic ester conversion of 96.7 percent.

The product was a nearly colorless liquid, giving a 93 percent transmittance at 425 mμ, as compared to 64 percent for the acid ester precursor of example 4.

This surfactant is useful as a wetting ad dispersing agent where frothing properties are undesirable. These values are shown in the tables below.

The detergency efficiency tests summarized in table I demonstrate a marked superiority of the nonionic 2 -hydroxylalkyl and 3 -alkoxy-2-hydroxypropyl phosphate esters over the analogous precursor anionic phosphates from which they are derived. The compounds of this invention are therefore highly useful as organic surfactants in laundering operations. They are particularly desirable where excessive foam generation is to be avoided, as is the case in commercial laundering machines and household washing machines having tumbling action.

TABLE I

DETERGENCY OF PHOSPHORIC ACID ESTER AND 2-HYDROXY-ALKYL OR 3-ALKOXY-2-HYDROXYPROPYL NONIONIC PHOSPHATE ESTERS DERIVED THEREFROM

Method: A Terg-O-Tometer, Model BD–101 was employed as the washing vessel. Wash cycle: 20 minutes at 140° F., Rinse cycle: 10 minutes at 140° F; 100 oscillations per minute; Water hardness: 150 p.p.m. pH: 11.0±0.1; **Volume**: 1 liter per test run.

Reflectance values measured with a Photovolt photoelectric reflection meter, Model 610, using a 610–Y search unit and a green tristimulus filter. Artificially soiled cotton fabric employed is supplied by Testfabrics, Incorporated, and measures 9 × 14 inches (14 g.).

W = Reflectance value of white portion before laundering (97).

S = Reflectance value of soiled portion before laundering (30).

S 1 = Reflectance value of soiled portion after laundering.

$$\text{Detergency efficiency, percent} = \frac{S1 - S}{W - S} \times 100.$$

Detergent builder: 1.74 g./1 sodium meta silicate, anhydrous;
0.02 g./1 carboxymethylcellulose.
Surfactant: 0.24 g./1, solids basis.

Surfactant	Reference: product of—	Detergency efficiency, (percent)	Increased detergency over anionic precursor taken as 100%* (percent)
Sodium salt of mono and di phosphoric acid of:			
Nonylphenol polyoxyethylate, 6 e.o.	Example 7	40.3	--
Nonylphenol polyoxyethylate, 9 e.o.	Example 6	34.3	--
Linear primary alkanol (C_{12}–C_{13}) polyoxyethylate, 6.5 e.o.	Example 1	35.8	--
Linear primary alkanol (C_{12}–C_{15}) polyoxyethylate, 9 e.o.	Example 2	25.4	--
Nonionic 2-hydroxypropyl phosphate ester of; Nonylphenol polyoxyethylate, 6 e.o.	Example 14	49.3	122.3
Nonionic 2-hydroxybutyl phosphate ester of:			
Nonylphenol polyoxyethylate, 9 e.o.	Example 15	41.8	121.9
Linear primary alkanol (C_{12}–C_{13}) polyoxyethylate, 6.5 e.o.	Example 9	45.5	127.1
Nonionic 2-hydroxyoctyl phosphate ester of; Linear primary alkanol (C_{12}–C_{15}) polyoxyethylate, 9 e.o.	Example 11	35.8	140.9
Nonionic 3-alkoxy (C_8–C_{10})-2-hydroxypropyl phosphate ester of:			
Linear primary alkanol (C_{12}–C_{13}) polyoxyethylate, 6.5 e.o.	Example 10	43.3	120.9
Linear primary alkanol (C_{12}–C_{15}) polyoxyethylate, 9 e.o.	Example 12	34.3	135.0

NOTE.—e.o. = moles ethylene oxide in the adduct; * Ratio of detergent efficiency of nonionic to precursor.

Of further significant value here, as well as in other cleaning operations, is the relative uniformity of froth level of these novel phosphate surfactants in soft and hard water. It will be noted from table II that the foam height of anionic phosphate esters fluctuates greatly based upon water hardness. The foam height values of the nonionic counterparts for hard and soft water are closely related.

The foaming properties and stabilities were determined using the Ross-Miles foam test, as described in *Oil and Soap*, 18:99–102 (1941). In this procedure a sample of surfactant solution is discharged from a reservoir through an orifice, to fall through a prescribed height into a pool of like solution. The temperature and pH were controlled to the value shown.

TABLE II.—FOAMING AND WETTING PERFORMANCE OF NONIONIC 2-HYDROXYALKYL PHOSPHATES AND THEIR ANIONIC PRECURSORS

[Solutions having an activity of 0.1%, pH 7.0± 0.2, at 25° C.]

	Hardness of water, p.p.m.	Ross-Miles foam Numbers, in mm.— Instant	60 seconds	300 seconds	Draves test in seconds
Anionic phosphate ester:					
Example 1	0	150	140	130	65
	200	45	30	20	
Example 6	0	155	140	135	39
	200	105	95	70	
Example 7	0	150	130	125	38
	200	40	35	30	
Nonionic phosphate esters:					
Example 9	0	100	95	90	24.5
	200	90	85	80	
Example 15	0	100	105	100	20
	200	110	105	100	
Example 14	0	75	70	70	30
	200	40	35	30	

As can be observed from this table II, the wetting properties of the nonionic species are also found substantially superior to those of the anionic precursors.

The wetting test employed was the Draves Test, synthron tape method, as adopted from the tentative procedures presented to the Auxiliaries and Testing Group Meeting of the American Association of Textile Chemists and Colorists, Atlantic City Convention, 1949.

The large reduction in time shows a large increase in wetting properties for the nonionic ester as compared with the precursor.

Particularly noteworthy is the ability of these compounds to couple water into the solvent solution and act as superior drycleaning agents.

The nonionic surface active 2 -hydroxyalkyl and 3 -alkoxy-2-hydroxylpropyl phosphate esters provide outstanding properties as lubricants and lubricating oil additives, to improve antiwear properties of mineral, vegetable and animal oils. Table III demonstrates the improvement in wear properties obtained by addition of these nonionic esters to white grease (similar to lard) or Industrial Pale Oil (mineral oil), using the Falex Lubricant Tester.

TABLE III.—FALEX TEST DATA ON FATTY AND MINERAL OILS WITH AND WITHOUT ADDITION OF NONIONIC 2-HYDROXYALKYL AND 3-ALKOXY-2-HYDROXYPROPYL PHOSPHATE ESTERS

Lubricant: percent by weight	Time Minutes	Time Seconds	Jaw load, lbs.	Torque, lbs./in.
White grease, 100%	2		250	4
	3		980	22
	3	40	1,150	28
	4		1,200	[1] 29
White grease, 90%; nonionic phosphate ester, Example 12, 10%	2		250	3
	3		950	18
	4		1,650	30
	5		2,100	32
	5	24	2,150	[1] 35
White grease, 99%; nonionic phosphate ester, Example 9, 1%	0		250	4
	1		1,000	22
	2¼		1,750	[1] 38
White grease, 97½%; nonionic phosphate ester, Example 9, 2½%	0		250	4
	1		950	24
	2¾		2,250	[1] 45
White grease, 95%; nonionic phosphate ester, Example 9, 5%	0		250	4
	1		950	20
	2¾		2,350	[1] 39
Pale oil, 100 SSU/100° F., 100%	0		250	5
	½		600	[1] 18
Pale oil, 100 SSU, 95%; nonionic phosphate ester, Example 12, 5%	0		250	5
	1		1,000	22
	1¾		1,600	[1] 28
Pale oil, 100 SSU, 80%; nonionic phosphate ester, Example 12, 20%	0		250	5
	1		1,000	22
	2¼		1,800	[1] 35

[1] Failure.

Table IV shows the performance of the indicated ester as an additive to white grease with the evaluation based on the Timken Lubricant Tester. Both testing devices are described in *Lubrication Engineering*, 24(8): 349–376 (1968).

TABLE. IV—TIMKEN LUBRICANT TEST DATA ON AQUEOUS EMULSION OR DISPERSION IN TAP WATER (HARD WATER) OF WHITE GREASE AND WHITE GREASE MODIFIED WITH NONIONIC PHOSPHATE.

Ester of Example 9

Dispersion of 5% white grease in tap water:
- 15 lbs ..... O.K.
- 20 lbs ..... Failure.

Emulsion of 4% white grease and 1% phosphate, Example 9:
- 15 lbs ..... O.K.
- 20 lbs ..... O.K.
- 25 lbs ..... O.K.
- 30 lbs ..... O.K.
- 35 lbs ..... Failure.

Table III shows that the addition of 10 percent by weight of the nonionic phosphate ester of example 12 to white grease provides nearly double the load bearing properties of the grease in the absence of the additive.

Table III also gives the performance of the nonionic phosphate ester of example 9 in incremental replacement of white grease. Nearly double the jaw load was registered with white grease containing only 2½ percent of this ester.

As will be seen from the table, the white grease failed at a jaw load of 1200 pounds. The addition of 10 percent of the ester of example 12 permitted the lubricant to withstand almost twice the load, i.e., 2150 pounds, before failure.

As little as 1 percent of the compound of example 9 permitted an application of 1.4 times the load tolerated by the grease alone. The addition of 2½ percent of the compound of example 9 increased the load from 1200 to 2250, i.e., about 1.8 times, and the addition of 5 percent doubled the load carrying capacity of the grease.

A similar result was obtained with Pale Oil. The addition of 5 percent of the compound of example 12 more than doubled, and the addition of 20 percent tripled, the load carrying capacity of the Pale Oil.

These nonionic phosphate esters may be used to provide emulsifying as well as antiwear properties. This is particularly desirable in the preparation of soluble oil cutting compounds, die casting lubricants, grinding fluids, etc.

The following composition, when poured into hard or soft water, forms instantaneous stable emulsions:

Pale Oil 100 SSU/100° F.	90.00*	
Nonionic phosphate, example 12		9.75
Morpholine	0.25 (to	
adjust the pH to 8 or above).		

*All parts by weight.

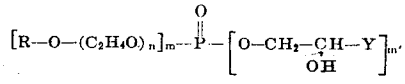
Freshly polished steel coupons immersed one-half in emulsions formed in 10 times and 30 times the volume of tap water were free of rust or corrosion below and above the surface level on standing for 1 week.

Utilizing the information given above, species of these nonionic 2-hydroxyalkyl and 3-alkoxy-2-hydroxypropyl esters may be prepared within the generic structure shown to give maximum performance for a given application.

While I have described particular embodiments of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, as set forth in the following claims.

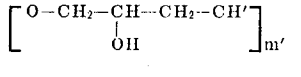
I claim:

1. Surface active nonionic phosphate esters chosen from the group consisting of the 2-hydroxyalkyl and 3-alkoxy-2-hydroxyalkyl phosphate esters conforming to the following general formula:

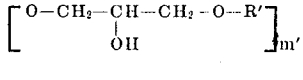


where R is a linear or branched alkyl group having carbon atoms in the range of eight to 18 carbon atoms, of which at least six carbon atoms are in an uninterrupted carbon-to-carbon chain; or an alkylphenyl group having carbon atoms in the range of eight to 15 carbon atoms in a linear or alkyl group, in which the alkyl constituent has at least four carbon atoms in an uninterrupted carbon-to-carbon chain, which may be branched; and Y is hydrogen or a methyl group, or an uninterrupted chain of carbon atoms in the range of two to 16 carbon atoms, or a methoxyalkyl group $-CH_2-O-R'$ where R' is a methyl radical or an alkyl radical of carbon atoms in the range of two to 18 carbon atoms; n is a number in the range of from two to 20; m is one or two; m' is one or two; and $m+m'$ equals three.

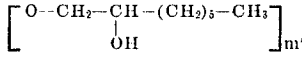
2. A composition of matter according to claim 1 in which R is alkyl group of from C_{12} to C_{15} or mixtures of said esters and the hydroxyalkyl ester radical is



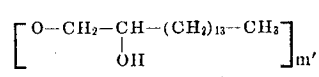
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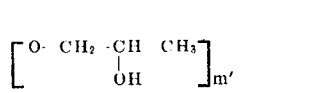
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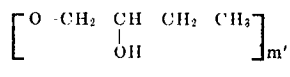


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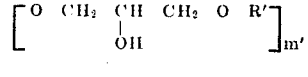


3. A composition of matter according to claim 1, in which R is an alkyl group C_{11} C_{15}, and mixtures of two or more of said nonionic phosphate esters.

4. A composition of matter according to claim 1, in which the hydroxyalkyl ester radical is

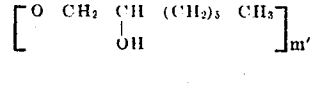


5. A composition of matter according to claim 1, in which the hydroxyalkyl radical of said ester is

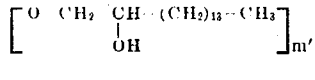


in which R' is n-octyl or n-decyl or mixtures of said esters.

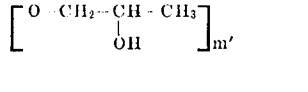
6. A composition of matter according to claim 1, in which the hydroxyalkyl radical is:



7. A composition of matter according to claim 1, in which the hydroxyalkyl ester radical is



8. A composition of matter according to claim 1, in which the hydroxyalkyl ester radical is



9. A composition of matter according to claim 1, in which n is a number in the range of from about six to nine.

10. A composition of matter according to claim 9, in which the R radical is nonylphenyl, or mixtures of said esters.

* * * * *

PO-1000
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,626,035 Dated December 7, 1971

Inventor(s) ROBERT ERNST

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the abstract, correct the formula to be as follows:

$$[R\text{-}O(C_2H_4O)_n]_m\text{-}P(=O)\text{-}[O\text{-}CH_2\text{-}CH(OH)\text{-}Y]_{m'}$$

1. Column 1, line 47: Change "m" to -m'-
2. Column 2, line 22: Change "1965" to -1956-
3. Column 3, line 45: Change "an" to -can-
4. Column 4, line 50: Change "$(C_{12}\text{-}C_5)$" to -$(C_{12}\text{-}C_{15})$-
5. Column 4, line 53: Change "57.07" to -570.7-
6. Column 4, line 64: Change "Pastry" to -Pasty-
7. Column 4, line 71: Change "$(C\text{-}C_{15})$" to -$(C_{11}\text{-}C_{15})$-
8. Column 5, line 29: Change "N-octyl" to -n-octyl-
9. Column 5, line 53: Change "Owith" to -reacted with-
10. Column 6, line 74: Insert -4.2- before "moles"
11. Column 8, line 45: Strike "100.6 mole" and insert in place thereof -Example 10) 0.6 mole-
12. Column 9, line 7: Change "an" to -and-
13. Column 9, line 39: Change "roe" to -rose-
14. Column 9, line 46: Change "eater" to -ester-

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,626,035 Dated December 7, 1971

Inventor(s) ROBERT ERNST

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

15. Column 9, line 73: Change "1,6 butylene" to -1,2 butylene-

16. Column 10, line 4: Change "plate" to -pale-

17. Column 10, line 33: Change "9.13" to -91.3-

18. Column 11, line 17: After "of' insert -n-octanol-

19. Column 11, line 17: Change the number "5" first occurrence to -in-

20. Column 12, line 9: Change "ad" to -and-

21. Column 12, lines 13 and 14: Change "2-hydroxylalkyl" to -2-hydroxyalkyl-

22. In Claim 2, line 1: Change "Claim 1" to -Claim 9-

23. In Claim 9, line 2: Insert -about- before "nine"

Signed and sealed this 20th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents