United States Patent Office 3,352,790 Patented Nov. 14, 1967

3,352,790

PROCESS AND COMPOSITIONS FOR DRY CLEANING

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No Drawing. Filed Feb. 21, 1964, Ser. No. 346,414
16 Claims. (Cl. 252—171)

This invention relates to improvements in the dry cleaning of fibrous textiles and related materials and more particularly to new and improved compositions for use with dry cleaning solvents, and to processes of dry cleaning wherein said improved compositions are employed.

It is well known that many types of fabrics and materials cannot be cleaned by the ordinary means of soap or detergents and water, such as are employed in laundering type operations since the presence of water deleteriously affects such materials. To provide effective cleaning for such materials, a dry cleaning process must be used. Dry cleaning processes employ organic solvents which are effective in removing from the materials treated most of the undesirable dirt, grease, dust and the like. It is also a common expedient in dry cleaning processes to add a small amount of water which, sufficiently dispersed in the dry cleaning fluid, will be effective to remove water-soluble stains without adversely affecting the materials treated.

It is therefore an object of this invention to provide new compositions, particularly suitable for use in dry cleaning operations.

It is a further object of this invention to provide new compositions suitable for use in all of the generally employed dry cleaning solvents.

It is a still further object of this invention to provide new compositions which give outstanding and improved cleaning ability by virtue of an outstanding detergency action coupled with an excellent ability to prevent soil redeposition on the materials treated.

It is another object of this invention to provide an improved process of dry cleaning in all types of dry cleaning solvents.

It is a further object of this invention to provide an improved process of dry cleaning wherein the usual dry cleaning solvents are employed in conjunction with minor amounts of water.

The compositions of the present invention comprise the usual organic dry cleaning solvent and a phosphate ester of a non-ionic surfactant hereinafter to be more fully described. In addition, other surfactants may be present as well as a small amount of water, e.g., 0.1 to about 10%.

Among the dry cleaning solvents one may use and which are normally employed in the dry cleaning industry are the following:

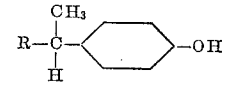
fluoro carbons e.g., trichlorotrifluoro ethane
naphtha
trichloroethylene
tetrachloroethylene
perchloroethylene
carbon tetrachloride
Stoddard Solvent, flash point 100° F.
Stoddard Solvent, flash point 140° F.

The phosphate esters of non-ionic surfactants which are herein contemplated are mono- and diphosphate esters and mixtures thereof which non-ionics contain from about 1 mole up to about 75 to 95% weight percent of alkylene oxide. The alkylene oxides or precursors thereof which may be employed to yield the corresponding oxyalkylene groups in the non-ionic surface active agents are those which contain from 2 to 4 carbon atoms such as ethylene

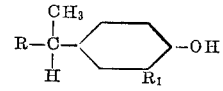
oxide, propylene oxide, butylene oxide, butylene dioxide, epichlorohydrin, isobutylene oxide, and the like. Since it is essential that the phosphate esters herein contemplated have solubility of a significant amount as hereinafter disclosed in the hydrocarbon or chlorinated hydrocarbon dry-cleaning solvent, the upper limit of ethylene oxide which may be used is about 75% by weight based upon the weight of the non-ionic surfactant. Above this amount the ethylene oxide condensates are too hydrophilic to have the requisite solubilities. With oxyethylene groups containing 3 carbon atoms, e.g., derived from propylene oxide, up to about 85% by weight thereof may be combined in the non-ionic surfactant. Using oxyyalkylene groups containing 4 carbon atoms such as derived from the interaction with butylene oxide up to about 95% of such grouping based upon the total weight of non-ionic surfactant may be employed. In addition, it is clear and obvious that mixtures of such oxyethylating reagents may be used whereby there results in the non-ionic surfactant variations in the oxyalkaline groups.

The non-ionic oxyalkylated products which are herein contemplated as precursors for the phosphate esters are well known in the art and are derived from a reactive hydrogen compound and the alkylene oxide as, for example, disclosed in U.S. Patents 2,213,477 and 1,970,578. In general, the reactive hydrogen compound is a hydrophobic moiety such as a phenol, alkylated phenol, thiophenol, higher alcohol, higher mercaptan, higher alkyl or aryl amide, higher alkyl or aryl sulfonamide, and the like containing a least about 8 carbon atoms. The reactive hydrogen compound may be a propylene or butylene oxide polymer (e.g., M.W. 400 to 4000), or the reaction product of an amine, e.g., ethylenediamine or an alcohol or phenol or the like with propylene or butylene oxide. The following illustrate some typical reactive hydrogen compounds suitable for reaction with ethylene oxide to yield non-ionic surfactants as precursors for the instantly contemplated phosphate esters:

nonylphenol (propylene trimer)
octylphenol (diisobutylene)
dodecylphenol (propylene tetramer)
diamylphenol
dibutylphenol
alkylphenols, where alkyl is C_4 to C_{18}
alkyl cresols, where alkyl is C_4 to C_{18}
mixed "coco" alcohols
lauryl alcohol (85% C_{12} alcohol)
lauryl alcohol (92% C_{12} alcohol)
tridecyl (oxo) alcohol
oleyl alcohol
hydrogenated tallow alcohol
R—OH prepared from olefins of C_8 to C_{22} by the "oxo" process, i.e., addition of $H_2C{=}O$ and hydrogenation to the alcohol R—OH where R=C_8 to C_{22}

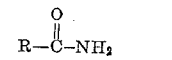


where R=n-C_4H_9 to n-$C_{22}H_{45}$



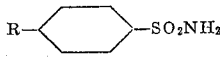
where R=n-C_4H_9 to n-$C_{22}H_{45}$

R—SH; R=C_8 to C_{22}



R=C_8 to C_{22}

:—SO_2NH_2 R=C_8 to C_{14}



:=C_6 to C_{18}

'olypropylene oxide of M.W. 400 to 2500

$I_2N—CH_2CH_2NH_2$+propylene oxide to M.W. 800 to 2500

(—NH_2 or X$(NH)_2$+propylene oxide to M.W. 400 to 2500

(—OH or X—$(OH)_2$+propylene oxide to M.W. 800 to 2500

(=residue of active hydrogen compound

The above types of compounds are then reacted with :thylene oxide and the like to yield the non-ionic used to)repare the phosphate esters.

The phosphate esters used in the present invention nay be prepared by numerous techniques. The preferred nethod involves the reaction of one mole of P_2O_5 with ! to 4.5 moles of the non-ionic surfactant as described ınd claimed in U.S. Patent 3,004,056 by Nunn and Hense ınd U.S. Patent 3,004,057 by Nunn. As described in he said Nunn and Hesse patent, the reaction between he P_2O_5 and the non-ionic polyoxyalkylene ether is :onducted under substantially anhydrous conditions and ıt a temperature below about 110° C. In its perferred 'orm, the reaction is carried out by adding the P_2O_5 ;radually, with vigorous agitation to the non-ionic sur- 'ace active agent in liquid form. The reaction is exo- hermic and cooling is in some cases necessary to keep he temperature below 110° C., since discolored and larkened products tend to be produced above this tem-)erature. The reaction proceeds continuously during the ıddition of the P_2O_5 and is preferably followed by main- enance of the reaction mixture at ambient temperatures ıp to 110° C. for an additional period of time after :ompletion of such addition to allow for complete solu- :ion of the P_2O_5 and reaction with the non-ionic sur- face active agent.

The exact chemical constitution of the products pro- duced by the above described reaction is not definitely known in view of the recognized tendency of the P_2O_5 to form complex products and polymers in such re- actions with hydroxylic compounds. In general, the product will usually contain about 20 to 45% of the secondary phosphate ester of the non-ionic agent, 30 to 80% of the primary phosphate ester, 0 to 40% of unreacted non-ionic agent, and small amounts of unidenti- fied by-products.

The following examples illustrate the preparation of such phosphate esters.

Example A

2.7 moles of a non-ionic surface active compound derived from dinonyl phenol condensed with 4 moles of ethylene oxide is reacted with 1 mole of P_2O_5 in the manner described in the examples of U.S. Patent 3,004,- 056. The product consists of about equal amounts of mono- and di-ester with about 10–15% unreacted non- ionic.

Example B

The procedure of Example A is repeated except that the non-ionic compound is derived from the interaction of nonyl phenol with 1.5 moles of ethylene oxide (ethyl- ene oxide content of condensate 29.2%).

Example C

The procedure of Example B is repeated except that 6.0 moles of ethylene oxide are condensed to yield a non-ionic containing 54.5% etthylene oxide.

Example D

Example B is again repeated except that about 10 moles of ethylene oxide are reacted to yield a conden- sation product containing about 64% ethylene oxide.

Example E

Example A is again repeated except that the reaction is carried out between tridecyl alcohol (obtained by the oxo process from using triisobutylene) and 9.75 moles of ethylene oxide to yield a product containing 68% ethylene oxide.

Example F

The procedure of Example A is repeated except that the non-ionic is a dodecyl phenol plus 2 moles of ethyl- ene oxide condensate.

Example G

The procedure of Example A is again repeated employ- ing as the non-ionic surface active agent a dinonyl phenol plus 5 moles ethylene oxide (40% ethylene oxide con- tent).

Example H

The procedure of Example A is once again repeated employing as the surfactant a dinonyl phenol plus 7 moles ethylene oxide (47% ethylene oxide content).

Example I

The procedure of Example A is still once again re- peated employing as the non-ionic surface active agent dinonyl phenol reacted with 1.5 moles of ethylene oxide to yield non-ionic product containing about 20% ethyl- ene oxide.

Example J

The above procedures are again repeated using as the non-ionic procedure the condensation product of dodecyl phenol with 1.8 moles of ethylene oxide.

Example K

In the following examples the procedure of Example A is reptated using the indicated non-ionic compounds:

(1) iso-otcyl alcohol+2.5 E.O.
(2) nonyl alcohol+3 E.O.
(3) dodecyl mercaptan+2 E.O.
(4) dodecyl mercaptan+9 E.O.
(5) cetyl mercaptan+4 E.O.
(6) dinonyl phenol+9.6 E.O.
(7) dinonyl thiophenol+6 E.O.
(8) soya bean oil amine+10 E.O.
(9) resin amine+15 E.O.
(10) iso-octyl amine+8 E.O.
(11) dodecyl benzene sulfonamide+10 E.O.
(12) decyl sulfonamide+6 E.O.
(13) oleic acid+15 E.O.
(14) stearic acid+12 E.O.
(15) stearamide+8.5 E.O.
(16) tetradecylbenzamide+12 E.O.
(17) polypropylene glycol (average M.W.=750)+2 E.O.
(18) polypropylene glycol (average M.W.=400)+6 E.O.
(19) dinonyl phenol+15 E.O.

By carrying out the above reaction in the presence of a small amount of a phosphorus-containing compound se- lected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid, preferably sodi- um hypophosphite or hypophosphorous acid, as described in said Nunn 3,004,057 patent, lighter colored or sub- stantially colorless reaction products are obtained.

While the presence of unreacted non-ionic is not detri- mental to the attainment of the objects of the present invention, the amount of non-ionic can be reduced, if desired, to a minimum of less than about 10% by in- corporating in the reaction mixture, a small amount of mineral acid such as phosphoric acid, hydrochloric acid or sulfuric acid. Since phosphorous pentoxide yields phos-

phoric acid in the presence of water, the latter can advantageously and preferably be used to form the acid "in situ." With the use of the mineral acid the amount of phosphorous pentoxide can also be increased to as much as 3 moles per mole of non-ionic reactant, thereby favoring the formation of the monoester in major amounts, i.e., substantially no diester.

Monoesters and diesters can also be prepared from the corresponding triesters by reacting the triester with phosphoric acid. By varying the ratio of non-ionic to acid, one can prepare either mono- or diester to the substantial exclusion of the other. A high ratio of triester to acid (2:1) produces diester whereas a low ratio (0.5:1) produces monoester.

Example L

Equimolar amounts of the non-ionic surface active compound of Example A and phosphorous pentoxide are heated at 90° C., while adding in the presence of about 0.4% water the P_2O_5 over a period of one hour. Then the reaction mixture is heated for 4 hours at 125° C. The final product is a monoester.

Example M

Example L is repeated employing one mole of a dodecyl phenol plus 2 moles ethylene oxide condensate and two moles of P_2O_5. The final product is a monoester.

Example N

Example L is again repeated using the following non-ionics:

A. octadecanol+3 moles ethylene oxide
B. hexadecanol+4 moles ethylene oxide
C. 1-eicosoanol+6 moles ethylene oxide
D. 1-doctriacontenol+7 moles ethylene oxide
E. dodecyl phenol+5 moles ethylene oxide
F. hexadecyl phenol+3 moles ethylene oxide
G. tri-n-octyl phenol+4 moles ethylene oxide
H. tri-n-octyl phenol+5 moles propylene oxide
I. dodecyl phenol+3 moles propylene oxide
J. dinonyl phenol+1.5 moles propylene oxide
K. diisohexyl phenol+2 moles propylene oxide
L. tri-n-butyl phenol+2 moles propylene oxide
M. tri-n-butyl phenol+3 moles propylene oxide
N. tri-n-butyl phenol+4 moles propylene oxide
O. tri-n-butyl phenol+3 moles ethylene oxide
P. hexadecanol+3 moles propylene oxide
Q. octadecanol+4 moles propylene oxide
R. butyl hexyl phenol+4 moles ethylene oxide
S. ethyl heptyl phenol+5 moles ethylene oxide
T. ethyl heptyl phenol+3 moles propylene oxide
U. ceryl alcohol+2 moles ethylene oxide
V. 1-octacosanol+4 moles ethylene oxide
W. 1-nonacosanol+7 moles ethylene oxide
X. 1-triacontenol+6 moles ethylene oxide
Y. 1-tetratriacontenol+5 moles ethylene oxide
Z. 1-tetratriacontenol+2 moles propylene oxide

Example O

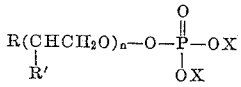
A phosphate triester of the non-ionic compound of Example A is prepared by reacting 3 moles of said non-ionic with 1 mole of phosphorous oxychloride in the presence of 1 mole of pyridine and 100 ml. of benzene. The $POCl_3$ is added dropwise to the other components at a temperature of about 0° C. and the temperature is held below 10° C. After all of the $POCl_3$ has been added, the mixture is refluxed for 3 hours and then the solvent is removed under vacuum distillation. The triester results.

The triester is converted to a monoester by adding 1 mole of phosphoric acid to 0.5 mole of the triester at about room temperature. The monoester results.

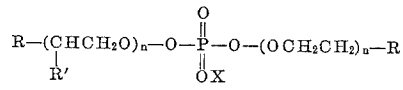
Example P

Example O is repeated except that 2 moles of triester are used in lieu of 0.5 mole. The diester results.

The mono- and di-phosphated products may be represented by the following formulae:

I 

and

II 

wherein R' represents H, methyl, ethyl, etc.; R represents the reactive hydrogen compound; X may be hydrogen or alkali metal, alkaline earth metal, ammonium, or amine (water soluble or insoluble) preferably lower aliphatic including hydroxyamines; and n=number of moles of alkylene oxide necessary to yield a final product containing 5 to 95% by weight thereof; mathematically this may be represented as follows:

$$\frac{44n}{\text{M.W of (R)}+44n}=0.05 \text{ to } 0.95$$

where R is the reactive hydrogen compound.

The phosphate esters which are herein contemplated are possessed of the following outstanding and desirable characteristics which are important in dry cleaning:

(1) They are readily soluble in the two types of solvents currently being used for dry cleaning, namely, Stoddard Solvent and perchloroethylene.

(2) They promote excellent carbon soil detergency and anti-redeposition properties by themselves in the two solvents.

(3) They are compatible with non-ionic and anionic surfactants and most organic solvents employed in dry cleaning thus rendering them suitable for formulating, if desired.

(4) They are manufactured in the form of free acids, thus offering wide latitude in both degree of neutralization and in selection of base used for neutralization. Among the bases which can be used are the following: sodium hydroxide, potassium hydroxide, barium hydroxide, methylamine, isopropulamine, ethylene diamine, various ethoxylated and unethoxylated fatty amines such as tall oil amine, soya amine, oleylamine, imidazolines, and aminoamides.

(5) They are extremely light in color, odorless and not subject to rancidity or breakdown. Consequently, no detrimental effects on fabrics can result due to these causes.

(6) The phosphate esters are excellent anti-static agents and so will reduce the danger of static charge build-up. This is important in the case of petroleum based solvents in the dry cleaning process.

(7) These products have the ability to "solubilize" certain amounts of moisture which is necessary in dry cleaning for the removal of water soluble stains such as salt and sugar.

(8) Only small amounts of water are necessary to effect outstanding removal of water-soluble products. This is important where larger amounts of water would cause shrinkage of woolens and the like.

The compositions of the present invention comprise from about 0.2 to about 10 parts by weight of the phosphate ester and 90 to 99.8 parts of the solvents. In a more concentrated form the compositions comprise 20–80 parts (or even 100 parts) by weight phosphate ester and 20–80 parts of a suitable vehicle in which the phosphate ester is soluble. In each instance the total parts should be 100.

The formulations hereinafter to be described where specific data is indicated for detergency and redeposition characteristics are tested as follows: 50 ml. of phosphate ester is dissolved in 50 ml. of selected dry cleaning solvent. 4 ml. of this concentrate is diluted to 100 ml. with the same solvent. To this 100 ml. in a mason jar there

re added 50 ¼" steel balls, one 3¾" x 4" clean woolen watch and one 3¾" x 6" carbon soiled woolen swatch nd then agitated in a Launderometer for ½ hour at oom temperature. The swatches are rinsed in fresh solent and dried. Reflectance readings are taken before and fter cleaning by means of a Photovolt Reflectometer, iodel 610. In the examples, the detergency values are xpressed as increase in reflectance units of the clean watch over the soiled swatch so consequently a higher alue indicates increased soil removal. Conversely, redeposition figures are expressed as decrease in reflectance nits of the clean swatch before and after the dry cleanng cycle so a lower figure indicates increased anti-soil edeposition properties.

In the following examples which are by way of illustration only, parts are by weight unless otherwise indiated.

Example 1

50 ml. of the sodium salt of a phosphate ester prepared s described below is dissolved in 50 ml. of Stoddard olvent: then 4 ml. of this concentrate is diluted to 100 nl. with Stoddard Solvent. This diluted solution is then sed to test a carbon soiled woolen swatch for detergency nd a clean woolen swatch for redeposition as described bove.

A. *Preparation of phosphate ester.*—2.7 moles of a onylphenol (propylene trimer) condensate with 9.5 noles of ethylene oxide is reacted with 1 mole of P_2O_5 n the presence of sodium hypophosphite following the rocedure described in the said Nunn U.S. Patent 3,004,-)57. The product consists of about equal amounts of nono- and di-ester with about 10–15% residual unreacted ion-ionic. Sodium hydroxide is used to neutralize the ree acid and bring the pH to about 7.0 whereby the odium salt is formed. The detergency in the Stoddard olvent shows an increase of 13.0 reflectance units and or redeposition a decrease of 7.9 units. In the following able a comparison with other detergents is shown.

TABLE I

	Detergency	Redeposition
(a) Example 1	13.0	7.9
(b) Dinonyl phenol plus moles ethylene oxide	9.6	14.2
(c) Nonyl phenol plus 6 moles ethylene oxide	0.6	40.1
(d) Isopropylamine dodecyl benzene sulfonate	11.4	9.0
(e) Commercial Product A	12.1	9.8
(f) Commercial Product B	10.9	10.9

From the above it is evident that the product of Example 1 is superior to all of the others in redeposition and detergency characteristics.

Example 2

Example 1 is repeated except that perchloroethylene is used as the solvent. In Table II the results are given, and a comparison with products (b) through (g) of Table I.

TABLE II

Product	Detergency	Redeposition
Example 2	19.4	3.8
(b)	14.3	17.8
(c)	13.1	18.9
(d)	15.4	10.1
(e)	18.2	8.7
(f)	13.1	16.9
(g) Nonyl phenol plus 9.5 moles ethylene oxide	12.4	20.5
(h) 1:1 mixture of isopropylamine dodecyl benzene sulfonate plus dinonyl phenol condensed with 7 moles ethylene oxide	10.5	16.5

Again it is clear that in perchloroethylene the product of Example 2 is far superior to all others in redeposition characteristics and much better than the others in detergency value. Only product (e) comes close to Example 2 in detergency but here redeposition is far poorer in the competitive product.

Example 3

Examples 1 and 2 are repeated employing 4 moles of a non-ionic derived from nonyl phenol and 6 moles of ethylene oxide reacted with 1 mole of P_2O_5 and converted to the sodium salt. This product is compared to products (b) through (h) above and the results are shown in Table III.

TABLE III

Product	Detergency		Redeposition	
	Perchloroethylene	Stoddard	Perchloroethylene	Stoddard
Example 3	22.0	14.5	6.3	4.9
(b)	14.3	9.6	17.8	14.2
(c)	13.1	0.6	18.9	40.1
(d)	15.4	11.4	10.1	9.0
(e)	18.2	12.1	8.7	9.8
(f)	13.1	10.9	16.9	10.9
(g)	12.4		20.5	
(h)	10.5	13.0	16.5	9.0

Example 4

Examples 1 and 2 are again repeated employing 3 moles of a non-ionic derived from dinonyl phenol and 7 moles of ethylene oxide reacted with 1 mole of P_2O_5 and converted to the sodium salt by neutralizing with 50% NaOH to a pH of about 6.5. The detergency and redeposition values are:

	Detergency	Redeposition
Perchloroethylene	19.2	2.4
Stoddard Solvent	15.9	2.2

Example 5

Examples 1 and 2 are once again repeated employing the phosphate ester sodium salt (from nonionic to P_2O_5 ratio of 2.7:1) of a nonionic derived from nonyl phenol and 4 moles ethylene oxide. Results are:

	Detergency	Redeposition
Perchloroethylene	19.6	5.0
Stoddard Solvent	13.8	5.9

Example 6

A phosphate ester (nonionic to P_2O_5 ratio of 2.7:1) of a nonionic derived from dodecyl phenol and 6 moles of ethylene oxide is used in the form of the sodium salt to repeat Examples 1 and 2. The results are:

	Detergency	Redeposition
Perchloroethylene	18.9	4.7
Stoddard Solvent	16.4	4.2

Example 7

Examples 1 and 2 are once again repeated employing the sodium salt of a phosphate ester (from nonionic to

P_2O_5 ratio of 2.7:1) of a nonionic derived from dinonyl phenol and 15 moles of ethylene oxide. The results are:

	Detergency	Redeposition
Perchloroethylene	21.7	1.4
Stoddard Solvent	18.1	2.6

Example 8

Example 1 is repeated except that the laundering cycle is 10 minutes and the phosphate ester sodium salt is derived from a nonionic to P_2O_5 ratio of 2.7:1 and the nonionic is prepared from tridecyl alcohol and 7 moles of ethylene oxide. The results are:

STODDARD SOLVENT

Detergency ---------- 11
Redeposition ---------- 3

Example 9

Example 8 is repeated at a concentration of 1% (rather than 2%). Results are:

Detergency ---------- 11
Redeposition ---------- 2

Example 10

Examples 8 and 9 are repeated employing the isopropylamine salt in lieu of the sodium salt. Results are:

Concentration, percent	Detergency	Redeposition
1	11	3
2	12	2

Example 11

Examples 8, 9 and 10 are repeated employing the salts of phosphate ester (nonionic to P_2O_5 ratio 3.0:1) of a nonionic derived from dinonyl phenol and 9.5 moles of ethylene oxide. Results are:

Concentration, percent	Salt	Detergency	Redeposition
1	Sodium	12	1
2	do	11	0
1	Isopropylamine	10	1
2	do	10	0

In the following table the results of Examples 8–11 are tabulated and compared with solvent alone and the salts of dodecylbenzene sulfonate:

	Detergency	Redeposition
Example 8 (2%)	11	3
Example 9 (1%)	11	2
Example 10:		
(2%)	12	2
(1%)	11	3
Example 11:		
Na salt:		
(2%)	11	0
(1%)	12	1
Isopropylamine salt:		
(2%)	10	0
(1%)	10	1
Sodium dodecyl benzene Sulfonate (2%)	9	4
Stoddard Solvent	6	8

Example 12

Examples 1 and 2 are again repeated employing the following nonionics:

Nonionic:	Percent alkylene oxide
A. Nonyl phenol + 15 moles ethylene oxide	75
B. Nonyl phenol + 4 moles ethylene oxide	44
C. Dinonyl phenol + 24 moles ethylene oxide	75
D. Dodecyl phenol + 10 moles ethylene oxide	63
E. Tri-octadecyl phenol + 1 mole ethylene oxide	5
F. Tri-octadecyl phenol + 30 moles ethylene oxide	61
G. Dinonyl phenol + 2 moles ethylene oxide	20
H. Hexadecyl phenol + 3 moles ethylene oxide	30
I. Nonyl phenol + 1 mole ethylene oxide	17
J. Lauryl alcohol + 4 moles ethylene oxide	49
K. Decyl mercaptan + 5 moles ethylene oxide	56
L. Oleyl mercaptan + 10 moles ethylene oxide	61
M. Octylamine + 8 moles ethylene oxide	73
N. Oleic sulfamide + 4 moles ethylene oxide	40
O. Oleic acid anilide + 20 moles ethylene oxide	71
P. Lauric acid amide + 3 moles ethylene oxide	40
Q. Dibutyl naphthalene sulfamide + 10 moles ethylene oxide	58
R. Tributyl phenol + 7 moles ethylene oxide	54

Example 13

The reactive compounds, i.e., the phenols, alcohol, mercaptans, amine, amides and sulfamides, of Example 12 are reacted with varying molar amounts of 1,2-propylene oxide and 1,2-butylene oxide to yield the corresponding methyl and ethyl substituted oxyethyl group. The results appear below in Table IV.

TABLE IV

Reactive Compound	Oxyalkylating Agent	Percent Alkylene Oxide
Nonyl phenol	5 moles propylene oxide	57
Do	10 moles propylene oxide	73
Do	20 moles propylene oxide	84
Do	5 moles butylene oxide	62
Do	1 mole butylene oxide	25
Do	11 moles butylene oxide	79
Do	25 moles butylene oxide	89
Do	35 moles butylene oxide	92
n-Octyl phenol	50 moles butylene oxide	95
Dinonyl phenol	5 moles butylene oxide	51
Do	10 moles butylene oxide	68
Dodecyl phenol	do	63
Tributyl phenol	do	63
Lauryl alcohol	do	70
Tridecyl alcohol	do	69
Tributyl phenol	5 moles propylene oxide	53
Do	10 moles propylene oxide	69
Do	15 moles propylene oxide	77
Do	5 moles butylene oxide	58
Do	10 moles butylene oxide	77
Do	20 moles butylene oxide	84
Decyl mercaptan	10 moles propylene oxide	77
Do	20 moles propylene oxide	87
Do	10 moles butylene oxide	80
Octyl amine	10 moles propylene oxide	82
Do	10 moles butylene oxide	85
Lauric acid amide	do	78

Example 14

Example E is repeated except that 6 moles of ethylene are used and the final product contains 56.9% ethylene oxide.

Example 15.—Preparation of magnesium salts

The phosphate ester products of Example K–6, Example 3 and Example 14, in free acid form in amounts of 844 g., 697 g. and 797 g., respectively, are added in separate vessels to 844 g., 697 g. and 797 g., respectively, of Stoddard Solvent. To the first two vessels there are added

29 g. of $Mg(OH)_2$ and to the third vessel, 50 g. of $Mg(OH)_2$ at room temperature with stirring. A slight exothermic reaction results and the temperature rises to 35–40° C. Stirring is continued for 12 to 16 hours at room temperature to complete the reaction. The reaction mixtures are filtered and found to have pH's of 6.9, 7.2 and 5.6, respectively.

Example 16

Example 15 is repeated except that the solvent is perchloroethylene.

Example 17

The detergency and redeposition tests of Examples 1 and 2 are repeated using the following phosphate esters:

A. disodium salt of ester of Example L.
B. diammonium salt of ester of Example M.
C. disodium salt of ester of Example N–E.
D. isopropylamine salt of ester of Example N–I.
E. magnesium salt of ester of Example N–J.
F. magnesium salt of ester of Example L.
G. monoethanolamine salt of ester of Example L.
H. diethanolamine salt of ester of Example L.
I. monosodium salt of ester of Example P.
J. magnesium salt of ester of Example P.

Excellent and comparable results are obtained.

The following formulations illustrate 100% active concentrates which are neutral, water-white, clear liquids:

A. 90 parts free acid of the phosphate ester (nonionic to P_2O_5 ratio of 2.7:1) of a nonionic derived from nonyl phenol and 9.5 moles of ethylene oxide, and 11 parts isopropylamine.

B. 95 parts free acid of the phosphate ester (nonionic to P_2O_5 ratio of 4.0:1) of nonionic derived from nonyl phenol and 6 moles ethylene oxide, and 10 parts isopropylamine.

C. 92.5 parts free acid of the phosphate ester (nonionic to P_2O_5 ratio 3.0:1) of nonionic derived from dinonyl phenol and 9.5 moles of ethylene oxide, and 7 parts isopropylamine.

D. 92 parts free acid of the phosphate ester (nonionic to P_2O_5 ratio 2.7:1) of nonionic derived from tridecyl alcohol and 7 moles of ethylene oxide, and 13 parts isopropylamine.

In addition to the amine salts which are specifically described and exemplified above, other amine salts and hydroxyamine salts may be used including salts of ethylene diamine, 1,2-propylene diamine, 1,4-butylene diamine, methyl ethyl amine, methyl isopropyl amine, ethyl isopropyl amine, diisopropyl amine, 2-aminoethanol, triethanol amine, 3-aminopropanol, and the like.

Other variations in and modifications of the described processes which will be obvious to those skilled in the art can be made in this invention without departing from the scope or spirit thereof.

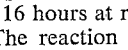
We claim:

1. A dry cleaning detergent composition comprising

(a) from about 90 to 99.8 parts by weight of a dry cleaning solvent and,

(b) as the detergent from about 0.2 to about 10 parts by weight of a phosphate ester of a nonionic surface active agent, said ester being selected from the class consisting of mono- and di-phosphate esters and mixtures thereof, in their free acid form, sodium salt form or amine salt form; said non ionic surface active agent having the molecular configuration of a condensation product of

(1) an organic compound containing a reactive hydrogen atom selected from the group consisting of R—OH, R—SH, R—COOH, R—NH_2,



and R—SO_2NH_2 compounds, wherein R is a hydrocarbon radical of from 8 to 60 carbon atoms, and

(2) at least one mole of an alkylene oxide containing 2 to 4 carbon atoms and up to about 75–95 weight percent of total combined alkylene oxide, the upper limit of 75% for ethylene oxide, an 85% upper limit for propylene oxide and the 95% upper limit for butylene oxide.

2. A dry cleaning detergent composition as defined in claim 1 wherein the detergent is derived from an alkyl phenol and ethylene oxide.

3. A dry cleaning detergent composition as defined in claim 2 wherein the alkyl phenol is nonly phenol.

4. A dry cleaning detergent composition as defined in claim 2 wherein the alkyl phenol is octyl phenol.

5. A dry cleaning detergent composition as defined in claim 2 wherein the alkyl phenol is dodecyl phenol.

6. A dry cleaning detergent composition as defined in claim 2 wherein the alkyl phenol is dinonyl phenol.

7. A dry cleaning detergent composition as defined in claim 1, wherein the detergent is derived from a fatty alcohol and ethylene oxide.

8. A dry cleaning detergent composition as defined in claim 7 wherein the fatty alcohol is lauryl alcohol.

9. A dry cleaning detergent composition as defined in claim 7 wherein the fatty alcohol is oleyl alcohol.

10. A dry cleaning detergent composition as defined in claim 7 wherein the fatty alcohol is tridecyl alcohol.

11. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is a petroleum based hydrocarbon.

12. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is Stoddard Solvent.

13. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is a chlorinated hydrocarbon solvent.

14. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is perchloroethylene.

15. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is a petroleum based hydrocarbon solvent and the nonionic surface active agent is a polyoxyalkylene ether of an alkyl phenol.

16. A dry cleaning detergent composition as defined in claim 1 wherein the dry cleaning solvent is a chlorinated hydrocarbon solvent and the nonionic surface active agent is a polyoxyalkylene ether of an alkyl phenol.

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