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DIALKYL POLYVINYL PHOSPHATE FLAME-RETARDANTS

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9 Claims. (Cl. 260—73)

This invention relates to flame-resistant textiles, and more particularly to compositions based on dialkyl polyvinyl phosphate resins with which the textiles are treated.

Heretofore, fabrics have been rendered less inflammable by treating them or the yarns from which they are made with a flame-retardant agent, based on insoluble hydrous oxides, highly halogenated compounds and phosphate derivatives.

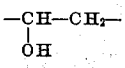
Fabrics treated with an insoluble hydrous oxide of a metal, such as titanium, bismuth, antimony, tin or similar amphoteric metal, are not entirely satisfactory since the fabric has a severe after-glow when subjected to flame, and also the volatile products thereby produced are usually toxic.

The halogenated compounds such as chlorinated paraffin and resins have an adverse effect on the "feel" of the fabric, and in addition, have the disadvantage that decomposition takes place slowly on storage, yielding small amounts of halogen acids which, in a relatively short time, tender or destroy the strength of the fabric. Impregnating agents based on inorganic phosphates likewise tender the fabric.

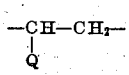
There has been a persistent search for many years for a treatment of fabrics to render them less inflammable, particularly in the search for a flame-retardant finish for textiles which does not tender or weaken the fabric over a relatively long period of time, and which is non-toxic, resistant to washing and does not adversely affect the feel and dyeing properties of the textile.

It is, therefore, an object of this invention to provide a composition suitable for treating textiles at any convenient stage in their production from carding to the finished fabric to render them flame-resistant. A further object is the provision of a flame-retardant finish which is exceptionally effective in reducing the inflammability and after-glow of fabrics and textiles treated, and which has substantially no adverse effect on the other properties of the fabric such as "feel" and dyeing. A still further object of this invention is the provision of a finish which, when applied to a fabric, does not decompose nor tender the fabric. Other objects will appear as the description of the invention proceeds.

These objects are accomplished by impregnating a fabric or its components at any stage of manufacture with a flame-retardant agent consisting essentially of phosphate esters of a derivative of a polymer which before esterification consists predominantly to exclusively of vinyl alcohol units of the structure

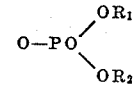


and contains a lesser proportion to zero of vinyl units of the formula



wherein Q is a radical as defined below, the degree of

phosphate esterification involving not less than 43% and not more than 82% of the number of all vinyl units present in the polymer, and the phosphate ester radical being a radical of form



wherein R_1 and R_2 are alkyl or halogeno-alkyl radicals of 1 to 8 C-atoms. The product may also be one in which the chains of the linear polymer are cross-linked through unesterified OH groups by a polyhydroxy methyl or an alkoxymethyl formaldehyde condensate.

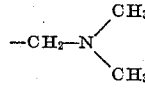
In general, these compositions are prepared by esterifying polyvinyl alcohol (or a copolymer as described below) with a dialkyl halophosphate in which case an organic base should be present as an acid acceptor. It will be apparent that the degree of esterification varies with the proportions of esterifying agent present, and the more vigorous the reaction conditions, the more complete the esterification will be. In order to avoid extensive hydrolysis of the esterification agent, it is preferable to use dry reagents.

An alternate procedure in which a dialkyl halophosphate is not used consists essentially of preparing the dialkyl vinyl phosphate polymers by reacting polyvinyl alcohol with the corresponding dialkyl phosphite in the presence of carbon tetrachloride and an aliphatic tertiary amine. Preferably the amine is at least as basic as triethylamine. The products of this reaction are chloroform, the amine hydrochloride and the ester.

The molecular weight of the polyvinyl alcohol used in either of the above methods is not critical, and may vary over a wide range depending on the properties desired in the final product. The polyvinyl alcohol may be of low, medium or high viscosity.

The nature of the radical Q depends on the mode of preparation of the initial polymer, and may be varied within reasonably wide limits. Thus, the initial polymer may be a polyvinyl alcohol obtained by hydrolysis of polyvinyl acetate. (Cf. E. R. Riegel, Industrial Chemistry, 4th edition, pages 457–458.) Often, however, the hydrolysis is not carried to completion, but only to an extent of about 86 to 90%; then the remaining unesterified vinyl acetate units in the polymer correspond to the second of the two formulas above, wherein Q is the acetate radical —$OCOCH_3$.

The initial polymer, however, may also be obtained by copolymerization of vinyl acetate with minor quantities of other vinyl compounds, for instance acrolein or dimethyl allylamine, followed by hydrolysis. Then Q may designate the radical introduced by said other vinyl compound, for instance the aldehyde radical —CHO or the dimethylaminomethylene radical



In similar manner other radicals Q may be introduced into the initial polymer, for instance, hydrogen, halogen, cyano, lower alkyl, alkoxy and aryl. In addition, the same polymer may still contain a minor proportion of vinyl units wherein Q is the acetate radical —$OCOCH_3$.

The products obtained according to this invention vary considerably in properties which are reflected by the selection of the R_1 and R_2 groups. When these groups contain from 1 to 4 carbon atoms, the products are very tacky, elastic solids. When the carbon atoms in these groups are increased to 8, the product becomes more soapy, softer and less tacky. As would be expected,

those bearing 1 or 2 carbon atoms in the alkyl groups are soluble in water, alcohol and acetone, but are insoluble in ether. Solubility in ether increases with the length of the alkyl groups.

All of the compositions which are not cross-linked contain some residual OH groups. By varying the composition of the R_1 and R_2 components in the above formula, a wide variety of products having a special combination of properties may be obtained. For example, the water-dispersing property of C_3 groups and the hydrophobic property of C_{12} to C_{18} alkyl chains may be incorporated into the same resin with C_1 to C_4 dialkyl polyvinyl phosphate groups for a balanced fabric finish combining flame-retardance, water-repellance and lubricity, with ease of application and durability. It has also been found that when the product is insolubilized through hydroxyl linkage to the above-defined multi-functional agents, the flame-retarding properties are greatly enhanced. All of the products are non-flammable, and are self-extinguishing without serious after-glow when removed from a flame. They are also readily applied to fabrics from solution or emulsion.

The cross-linking agents referred to include all types of formaldehyde condensation products with other compounds such as phenols, urea, melamine, ketones etc. The preferred ones are the common resin-forming materials used for treating textiles, such as the methylol ureas, methylol melamines, 1,3-bis(hydroxymethyl)-2 imidazolidone and their lower alkyl ethers. These cross-linking agents react through the hydroxyl groups of the polymers when heated therewith in the presence of mildly acidic or acid-generating catalysts such as diammonium acid phosphate, zinc nitrate, tartaric acid etc. One method of treating fabrics involves effecting the cross-linking in situ on the fabric, in which case the finish becomes permanently attached.

It has been found that the amount of finish to be applied varies with the fabric, and the degree of flame-resistance desired. The phosphate resin alone gives satisfactory flame-retardance according to the test described below when 2.5% to 3.0% P, based on the weight of the fabric is present. When combined with a melamine resin, as little as 1.5% P and 1.3% N is sufficient.

The test referred to above is that described as Tentative Test Method 34–37 "Evaluation of Fire-Resistant Textiles," AATCC Year Book, 1950, p. 118.

The following examples are given by way of illustration only and no limitation is intended thereon, since the reagents mentioned in the examples may be replaced in equivalent amount by any falling within the above definition.

EXAMPLE I

In a suitable reactor were placed 300 cc. dry benzene and 11 g. of a commercial low viscosity polyvinyl alcohol which was 86–90 per cent hydrolyzed. A small amount of water was removed as an azeotrope. Technical diethyl chlorophosphate (51.5 g.) was added and the mixture stirred and heated to 82° C. in 15 minutes. Twenty grams anhydrous pyridine was added and a swollen red, plastic mass formed during two hours heating. The liquid was decanted and the soft gel solid washed thoroughly with water. On air drying, the product weighed 16.6 g. and contained 13.6% P.

EXAMPLE II

The reaction was repeated using a commercial 100% hydrolyzed, low viscosity polyvinyl alcohol and 26.8 g. 2,6-lutidine in place of pyridine. The reaction mixture was refluxed 18 hours. The product was separated by steam-distilling the benzene and 2,6-lutidine while neutralizing the mass with sodium carbonate, and the aqueous layer was decanted.

The red jelly was oven dried at 45° C. three days. The diethyl polyvinyl phosphate weighed 23.9 g. and contained 13.0% P which corresponds to 43% of the hydroxyl groups esterified with the diethyl phosphoryl group.

EXAMPLE III

The experiment of this example is similar to Examples I and II, except that the reaction was carried out in pyridine. In a reactor were placed 11 g. low viscosity, 86–90 per cent hydrolyzed polyvinyl alcohol, 100 cc. anhydrous pyridine and 20 cc. benzene. The polyvinyl alcohol was dried by distilling out the water-benzene azeotrope. The reaction mixture was cooled to 18° C. and 43.0 g. diethyl chlorophosphate added in one-half hour at 18° to 27° C. A white precipitate appeared immediately, and the mixture became syrupy as the polyvinyl alcohol disappeared. The mixture was stirred at room temperature for about 16 hours. The pyridine hydrochloride was neutralized with saturated sodium carbonate solution until the pH was 8. A clear, colorless syrup resulted, which was poured onto 500 g. ice. An attempt to extract the product with ether was unsuccessful, but an intermediate gummy layer formed which was isolated and dried in a vacuum oven at 45° C. The glassy, yellow solid weighed 27.6 g. and contained 12.9% P. It swelled to a soft gel in water and dissolved in alcohol.

An alcohol solution was used to impregnate cotton cloth. A mixture of 9.0 g. of the diethyl polyvinyl phosphate, 40 g. of 95% alcohol, 3.0 g. of methylated methylolmelamine resin and 0.5 g. tartaric acid was padded onto 8 oz. cotton herringbone twill. An add-on of 29.6% in the weight of the cloth was obtained. The cloth contained 2.46% P and 2.2% N and gave a char-length of 4½ inches with no after-glow in the standard burning test method described above. After washing in 0.5% soap solution (AATCC No. 1, doubled amounts), the cloth gave 2½ inches char-length and contained 2.0% P and 2.1% N, showing a considerable degree of permanence of flame-retardance has been achieved.

EXAMPLE IV

In this example two runs were made using technical dibutyl chlorophosphate in the first and relatively pure ester in the second. Both gave about the same results. Commercial low viscosity 86–90 per cent hydrolyzed polyvinyl-alcohol was dried in an oven at 80° C. for several hours. Twenty-two g. of the dry powder was swollen in 400 cc. anhydrous pyridine by heating at 60–70° C. for one-half to one hour and cooled to 15° C. A commercial technical grade of dibutyl chlorophosphate (120 g., a slight excess) was run in rapidly. The temperature rose to 23° and was lowered by cooling to 0° C. for one-half hour. The mixture became smooth as stirring was continued for several hours and it gradually warmed to room temperature. The mixture was neutralized with sodium carbonate and the pyridine steam-distilled. The product was separated by decantation and weighed 138 g. while still somewhat wet. A dried sample contained 12.0% P, which corresponds to 67% of the theory for complete esterification of the polyvinyl alcohol. The product readily dissolved in acetone, alcohol-chloroform, and benzene, and was insoluble in water and ether. The product was very tacky. It was non-flammable.

The above procedure was repeated using 11 g. of a commercial medium viscosity, 91–93 per cent hydrolyzed polyvinyl alcohol and 60 g. of di(n-butyl) chlorophosphate (added at 0° C.) and gave 55.8 g. of a product containing 12.6% P. The weight of product and phosphorus content correspond to 82% complete esterification of the polyvinyl alcohol. This product was not soluble in common solvents, but swelled to a thick gel in alcohol, pyridine or dimethyl formamide.

Cotton herringbone 8 oz. fabric, treated with di(n-butyl) polyvinyl phosphate in acetone solution to give an add-on of 26% of resin on weight of the cotton, gave a char-length of 2½ and 3½ inches in duplicate determinations by the standard fire resistance test as described above. Untreated cotton was totally consumed.

The cloth sample was washed according to a standard laundering procedure (AATCC No. 1, 1950, Yearbook, p.

85) in the Launderometer. The cloth suffered a loss in weight of 7.2% and was now not sufficiently flame-resistant to pass the burning test. The fabric was very sticky when wet. Another sample impregnated with 25% of the resin (2.4% P) was washed (AATCC No. 3) and lost 18% of its weight (1.0% P now). Another similar cloth sample was treated with an acetone solution containing di(n-butyl) polyvinyl phosphate to give an add-on of 36%. The dried cloth was then treated with 1.5 g. of 50% aqueous solution of dimethylol ethylene-urea and 0.2 g. of tartaric acid in 10 g. of water. The cloth was dried and then cured at 150° C. for one minute. The sample was laundered (AATCC No. 3) and lost only 2% of its weight; (contained 2.4% P). Another wash (AATCC No. 3) removed 16% of its weight, and the cloth now contained only 1.5% P.

An even more permanent finish was produced by a solution containing the following:

15 g. di(n-butyl) polyvinyl phosphate (11.9% P)
30 g. 95% alcohol
3 g. commercial methylated methylolmelamine resin
10 g. water containing 0.5 g. diammonium hydrogen phosphate

The solution was padded on cotton fabric (same as above) at two different loadings and the following results obtained. The washes were done in the Launderometer, AATCC No. 1, repeated four times and eight times.

Sample No.	Add-on of Resin, percent	Before	Analysis		Char-Length		Weight of Cloth		
			After 4 Washes	After 8 Washes	Before, inches	After 4 Washes, inches	Before, g.	After 4 Washes, g.	After 8 Washes, g.
A	36.2	3.2% P 1.8% N	2.0% P	1.93% P	3¼	2¾	6.66	6.40	6.27
B	29.8	3.1% P 1.3% N	1.5% P	1.49% P	3⅜	3½	6.16	5.97	6.00

EXAMPLE V

A commercial low viscosity 86–90 per cent hydrolyzed dry polyvinyl alcohol (11.0 g.) and 200 g. dry pyridine were heated and stirred at 40–80° C. for one-half hour. Dry carbon tetrachloride (316 cc., a 4-fold excess), was added and 98 g. of a commercial di(n-butyl) hydrogen phosphite (a 2-fold excess), was run in. No heat was evolved, but when heated to 70° C. and 18 cc. dry triethylamine added, the temperature rose to 86° C. and the mixture refluxed. The reaction mixture darkened and thickened. Another 18 g. of dry triethylamine was added after two hours without heating. The temperature rose from 35 to 43° C. and the mixture grew thicker. After standing overnight, the solvents were steam-distilled while neutralizing the triethylamine hydrochloride with 115 cc. of 33% sodium carbonate solution. The brown solid was collected, washed with water, acetone and dried. The di(n-butyl) polyvinyl phosphate weighed 25.2 g. and contained 11.6% P by analysis. It was swollen by 95% alcohol.

EXAMPLE VI

Polyvinyl alcohol (4.4 g.) in 160 g. carbon tetrachloride was treated with 20 g. of commercial diethyl hydrogen phosphite and 13 g. triethylamine. The mixture grew warm and refluxed. The mixture was stirred and heated to 80–90° C. for 2 hours. The solid was collected and washed with ether, and then with 95% alcohol. The swollen gel was dried. It weighed 10.5 g. and contained 12.8% P and 2.6 N (some triethylamine hydrochloride contaminated the product).

EXAMPLE VII

Di(2,3-dibromopropyl) chlorophosphate was prepared from 2,3-dibromopropanol-1 and phosphorus trichloride, followed by chlorination.

Phosphorus trichloride (45.8 g., 0.33 m.) was added dropwise with stirring to 218 g. (1.0 m.) 2,3-dibromopropanol-1 (B. P. 103°/15 mm.) at 6–9° C. The solution was diluted with 240 g. of dry carbon tetrachloride and cooled to 0° C. Chlorine gas (24 g.) was bubbled in at 2–4° C. over 55 minutes until a green color persisted and nitrogen swept out hydrogen chloride for 16 hours at 2–9° C. A total of .96 equivalent of acid were generated. The residue, after removing the carbon tetrachloride by distillation down to 35° C. at 15 mm. pressure, weighed 246.2 g. (theory 251 g.).

A commercial low viscosity, 86–90 per cent hydrolyzed polyvinyl alcohol (4.4 g.) and 100 g. dry pyridine was stirred and heated to 60° C. for one hour before cooling to 0° C. Eighty grams of the product above containing 0.1 mol $(BrCH_2CHBrCH_2O)_2POCl$ and 0.1 mol $BrCH_2CHBrCH_2Cl$ was added in eight minutes at 0–2° C. The temperature was maintained at 0–4° C. for 6 hours, and 100 cc. glacial added. After standing 16 hours at a temperature of 4–15° C., the opaque solution was precipitated in water. The white gum which formed was washed with water, carbon tetrachloride and ether and dried. The product was a soft gum which weighed 48 g. (theory 52.3 g.).

An aqueous pyridine dispersion containing 28% solids was made from 21.7 g. of the above product with pyridine and water. The emulsion was used to impregnate cotton cloth. A cloth sample impregnated with 34.8% of its weight of the resin contained 1.5% P and 11% Br. It gave a satisfactory test when subjected to burning as described above. After washing in standard AATCC No. 1 wash, the cloth contained 1.1% P and was still flame-resistant (3¾ inch char-length). A more severe wash (AATCC No. 4, doubled amounts) did not remove the resin since a char-length of 3½ inches resulted in the standard test. No after-glow was observed.

EXAMPLE VIII

The procedure of Example IV was repeated using low viscosity, 86–90 per cent hydrolyzed polyvinyl alcohol (4.4 g.) in 100 g. dry pyridine, treated with 30.6 g. of a commercial technical grade dioctyl chlorophosphate at 29–34° C. The mixture was heated 60° C. for one hour, and the appearance was clear and smooth with a precipitate of pyridine hydrochloride settled out. After standing about 16 hours, the mass was neutralized, steam-distilled and the product was separated by decanting off the salt solution. The dioctyl polyvinyl phosphate was a soft jelly of 28% solids content (8.9% P). Ether extracted a portion of the product from the gel saturated with salt, and after evaporation of the solvent, a white, flaky solid was obtained which contained 9.0% P. It was readily soluble in water to give a soapy solution. The gel itself possessed a slight tackiness when dry. The solid was soluble in 95% alcohol. The phosphorus analysis corresponds to about 58% complete esterification.

EXAMPLE IX

The procedure of Example IV was again repeated using di(sec.-butyl) chlorophosphate prepared from sec.-butyl alcohol and phosphorus trichloride in carbon tetrachloride solution, followed by chlorination of the intermediate di(sec.-butyl) hydrogen phosphite. The chlorophosphate was not distilled, but contained 13.6% P and required the correct amount of standard alkali when titrated in alcohol-water solution.

The di(sec.-butyl) polyvinyl phosphate was obtained as a brown, viscous solid weighing 74.5 g. while still somewhat wet, and an oven-dried sample contained 12.4% P. This product was readily dispersed in water to give a milky emulsion. It was very tacky. The product was self-extinguishing when subjected to burning.

When applied to cotton cloth (as described above), to give add-on of 32.4% and 44.5%, the corresponding flame-test values were 2¾ inches and 3¼ inches, respectively, with no after-glow. After two washes, the values were 2½ and 3 inches, respectively, with no after-glow.

EXAMPLE X

A. The procedure of Example IV was used. From 17.6 g. of low viscosity, 86–90 per cent hydrolyzed polyvinyl alcohol and 70 g. distilled diisopropyl chlorophosphate (B. P. 72–89°/11 mm., N_D^{25} 1.4148; found 15.23% P, 17.0% Cl) in 240 g. dry pyridine was obtained 72.8 g. of gummy solid containing 13.0% P. If all the hydroxyl groups had been esterified with diisopropyl phosphoryl groups, the product would contain 14.9% P.

Diisopropyl polyvinyl phosphate fabric impregnation from aqueous emulsion

Diisopropyl polyvinyl phosphate (15.0 g.) was emulsified in 150 cc. water containing about 1.0 g. oleic acid and enough sodium hydroxide to bring the pH between 7 and 8. An opalescent emulsion resulted on stirring. To this emulsion was added 3.0 g. of a commercial methylated methylol melamine resin and 0.5 g. of diammonium hydrogen phosphate and the dispersion remained stable.

The emulsion was padded onto cotton cloth to give an add-on of 28.6%. The cloth was heated to 150° C. for 5 minutes, and was not noticeably stiffened. Strips 2½ inches wide were washed in 200 cc. 0.5% tallow soap solution at 160° F. for varying times and subjected to the standard burning described above. The data are recorded below.

Sample	Before Wash	After 1½ hour wash	After 2 hour wash
Cloth wt.....g..	5.96	5.70	5.56
I Analysis:			
P.....percent..	2.71	1.78	2.15
N.....do....	0.92	0.85	0.77
Flame-test (char length).....inches..	[1] 2⅜	3¾	4¼

[1] No after-glow observed in any test.

A different formulation was used with the same resin.

15 g. diisopropyl polyvinyl phosphate
25.0 g. 95% alcohol
10.0 g. water
3.0 g. commercial methylated methylol melamine resin
0.5 g. tartaric acid

Cloth samples impregnated with the resulting smooth solution were dried and cured at 150° C. for 5 minutes. The fabric was noticeably stiffened, but was softened again by washing. The 2½ inch strips were washed as above and tested for flame-retardance. The following results were obtained. Sample one had an add-on of 23%.

Sample	Before Washing	After ½ hr. wash at 160° F.	After 1 hr. wash
Cloth wt.....	5.48	5.22	5.21
P Analysis.....	2.01	1.38	1.38
N Analysis.....	.....	.....	1.28
Flame Test (char-length).....inches..	.....	3	2⅜

Another sample had a resin add-on of 30%.

Sample	Before Washing	After ½ hr. wash at 160° F.	After 2 hrs. wash
Cloth wt.....	5.48	5.51	5.37
P Analysis.....	2.51	1.80	2.14
N Analysis.....	.....	.....	1.56
Flame Test (char-length).....inches..	2¾	2½	2¼

The results show a considerable degree of durability of flame-retardance has been achieved.

B. Another preparation of diisopropyl polyvinyl phosphate was made as above in X—A, but using diisopropyl chlorophosphate which contained a small amount of monoisopropyl dichlorophosphate as evidenced by extensive cross-linking during reaction with polyvinyl alcohol in pyridine solution. An aqueous acetone solution of 20% solids was made up from the tight gum obtained after thorough water washing and this solution was applied to cotton fabric without additional cross-linking resin. This particular resin finish was durable to a commercial laundering, since a half-hour wash at 160° F. in 0.25% soap and 0.1% soda ash in a wash wheel actually improved the flame-resistance of the cloth. The char-length was reduced from 5⅞" to 4½". The fabric was quite soft after washing.

C. Another preparation which was also similarly cross-linked was applied as a viscous aqueous alcohol solution of 22.5% solids together with 5% of a methylated methylol melamine resin and 5.0% of a monomeric phosphate ester to soften the finish. An improvement in the hand of the treated fabric was observed and the finish was durable to numerous commercial launderings (as in X—B). The results are recorded below.

Sample	Plasticizer	Add-On, percent	No. of times washed	Char-Lengths, inches	
				Initial	Washed
1.....	Tricresyl phosphate.....	32.5	1	5	3¼
2.....	A commercial alkyl aryl phosphate (M. W. 362.4).	26	1	5⅛	3¼
			4	5⅛	3⅜
			8	5⅛	3½

A single wash improved the flame resistance as observed previously. This is probably because a small amount of impurity such as salt in the aqueous solution which was applied has been washed out.

Dimethyl polyvinyl phosphate

Dimethyl chlorophosphate was made from anhydrous methanol and phosphorus trichloride by the method of Hardy and Kosolapoff (U. S. 2,409,039). The product distilled at 72–78° at 15 mm. pressure; it had N_D^{24} 1.4110 and contained 21.0% P and 23.0% Cl (theoretical values are 21.4% P and 24.6% Cl). It was used immediately in a reaction with 90–96% hydrolyzed low viscosity polyvinyl alcohol. Forty-four grams of the polyvinyl alcohol was heated and stirred with 600 g. dry pyridine at 60° C. for one hour. The mixture was cooled to 0° C. and 164 g. of dimethyl chlorophosphate (a 14% excess) was dropped in slowly at 0° with strong cooling. A white crystalline precipitate formed immediately and the mixture grew very thick. After all the dimethyl chlorophosphate was added, the reaction mass stood overnight at room temperature. The mixture was gelled, but thinned out to a thick syrup in aqueous solution when steam distilled to remove the pyridine while neutralizing with aqueous alkali. The product could not be readily separated from the salt formed by neutralization, but was applied as such to fabric. The cloth was stiffened, but was flame-resistant at a loading of about 25% with 5% methylated methylol melamine. A char length of 4½ inches was observed. It was not durable to washing. Evidently a minor amount of probably methyl dichloro-

phosphate contaminated the dimethyl chlorophosphate and was responsible for the cross-linking during reaction with the polyvinyl alcohol.

EXAMPLE XI

A low viscosity ((*n*)=0.34) copolymer containing 5% acrolein units and 95% vinyl alcohol units, was prepared from vinyl acetate and acrolein by polymerization in alcohol solution, followed by hydrolysis of the acetate portion to hydroxyl groups by treatment with methanol and sodium methoxide. The copolymer (11.0 g.) in 200 cc. dry pyridine was heated to 65° C. for about one-half hour and then cooled to 5° C. while 50 g. of di(n-butyl) chlorophosphate was added. An exothermic reaction began and a crystalline precipitate formed at 5 to 10° C. The mixture was allowed to stand overnight and then heated to 90° C. The insoluble portion was filtered off and washed with sodium carbonate solution and water. The solid was air-dried and dried in vacuo at 60° C. It weighed 15 g. and contained 12.14% P by analysis. The pyridine filtrate was poured into water, but no solid precipitated because of the great proportion of pyridine present.

EXAMPLE XII

A copolymer containing 10% combined acrolein and 90% vinyl alcohol units similar to the material above was also used. The reaction was run at 6–10° C. and stood overnight at room temperature. The mass of crystalline precipitate and pyridine solution was neutralized by addition of 12.3 g. of sodium hydroxide in 46 cc. water and the neutral solution steam-distilled to remove the pyridine. The solid was collected on a Buchner funnel and the filtrate discarded. A portion of the product emulsified in the distilled water used for washing the salts out of the product. This filtrate was coagulated to give a transparent gum weighing 3.0 g. and containing 11.9% P. The product on the funnel was dried at 60° C. in vacuo for 3 days. It weighed 22.4 g. and contained 12.5% P.

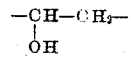
EXAMPLE XIII

The method of Example XII was employed. The copolymer used contained 1.19% N or about 7.2% dimethylallylamine and was prepared by polymerizing vinyl acetate with N,N-di-methylallyl amine and hydrolyzing the intermediate copolymer. The product of the esterification with di-(n-butyl) chlorophosphate was readily emulsified in water to give a thick cream. When dry, it weighs 32.2 g. and contains 13.0% P and .35% N.

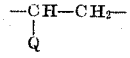
It is apparent that many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, and therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

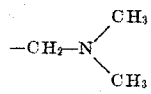
1. A fire-retarding compound being a phosphate ester of a polymer which before esterification consists predominantly to exclusively of vinyl alcohol units of the structure



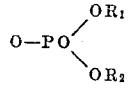
and contains a lesser proportion to zero of vinyl units of the formula



wherein Q is a radical selected from the group consisting of the acetate radical —O—$COCH_3$, the aldehyde radical —CHO, and the dimethylaminomethylene radical



the degree of phosphate esterification involving not less than 43% and not more than 82% of the number of all vinyl units present in the polymer, and the esterifying phosphate radical being a radical of form



wherein R_1 and R_2 are aliphatic radicals of from 1 to 8 C-atoms and containing no elements other than carbon, hydrogen and halogen.

2. The compound of claim 1 in which R_1 and R_2 are ethyl.

3. The compound of claim 1 in which R_1 and R_2 are normal butyl.

4. The compound of claim 1 in which at least one of the R's is isopropyl.

5. The compound of claim 1 in which the chains of the esterified polymer are cross-linked through unesterified OH groups.

6. The compound of claim 1 in which the chains of the esterified polymer are cross-linked with a monoalkyl dihalophosphate.

7. A fabric treated with the compound of claim 1.

8. A fabric treated with the compound of claim 1, the phosphorus content of the treated fabric being from 1% to 3% by weight.

9. A fabric rendered fire-resistant by treatment with the compound of claim 1 and a plasticizer.

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