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FLAME-RETARDING OF TEXTILES

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This invention relates to new textile fiber and plastic compositions which are resistant to burning. It relates particularly to flame resistant cellulose acetate compositions and to new compositions of matter which impart flame resistance to cellulose acetate and similar materials.

Because of their inherent properties of good resistance to abrasion and because of their excellent resilience, cellulose acetate fibers have appeared to be well suited for the replacement of more expensive wool, in whole or in part, in the manufacture of certain types of rugs and floor covering materials. However, when such rugs are made from untreated cellulose acetate fibers, they are very prone to rapid burning.

Many attempts have been made to treat ordinary flammable textile materials, and cellulose acetate in particular, in such a manner as to reduce their tendency to burn freely when ignited, or to inhibit their ignition altogether. There is extensive published art in this field, and attention is called in particular to "Flameproofing of Textile Fibers," by Little, Reinhold Publishing Company, 1947.

Many inorganic salts will reduce or inhibit the burning of textiles if applied in sufficient quantity, but the required quantity is usually sufficient to cause the materials to become stiff and boardy. Furthermore, such salts are readily removed by washing, and this type of treatment has had limited application and is of little value where repeated laundering may be contemplated. When applied particularly to cellulose acetate fibers which might be used in rugs, most of these prior art methods have caused an undesirable increase in weight, a loss of resilience in the finished rug, a serious loss in the case of dyeing the fabric or any combination of these deficiencies. Also, the lack of fastness to washing inherent in many of these proposed treatments has limited their application in floor-covering materials which are frequently cleaned by scrubbing with aqueous detergents.

It is among the objects of this invention to produce synthetic textile fibers and plastic compositions, and particularly cellulose acetate compositions, which are resistant to burning, have suffered no loss in tensile strength, exhibit satisfactory hand and resiliency and which have softening or melting points which are not significantly different from those of the untreated compositions.

A further object is the preparation of certain new flame-retarding compositions particularly adapted to impart these desirable properties to cellulose acetate and like compositions.

These and other objects of this invention are accomplished by incorporating ferric pyrophosphate-hydrous metal oxide flame-retarding compositions in solutions of cellulose acetate or other similar materials and spinning fibers or casting films therefrom. More specifically, the objects of this invention are attained by preparing new and improved flame-retarding agents comprising iron pyrophosphate compositions which have been treated with compounds of titanium, zirconium or antimony, and then

incorporating these agents in solutions of cellulose acetate or like material from which flame resistant fibers may be spun. The spun fibers and materials made therefrom retain this property through repeated washing with aqueous detergent solutions.

In one embodiment of this invention the treated iron pyrophosphate is prepared by a simple reaction between a solution of a ferric salt, such as ferric sulfate and a solution of an alkali pyrophosphate, such as tetrasodium pyrophosphate, followed by treatment with a solution of titanyl sulfate and adjustment of the pH to about 3.0. After filtration, washing and drying, there is obtained a dry powder which contains both iron and titanium, the latter being preferably in a minor proportion. When this new flame-retarding agent is dispersed in a cellulose acetate spinning solution and fibers spun therefrom, they are not only initially resistant to ignition and burning, but they retain this property throughout any ordinary processing and cleaning operation. Furthermore, the hand and resilience of such fibers are substantially equivalent to those of similar fibers containing no flame-retarding agent; their dyeing properties are unimpaired; and they show only a very faint yellowish to brownish color.

The following examples illustrate this invention in more detail. Unless otherwise specified, all parts are by weight.

EXAMPLE I

280 parts of ferrous sulfate ($FeSO_4.7H_2O$) is dissolved in about 1,000 parts of water. To this solution are added in turn, a solution of 49 parts of sulfuric acid in about 75 parts of water, and a solution of 19 parts sodium chlorate in 100 parts of water. The mixture is heated to about 82° C., held at that temperature for about 30 minutes and finally diluted to a volume equivalent to about 3,000 parts at about 35° C. A separately prepared solution of tetrasodium pyrophosphate containing 190 parts of $Na_4P_2O_7$ in 2500 parts of water at about 35° C. is added to the iron solution over a period of about 40 minutes. The resulting slurry is practically white and has a pH of about 1.9 to 2.3. It is heated to 82° C. and held at this temperature for about one hour. At the end of the heating period at 82° C., a solution of 32 parts of titanyl sulfate ($TiOSO_4$) in about 200 parts of water is added to the slurry while stirring. Because of the free acid normally present in a titanyl sulfate solution, the pH drops to about 1.0, but it is brought back to about 2.8 to 3.0 by the addition of about 75 parts of sodium carbonate in about 500 parts of water. The mixture is then stirred for about 15 minutes, and the precipitate is isolated by filtration. It is washed free of sulfate ion, dried at about 60° C., and pulverized. About 265 parts of a substantially colorless powder is obtained.

EXAMPLE II

A zirconium modified ferric pyrophosphate is obtained by following the procedure of Example I, except that 64 parts of zirconium oxychloride ($ZrOCl_2.8H_2O$) dissolved in about 250 parts of water is used instead of the titanyl sulfate. Approximately 20 parts of sodium carbonate is required to adjust the final pH to 2.8 to 3.0. About 275 parts of a powder substantially similar in appearance to that of Example I is obtained.

EXAMPLE III

An antimony modified ferric pyrophosphate composition is obtained by replacing the titanyl sulfate of Example I with 46 parts of antimony chloride ($SbCl_3$) dissolved in about 250 parts of water containing free hydrochloric acid. Approximately 60 parts of sodium carbonate is required to make the final pH adjustment, and the final yield is about 270 parts of a powder which is

very similar in appearance to the products of Examples I and II.

EXAMPLE IV

In order to use the flame-retarding agents prepared in Examples I to III inclusive, it is necessary that they be dispersed in a very finely divided form in the cellulose acetate solutions from which the fibers or the thin plastic films are formed. One convenient method of obtaining the pigment in this divided form is to disperse it in a concentrated form in a solution of cellulose acetate by grinding in a ball mill. To avoid contamination with any metallic substance, it is desirable to make such a dispersion in a porcelain lined ball mill using grinding balls of some ceramic composition such as porcelain. A convenient grinding formula comprises 180 parts of flame-retarding agent, 300 parts of a 16% solution of cellulose acetate in acetone and 720 parts of acetone in a mill of such a size that it is not more than about two-thirds full when the complete charge is in it. This charge is ground for about 72 hours under conventional ball milling conditions, and then it is discharged from the mill and separated from the grinding balls. The resulting composition contains 15% flame-retarding agent and 4% cellulose acetate in a slightly viscous suspension, and it is ideally suited for mixing with additional quantities of cellulose acetate solution to make compositions from which either cellulose acetate fibers or thin plastic films may be formed.

To obtain thin plastic films of cellulose acetate polymer containing the metallic pyrophosphate flame-retarding agents of this invention, one may mix 6.7 parts of the 15% solution prepared in Example IV with 148 parts of a 16% solution of cellulose acetate to give a composition which contains 4% of the flame-retarding agent based on the dry cellulose acetate. This composition should be thoroughly mixed for at least one hour with adequate means to prevent loss of solvent and a film of about .015 inch (wet film thickness) is cast on a sheet of plate glass and dried 30 to 40 minutes at about 70° C. to evaporate the solvent.

To test these films for flammability, strips measuring about one inch by five inches are cut and suspended with the longer dimension held vertically. A small gas flame, about ¼ to ½ inch long from a fine glass tip, is then played for about two seconds on the lower end of the film. Observations may be made with respect to:

A. Ease of ignition
B. Ease of propagation or lack of propagation of flame
C. Relative amount of volatile combustible gases evolved
D. Degree of softening of polymer during burning
E. Tendency to after-glow in residue

The following table summarizes the first two of these properties with respect to compositions made from the flame retardants of Examples I to III inclusive:

Table 1.—Films as cast

	Untreated Control	Ex. I	Ex. II	Ex. III
Ease of Ignition	Easy	DNC [1]	DNC	DNC.
Propagation of Flame	Rapid	None	None	None.

[1] DNC—Did not catch.

Portions of the same films were washed by soaking for about one hour in clear water, dried and then tested for flammability as above. The following Table 2 summarizes the properties of these compositions after washing:

Table 2.—Films after washing

	Control	Ex. I	Ex. II	Ex. III
Ease of Ignition	Easy	DNC	DNC	DNC.
Propagation of Flame	Rapid	None	None	None.

EXAMPLE V

In the manufacture of cellulose acetate fibers containing metallic pyrophosphate flame-retarding agents according to the disclosures of this invention, it is preferred to make such fibers containing approximately 2% of the pyrophosphate based on the weight of the finished fiber. Dispersions of the flame-retarding agents of Examples I, II, and III prepared according to the disclosures of Example IV comprise suitable starting materials to be incorporated with additional solution of cellulose acetate to provide the spinning solutions from which the fibers are spun.

As illustrative of a suitable spinning solution, one may dissolve 700 parts of a suitable grade of cellulose acetate in 2,200 parts of acetone and, when solution is complete, one may add 100 parts of a dispersion of Example IV. The resulting composition, which comprises about 24% of cellulose acetate, is filtered according to standard procedure and then pumped to the spinnerets so arranged as to give any desired type and size of fiber. The proportions of ingredients listed yield a fiber which contains approximately 2% of the modified pyrophosphate based on the weight of the final dry fiber. The fibers are then used as a deep pile in woven rugs which may then be tested for inflammability both as originally woven and after repeated launderings with aqueous detergents. In one method of making such a test for flammability, a small flame is applied for 10 seconds to the lower end of a strip of rug held at a 45° angle to the horizontal as in the AATCC test (see Little, "Flameproofing of Textile Fibers," page 106), and the flame is then withdrawn and the behavior of the fabric observed as to:

A. Whether ignition took place
B. Whether the flame continued after the withdrawal of the igniting flame

Accompanying Table 3 shows the results of such test on fabrics containing 2% of the flame-retarding agent of Example I, before they had been washed, and Table 4 summarizes a similar series of tests on the same fabrics after ten successive washings.

Table 3.—Textiles before washing

	Control	Ex. I
Ease of Ignition	Easy	Did not catch.
Propagation of Flame	Burns rapidly	None.

Table 4.—Textiles after 10 launderings

	Control	Ex. I
Ease of Ignition	Easy	Did not catch.
Propagation of Flame	Burns	None.

The ferric pyrophosphates, which are starting materials in the process of preparing the flame retardants of this invention, are known compositions of matter. As is evident from Example I, they are prepared by reacting a water soluble pyrophosphate and a soluble ferric salt. The most readily available source of the pyrophosphate ion is tetrasodium pyrophosphate ($Na_4P_2O_7$), and this salt may be preferred for economic reasons. Potassium pyrophosphate and the corresponding acid salts, such as $Na_4H_2P_2O_7$ or $K_2H_2P_2O_7$ could be used with equal facility. The most readily available iron salt is ferrous sul-

fate which may be oxidized to supply the ferric ions for the reaction. Reacting proportions may vary from as low as about 0.6 mol of pyrophosphate up to about 1 mol of pyrophosphate per mol of iron. To prepare the titanium modified ferric pyrophosphate any water soluble titanium salt may be used. However, the most practical salt for such purpose is titanyl sulfate ($TiOSO_4$). This is a common intermediate compound in the preparation of titanium compounds from its ores, and it may also be readily prepared by dissolving a hydrous titanium oxide in excess sulfuric acid. The salt is only soluble in solutions containing substantial excess of acid, and it is necessary to introduce a neutralization step whenever the salt is used. The corresponding titanium oxychloride ($TiOCl_2$) could also be used, and in the treatment with zirconium shown in Example II, it is zirconium shown in Example II, it is zirconium oxychloride which is the most readily available and preferred salt for use. In the treatment with antimony, shown in Example III, the antimony chloride ($SbCl_3$) is the most readily available salt, and it requires free acid in the solution for complete solubility. In none of these cases, however, is it intended to imply that there is any limitation on the particular form of antimony or zirconium used other than to require the use of a water or acid soluble compound.

In the treated ferric pyrophosphates of Examples I, II and III, it is preferred to use about 0.2 mol of the titanium or other treating salt per mol of iron. However, this amount of treating salt may vary from about 0.1 mol to 0.3 mol without materially changing the properties of the resulting compositions. On the other hand, there is no evidence of significant advantage in amounts above 0.2 mol, but as the amount is significantly decreased below this point, a loss in effectiveness is observed. The composition of such products is as follows:

	Percent
Iron as Fe_2O_3	30–40
Phosphorus as P_2O_5	40–50
Ti, Zr or Sb as its oxide	4–10

The balance of the composition will be essentially water, but there will also be present in the flame retardants of this invention a small amount of sodium or other alkali metal from the process which prepared the ferric pyrophosphate.

In the product of Example II, the zirconium as ZrO_2 is equivalent to about 9.1% while the antimony as Sb_2O_3 in the product of Example III is about 7.4%. Analysis of such products made with a titanium salt as the treating agent show:

	Range	Typical
	Percent	*Percent*
Iron as Fe_2O_3	30–40	36.1
Phosphorus as P_2O_5	40–50	48
Titanium as TiO_2	4–6	4.7

The actual compounds present in these treated products are difficult to determine, but the properties are consistent with the proposition that the treating agent is precipitated on the freshly precipitated ferric pyrophosphate as a hydrous metal oxide which becomes an intimate part of the over-all composition.

In the preparation of cellulose acetate compositions containing the flame-retarding agents described in this invention, it is necessary that these agents be dispersed in extremely small particle sizes before they may be used. This requirement of extreme dispersion is particularly important in the preparation of fibers for several reasons. Particles of any appreciable particle size might either clog the filter before the spinneret or clog the holes in the spinnerets themselves; or if it did pass through the spinneret, a large particle might weaken the very fine filaments and cause breaks during their subsequent processing. Also, particles of any significant size may impair the appearance of either fibers or films. Consequently, it is necessary to introduce a step which disperses the flame-retarding agents in the spinning solutions, but the particular method by which this is done is not in any way a part of this invention. It is very convenient to use techniques generally applicable to the dispersion of pigments in liquid compositions such as grinding in a ball mill in a fluid medium, and the process of Example IV in which the fluid medium is a solution of a small amount of cellulose acetate in an appropriate solvent, such as acetone, is merely typical of such processes. Dispersion can be effected in the solvent alone, but experience has shown that it is more effectively done in the presence of a small amount of cellulose acetate. Other dispersing agents could be used if one desires them in the subsequent spinning solutions. The amount of solids in this dispersion preparation is not important, except that it must be low enough to maintain a suitable consistency for effective ball milling. Other effective methods of dispersion in such liquid compositions include grinding on roller mills, passing through homogenizers, and plastic milling in compositions of high viscosity such as cellulose acetate containing only a small amount of solvent, or even molten cellulose acetate.

The preparation of cellulose acetate films and fibers is a very complex art in which the exact composition of the solutions from which the films are cast or the fibers are spun may be varied widely in a manner well known in the art to obtain particular properties in the resulting films or fibers. The only point in these possible variations which is significant to this invention is the introduction of the preferred modified pyrophosphates to confer upon the compositions fire retardant properties. In the introduction of these modified pyrophosphates, it is convenient, as shown in Examples IV and V, to add a desired amount of a dispersion prepared as in Example IV to a composition suitable for the ultimate desired purpose in such amounts as will give from about 0.5% to about 5% of the modified pyrophosphate on the basis of the final cellulose acetate composition. In the case of the preparation of cellulose acetate fibers, it is preferred to add this separately prepared dispersion of the modified pyrophosphate to the spinning solution just prior to its filtration before spinning. A significant improvement in fire retardant properties of cellulose acetate fibers is obtained with as little as 0.5% of the modified pyrophosphates, and very highly desirable products are obtained in the range of 1 to 2%. Fibers made in this way show substantially no change in properties when compared to fibers containing no pyrophosphate. The fibers can be further dyed, or colored pigments may be introduced into the spinning solution to obtain any desired color. It is not intended to exclude the possibility of using the novel compositions of this invention in amounts above the preferred maximum of 5%, but the introduction of such larger amounts frequently may result in an alteration of the properties of the fiber, and it is also economically unattractive.

This invention has been set forth as having its principal utility in imparting flame resistance to "cellulose acetate" by which term is meant the acetone soluble polymer commonly obtained by partially hydrolyzing cellulose triacetate so that it contains 2.3 to 2.5 acetate groups per structural unit in the cellulose chain. This is the most widely used modification, but it is contemplated that true cellulose triacetate which can be spun from chloroform solution, for instance, can be made flame resistant in a comparable manner. A number of other cellulose esters and ethers have been used for special effects, such as cellulose butyrate or cellulose propionate, as well as mixed esters containing both acetate and butyrate or propionate groups. These are also

formed into fibers or films from acetone solutions, and they can be made flame resistant in the manner set forth above. The cellulose ethers such as ethyl cellulose and benzyl cellulose may also be formed into films from solvent solutions, and flame resistance may be imparted by incorporating the metal pyrophosphates of this invention.

Cellulose acetate fibers made according to the disclosures of this invention offer many advantages with respect to freedom from flammability over prior art cellulose acetate fibers. For the first time, cellulose acetate fibers have been given a flame resistant treatment which does not significantly alter the other properties of the fibers. There is no significant lowering of the softening point; there is no significant change in the resilience or hand of the textiles made therefrom; and there is no loss in the ability to dye the textiles. In particular, it is believed that these products open for the first time the wide-scale use of cellulose acetate in the manufacture of rug fibers. Such products are also potentially useful in many other applications of cellulose acetate such as in knit goods or the like, and these fire resistant products would offer marked advantages over products currently available.

I claim:

1. A flame-retarding composition of matter consisting essentially of a major amount of ferric pyrophopsate and a minor amount of a hydrous metal oxide, the metal of said oxide being selected from the group consisting of titanium, zirconium, and antimony, said composition containing 30–40% iron calculated as Fe_2O_3; 40–50% phosphorus as P_2O_5; 4–10% metal as the metal oxide; the balance being essentially water.

2. The composition of claim 1 in which the metal of the hydrous metal oxide is titanium.

3. The composition of claim 2 in which titanium as TiO_2 is 4–6%.

4. The composition of claim 1 in which zirconium as ZrO_2 is about 9.1%.

5. The composition of claim 1 in which antimony as Sb_2O_3 is about 7.4%.

6. A process for preparing a composition adapted to impart flame retardant properties to cellulose materials which comprises contacting a ferric pyrophosphate in an aqueous medium with a metal salt selected from the group consisting of titanium, zirconium, and antimony salts, which are water and acid soluble, in the ratio of 1 mol of ferric pyrophosphate to 0.1–0.3 mol of the metal salt, adjusting the pH to between 2.8 and 3 and recovering the flame-retarding composition from the aqueous medium.

7. The process of claim 6 in which the metal salt is a titanium salt in an amount of about 0.2 mol per mol of ferric pyrophosphate.

8. The process of claim 7 in which the titanium salt is titanyl sulfate in an amount of about 0.2 mol per mol of ferric pyrophosphate.

9. The process of claim 6 in which the metal salt is a zirconium salt in an amount of about 0.2 mol per mol of ferric pyrophosphate.

10. The process of claim 6 in which the metal salt is an antimony salt in an amount of 0.2 mol per mol of ferric pyrophosphate.

11. A flame retardant cellulose material consisting essentially of a major amount of a cellulose derivative selected from the group consisting of cellulose ethers and cellulose esters and a minor amount sufficient to impart flame retardant properties to said cellulose derivative of a ferric pyrophosphate-hydrous metal oxide composition, the metal of said oxide being selected from the group consisting of titanium, zirconium, and antimony, and said composition containing 30–40% iron calculated as Fe_2O_3; 40–50% phosphorus as P_2O_5; 4–10% metal as the metal oxide; the balance being essentially water.

12. A flame retardant cellulose material consisting essentially of a major amount of a cellulose derivative selected from the group consisting of cellulose ethers and cellulose esters and from 0.5 to 5% by weight of a ferric pyrophosphate-hydrous metal oxide composition, the metal of said oxide being selected from the group consisting of titanium, zirconium, and antimony, and said composition containing 30–40% iron calculated as Fe_2O_3; 40–50% phosphorus as P_2O_5; 4–10% metal as the metal oxide; the balance being essentially water.

13. The flame-retardant cellulose material of claim 12 in which the cellulose derivative is cellulose acetate, and the metal oxide is TiO_2 in an amount ranging from 4–6% of the ferric pyrophosphate-hydrous metal oxide composition.

14. The flame-retardant cellulose material of claim 12 in which the cellulose derivative is cellulose acetate, and the metal oxide is ZrO_2 in an amount of about 9.1% of the ferric-pyrophosphate-hydrous metal oxide composition.

15. The flame-retardant cellulose material of claim 12 in which the cellulose derivative is cellulose acetate, and the metal oxide is Sb_2O_3 in an amount of about 7.4% of the ferric pyrophosphate-hydrous metal oxide composition.

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