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METHOD OF FLAMEPROOFING COMBUSTIBLE MATERIAL

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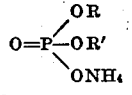
10 Claims. (Cl. 91—68)

This invention relates to the treatment of normally combustible solid materials including wood, textiles such as cotton, rayon, linen, etc., sheetings such as Cellophane, paper, cardboard, wallboard, and the like, whereby the flammable characteristics are reduced very substantially if not actually eliminated.

It is known that di ammonium phosphates, $(NH_4)_2HPO_4$ and mono ammonium phosphate, $NH_4H_2PO_4$ are useful as flameproofing agents. For this purpose the phosphate salt is usually dissolved in water and applied to the flammable object under conditions which leave on drying sufficient salt residue to accomplish the intended purpose. Although this procedure is entirely satisfactory for many purposes it can not be used generally. For example, since the inorganic residue appears as a crystalline deposit it is unsuitable when used in connection with light fabrics and paper, notably Cellophane. It is also known that fabrics and sheeting must be treated in order to overcome normal brittleness and harshness. For this purpose hygroscopic agents such as glycerine are used. However, glycerine by itself has no fire retarding properties, and moreover, it decomposes at elevated temperatures to form acrolein whose vapor is extremely irritating to eyes and mucous membranes.

I have now discovered that the alkyl ammonium phosphate salts impart the excellent flame resisting qualities of inorganic ammonium phosphate (despite the fact that they contain organic constituents and might be assumed to have less or no useful fire-retarding characteristics). Equally important is the fact that the deposits of the organic phosphate salts leave no visible crystalline residue on materials such as fine fabrics, sheeting, etc., and that the use of the salts reduces or entirely disposes of the need for glycerine while at the same time avoids the acrolein formation when exposed to high temperatures.

By alkyl ammonium phosphate salts I mean salts of the following general formula:



in which R is an alkyl group and R′ is a radical selected from the group consisting of H, NH_4 and R. These salts are also generally known as ammonium salts of alkyl phosphoric acids.

The methods by which the organic salts are made form no part of the present invention. Various methods are used. In general, the salts are made conveniently by reacting ammonia or aqua ammonia with the alkyl phosphoric acid. In as much as the salts are used most conveniently as aqueous solutions no evaporation is necessary when using aqua ammonia. The alkyl phosphoric acid is obtained conveniently by reacting phosphorus pentoxide (P_2O_5) with an excess of alcohol or alternately by reacting pyro, meta, or tetraphosphoric acid with alcohol, preferably anhydrous. Excess alcohol may be stripped and recovered from the neutralized acid by simple distillation of the aqueous salt solution or steam distillation of the aqueous salt solution. Excess ammonia, if any, may be recovered by the same means and simultaneously.

Salts contemplated by the present invention include the dialkyl ammonium phosphates and the monoalkyl ammonium phosphates of the type included in the above disclosed general formula. In general one can obtain mixtures of the mono and di alkyl phosphoric acids more conveniently than either one of the materials particularly when using meta or pyro phosphoric acid or P_2O_5 and for my purpose the mixture is equally suitable or even preferred under some conditions. Thus, a mixture of mono and di ethyl ammonium phosphates results when anhydrous ethyl alcohol is reacted with P_2O_5 and subsequently is neutralized with aqua ammonia. I have also found that the mono alkyl mono ammonium phosphates and the mono alkyl di ammonium phosphates of the above general formula are suitable for my purpose and that mixtures are especially useful where both hygroscopic and fire retardation are required to a high degree.

I prefer to use an alkyl salt in which the alkyl group is derived from an alcohol that is relatively water soluble such as methyl, ethyl, propyl, butyl, or amyl, or mixtures of these.

Under some conditions of manufacture there is formed a certain amount of the ammonium salt of alkyl phosphoric acid. This material may be used alone or in admixture with the ortho phosphate salts.

One convenient procedure which I have used consists in adding one mole of P_2O_5 slowly to approximately four moles of absolute ethyl alcohol and thereafter neutralizing the reaction mixture with aqua ammonia to a methyl orange neutrality. The product obtained after the evaporation of the excess alcohol and water has a pH of 4.7% and contains 9.9% combined NH_3. An analysis of this material indicates that the following materials are present in substantially the percentages shown:

	Per cent
Di ethyl mono ammonium phosphate	67.2
Mono ethyl di ammonium phosphate	18.2
Mono ethyl mono ammonium mono hydrogen phosphate	12.1
Mono ammonium di hydrogen phosphate	2.4

Usually there is so small an amount of residual alcohol or ammonia in the product that the solution as formed may be used without further processing for many purposes. However, when

the residual alcohol or ammonia is large or must be removed distillation, preferably under reduced pressure conditions, may be used effectively.

The following examples illustrate embodiments of the present invention:

Example 1.—A mixed ethyl ammonium phosphate such as described above is made up in an 8.3% aqueous solution. A cotton cloth is thoroughly saturated with an 8.3% aqueous solution of ethyl ammonium phosphate of the above composition. Subsequently the excess solution is removed by manual wringing and the cloth is finally allowed to dry. The dried fabric has an excellent soft feel and is not inflammable whereas the untreated cotton fabric is relatively harsh and has the flammable characteristics of ordinary cotton cloth.

Example 2.—Strips of Cellophane were soaked in water to remove glycerine after which some of these strips were suspended in air to dry. Other strips so treated were immersed in the solution as described in Example 1 and were allowed to drain and dry in air. The untreated materials were flammable and moreover had a harsh and brittle feel typical of sheeting which contains no glycerine. On the other hand the treated material charred under the flame but was not flammable and had a soft flexible feel comparable to that of the original samples before the removal of the glycerine. The salt appears to be uniformly distributed and does not impair the transparency of the sheeting. This is to be contrasted with the inorganic ammonium phosphates which leave a white crystalline deposit on the sheeting in sufficient amount to impair the transparency of the sheeting.

Example 3.—By substituting the corresponding methyl ammonium phosphate for the ethyl phosphate salt of Example 1, which methyl ammonium phosphate is obtained in a manner analogous to that described above for the ethyl ammonium phosphate, one obtains a product which when applied to flammable materials such as cotton, Cellophane, etc., renders them non-inflammable and imparts a desirable feel to the material.

The exact method of applying the alkyl ammonium phosphate salts can be varied widely. However, in general, the procedure which I have found most convenient is analogous to that used with other water-soluble treating agents. I may add the salt directly to the sizing as is the practice with glycerine containing sizing. It is to be noted that when so used the sized material not only has the desired feel but also has the added quality of non-inflammability that is not obtained with glycerine as is pointed out above. It is to be understood that the phosphates contemplated by the present invention may be used as partial or total substitutes for glycerine or inorganic ammonia phosphates.

It is to be understood in the claims when I use the expression salt of phosphoric acid it is to include not only the salts of ortho but also the salts of pyro phosphoric acid. It is also to be understood that the mixtures of salt such as mono ammonium or di ammonium salt of phosphoric acid and also mixtures containing mono alkyl and di alkyl ammonium salts are specifically comprehended herein and further that minor amounts of ammonium phosphates from the methods of making alkyl ammonium salts may be present without departing from the spirit of the present invention.

What I claim is:

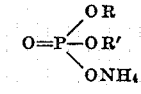
1. The method of rendering flammable materials fire resistant characterized in that there is applied thereto an aqueous solution of an ammonium salt of an alkyl phosphoric acid, in which the alkyl group has from one to five carbon atoms, after which the materials thus treated are dried.

2. A sheeting of cellulosic material having applied thereto an ammonium salt of an alkyl phosphoric acid in a sufficient amount to render the same flexible and non-inflammable, the alkyl group of said salt having from one to five carbon atoms.

3. A normally flammable cellulosic material comprising a regenerated cellulose sheeting, having applied thereto an ammonium salt of an alkyl phosphoric acid in sufficient amount to render the material substantially non-inflammable, the alkyl group of said salt having from one to five carbon atoms.

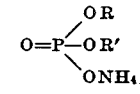
4. As an article of manufacture a flammable material having incorporated therewith an ammonium salt of ethyl phosphoric acid in sufficient quantity to render said material substantially fireproof.

5. As an article of manufacture a flammable material having incorporated therewith a phosphoric acid derivative of the following general formula:



in which R is an alkyl group containing from 1 to 5 carbon atoms and R′ is a radical selected from the group consisting of H, NH_4 and R, said derivative being present in sufficient quantity to render said material substantially fireproof.

6. As an article of manufacture a flammable material having incorporated therewith a mixture of phosphoric acid derivatives of the following general formula:



in which R is an alkyl group containing from 1 to 5 carbon atoms and R′ is a radical selected from the group consisting of H, NH_4 and R, said mixture being present in sufficient quantity to render said material substantially fire-proof.

7. As an article of manufacture a flammable material having incorporated therewith a phosphate salt mixture comprising the mono ammonium salt of monoethyl phosphoric acid and the mono ammonium salt of diethyl phosphoric acid, said mixture being present in sufficient quantity to render said material substantially fire-proof.

8. As an article of manufacture a flammable material having incorporated therewith a phosphate salt mixture comprising the mono ammonium salt of monomethyl phosphoric acid and the mono ammonium salt of dimethyl phosphoric acid, said mixture being present in sufficient quantity to render said material substantially fire-proof.

9. The method of rendering flammable materials fire resistant which comprises saturating said materials with a relatively dilute aqueous solution of a phosphate salt mixture comprising the mono ammonium salt of a monoalkyl phosphoric acid and the mono ammonium salt of a dialkyl phosphoric acid, the alkyl groups in said

salt mixture containing from 1 to 5 carbon atoms, and then drying the materials thus treated.

10. The method of rendering flammable materials fire resistant which comprises saturating said materials with a relatively dilute aqueous solution of the salt mixture obtained by reacting one mole of phosphorous pentoxide with four moles of an absolute alkyl alcohol containing from 1 to 5 carbon atoms, neutralizing the reaction product with aqua ammonia and evaporating excess alcohol and water, and then drying the materials thus treated.

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