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PROCESS OF TREATING CELLULOSIC AND SIMILAR MATERIALS

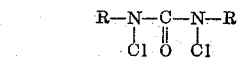
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3 Claims. (Cl. 117—138.5)

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This invention relates to a process of treating cellulosic materials, or materials similar in nature or composition to the cellulosic materials, such as starches, esters of cellulose, or regenerated cellulose materials, to render them resistant to degradation by the action of acids and unstable chlorinated compounds which yield acid when subjected to conditions of temperature and/or high humidities. Chlorinated paraffins, tetrachloroethane, and products of the general structure



where R is an alkyl group, are typical examples of unstable chlorinated compounds which react in this manner.

This application is a continuation-in-part of my copending application, Serial No. 591,428, filed May 1, 1945, which is now abandoned.

The cellulosic materials herein referred to could be textiles made from cotton, linen, jute, ramie, or regenerated cellulose, materials made from wood pulp such as paper, and materials made of modified cellulose such as cellulose acetate, nitrocellulose, etc.

The cellulosic materials, or materials similar in nature to cellulose, when treated with highly chlorinated compounds will degrade or hydrolyze when exposed to heat and moisture. These materials are readily degraded by acid in solution or acid formed from the breakdown of unstable chlorinated compounds which have been used to treat the cellulose materials. The action of the acid in either case is to convert the cellulose to a weaker hydro-cellulose, thus "tendering" or weakening the fiber. The degree to which "tendering" will take place depends to a large extent upon the temperature at which drying is effected, as well as the humidity conditions prevalent during exposure to the drying temperatures. Cotton which has been tendered by acid has undergone chemical change, evidenced by a slight increase in the percentage of hydrogen and oxygen. This product formed by the action of acid on cellulose is known as hydro-cellulose. The extent of this degradation of cellulose depends on the temperature, the concentration of the acid formed, and the length of time such cellulosic materials are exposed to the action of the acid. Degradation implies the impairment and even the destruction of the strength of cellulosic materials. I have observed an appreciable loss in the tensile strength of a cotton fabric thoroughly wetted in certain acid solutions and dried.

An object of this invention is to provide a process for treating cellulosic materials or materials of a similar nature to inhibit the degradation thereof when subjected to the action of acids, as, for example, hydrochloric, sulphuric, phosphoric or oxalic acid, or compounds which break down to form any one of these acids. An

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example of such a compound is a highly chlorinated hydrocarbon liberating hydrochloric acid in the presence of high temperatures and moisture.

A further object of the invention is to provide a process for treating fabrics such as cotton or other cellulosic fabrics, whether or not such fabrics have been treated or sized with resins, starches or other materials so that when such fabrics are exposed to acid in solution, the fabrics will be rendered partially or totally immune to attack by such acid agents.

I have found that cellulosic materials or other materials of a similar nature or composition may be protected against degradation by treating with an aqueous solution containing alkali-metal molecularly dehydrated phosphate, such as the water soluble sodium, potassium, lithium, and ammonium phosphate glasses or the crystalline tetrasodium pyrophosphate and sodium tripolyphosphate. The alkali-metal phosphate glasses may be generally designated by the formula

$$XM_2O.1P_2O_5$$

where M is an alkali-metal or the ammonium radical, and X is a number ranging from zero to two. The alkali-metal phosphate glasses may be prepared over a wide range of composition as indicated by a ratio of $M_2O:P_2O_5$ of from less than 0.8:1 to about 1.7:1. The broad range of this ratio extends from glassy P_2O_5 where the ratio of $M_2O:P_2O_5$ is 0, to a ratio of 2:1 which is that of the pyrophosphate composition.

This invention may be practiced or applied in various procedures. For example, the cellulosic materials may be impregnated in a solution containing a molecularly dehydrated phosphate before such materials have been exposed to the action of the aforementioned acid degrading agents. The solutions should have a concentration of at least 0.5% of molecularly dehydrated phosphate, but may contain as high as 2% or 3%. I have found that a solution containing a concentration of 1% of molecularly dehydrated phosphate, such as a sodium phosphate glass having a ratio of $Na_2O:P_2O_5$ of about 1.1:1, will produce very good protective results when measured by the tensile strength of the cellulose fabric after action of acid agents which normally cause degradation.

I may also utilize the invention by immersing the cellulosic materials in an aqueous solution containing about from 0.5% to about 3% of a molecularly dehydrated phosphate followed by removing the materials from the solution and drying them, when drying is practicable. After drying, the materials may be treated in acid solutions or with highly chlorinated hydrocarbons. I have found that little or no degradation of the cellulosic materials occurs when fabrics or cellulose are treated with acids or acid-liberating materials following a treatment in a solution containing a molecularly dehydrated phosphate as

above described. When the cellulosic materials have been treated in a solution of molecularly dehydrated phosphate, I prefer, as above stated, that the material be dried after removal from such solution. However, I have found that even though not dried, these materials are protected against degradation by acid.

Molecularly dehydrated phosphates may be added directly to an acid solution or to solutions of unstable chlorinated compounds when these solutions are to be used for treating cellulose. Cellulose materials treated in this manner are protected against degradation, thereby preventing conversion of cellulose to hydrocellulose.

Instead of first treating the cellulosic materials in a solution containing a molecularly dehydrated phosphate, I may treat such materials in a solution containing both acid or acid-forming compounds and molecularly dehydrated phosphate. When a mixture of the molecularly dehydrated phosphate and acid are used, the amount of molecularly dehydrated phosphate in the mixture with relation to the solution should be such as to provide a concentration of at least 0.5%.

When mixtures of molecularly dehydrated phosphates and unstable compounds which liberate acid under favorable conditions are employed, the proportions of phosphate to acid-liberating product may vary from about 2:1 to about 20:1. If such a mixture, when added to water, produces an acid concentration of 0.50%, the contration of phosphate would be 1.0% for the 2:1 ratio mixture and 10% for 20:1 ratio mixture.

An example of my process is where I treated a cotton broadcloth material that had been properly bottomed by the progressive Jig process (desizing and caustic boil) in a solution of 0.5% hydrochloric acid. The goods were removed from this solution and allowed to dry in the air. At the end of eight hours the cloth was dry and partial degradation of the cellulose had taken place. Another piece of the same broadcloth was passed through an aqueous solution containing 0.5% hydrochloric acid and 1% sodium phosphate glass, the glass having a ratio composition of $Na_2O:P_2O_5$ about 1.1:1. After removal from this solution, the cloth was dried. Very little degradation of the second piece of fabric was noticed.

The following table will show the benefits derived from the addition of molecularly dehydrated phosphate to an acid solution to inhibit the degradation of cellulose treated in such solutions:

Acid Solution	Tensile Strength (lb./in.²)	
	Air Dried	Treated at 100% relative humidity at 70° C. for 19 hrs.
Control	75.4	62.0
0.25% H_2SO_4	48.6	9.9
0.25% H_2SO_4+0.5% phosphate	55.3	24.7
0.25% H_2SO_4+1.0% phosphate	59.1	32.8
0.25% HCl	46.7	21.2
0.25% HCl+1.0% phosphate	58.2	50.0

It will be noted that there is a moderate superiority in the tensile strength of air dried samples which have been treated with the inhibited acid. However, in the case of those subjected to an elevated temperature and 100% relative humidity, the tensile strength loss is markedly reduced by the addition of phosphate to the acid solutions. Obviously, the improvement in tensile strength is highly desirable, particularly where the finished fibers are to be woven into fabrics exposed to the severe climatic conditions of humidity at elevated temperatures.

Having thus described the invention, what I claim as new and desire to secure by Letters Patent is:

I claim:

1. The method of treating materials of the class consisting of cellulose, cellulose coated with resins, cellulose coated with starch, and cellulose coated with mixtures of resins and starch to thereby inhibit degradation thereof when contacted with acid which consists in wetting said materials with an aqueous solution containing from about 0.5% by weight to about 10.0% by weight of an alkali-metal molecularly dehydrated glassy phosphate having a molar ratio of M_2O to P_2O_5 of from about 0.8:1 to 1.7:1, where M is a member of the group consisting of ammonium, lithium, sodium and potassium, removing said materials from contact with said solution and drying the same, the phosphate retained by said materials inhibiting degradation thereof when wetted with acid.

2. The method of treating materials of the class consisting of cellulose, cellulose coated with resins, cellulose coated with starch, and cellulose coated with mixtures of resins and starch to thereby inhibit degradation thereof when contacted with acid which consists in wetting said materials with an aqueous solution containing from about 0.5% by weight to about 10.0% by weight of an alkali-metal molecularly dehydrated glassy phosphate having a molar ratio of M_2O to P_2O_5 of from about 0.8:1 to 1.3:1, where M is a member of the group consisting of ammonium, lithium, sodium and potassium, removing said materials from contact with said solution and drying the same, the phosphate retained by said materials inhibiting degradation thereof when wetted with acid.

3. The method of treating materials of the class consisting of cellulose, cellulose coated with resins, cellulose coated with starch, and cellulose coated with mixtures of resins and starch to thereby inhibit degradation thereof when contacted with acid which consists in wetting said materials with an aqueous solution containing from about 0.5% by weight to about 10.0% by weight of an alkali-metal molecularly dehydrated phosphate having a molar ratio of alkali-metal oxide to phosphorus pentoxide (P_2O_5) of from about 0.8:1 to 2:1, the alkali-metal of said alkali-metal oxide being selected from the group consisting of sodium, potassium, lithium and ammonium, removing said materials from contact with said solution and drying the same, the phosphate retained by said materials inhibiting degradation thereof when wetted with acid.

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