

1

2,949,385

FIRE-RETARDANT PROCESS

John E. Malowan, Dayton, and Morris L. Nielsen, Centerville, Ohio, assignors to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Filed Jan. 27, 1953, Ser. No. 333,601

1 Claim. (Cl. 117—138)

This invention relates to the treatment of cellulosic materials in order to improve their resistance to fire.

It is an object of the invention to provide a method for rendering cellulosic materials fire-resistant. It is another object of the invention to provide flame-resistant cellulosic products. Still another object of the invention is the modification of textile fibers and other combustible materials containing cellulose to render the same resistant to fire.

It is known in the prior art that cellulosic materials such as textile products can be modified to improve their resistance to fire by treatment with phosphorus compounds. For example, U.S. Patent 2,401,440 describes the treatment of cellulosic products such as alkali cellulose by treatment first with phosphorus oxychloride and then with ammonia. While the products produced by the process described in this patent contain chemically bound phosphonamide groups, the treatment involved the use of chemical reagents which the textile processing industry was not generally equipped to handle. For this reason a simpler method which could be used in the ordinary textile plant without special equipment or skills was greatly to be desired.

In accordance with the terminology which has been developed in this field "fire-resistance" and "flame-resistance" result from the treatment of a base material such as cloth with various chemicals so that it becomes resistant to the propagation of flame across its surface after the igniting flame has been removed; that is, a flame-resistant material will not support combustion independently of an external source of heat. In contact with an open flame, however, or at elevated temperatures, flame-resistant cellulosic material can be expected to char and decompose.

The products of the present invention exhibit the properties of fire-resistance or fire-retardancy, while at the same time maintaining to a large degree the original "hand" of the material. The color, physical appearance and the property of softness are not substantially affected by the present treatment.

It has been found that an improved fire-retardant treatment of combustible cellulosic materials such as cotton and other cellulosic derivatives including cellulose acetate, cellulose nitrate, and regenerated cellulose may be provided with the hydrolyzed water-soluble, nitrogen- and phosphorus-containing product described in copending application Serial No. 333,602, filed January 27, 1953, now Patent No. 2,749,233, which application is assigned to the same assignee as is the present case. This treatment results in the production of a permanent flame-resistant material of excellent "hand," which exhibits substantially the physical appearance and property of softness of the untreated fabric.

According to the copending application referred to above, the nitrogen- and phosphorus-containing products utilized in the present invention are produced by the hydrolysis of the substantially water-insoluble reaction product of phosphorus oxychloride and ammonia, which is

2

obtained from a reaction carried out at a temperature in the range of from 155° C. to 200° C. The said hydrolysis is conducted by treatment of the aforementioned condensation product with from 10% to 35% by weight of water at a temperature in the range of from 80° C. to 150° C. at a pressure of about 2 atmospheres or more. The hydrolysis may also be conducted in the presence of minor proportions of dilute mineral acids or bases as catalysts. The above reaction results in the production of a water-soluble product forming viscous solutions with water. The molecular weight of the water-soluble hydrolysis product is preferably in the range of from 200-250. Solutions containing up to 50% by weight of solids may readily be prepared.

The nitrogen-phosphorus atomic ratio of the hydrolyzed product lies in the range of 1.25:1 to 1.9:1, which represents a product desirable from the standpoint of providing a material which may combine with an organic resin in a fire-retardant composition to release nitrogen compounds as gases upon exposure to fire. Consequently, when a resin is present, the entire coating composition swells to provide a porous insulating layer when subjected to extreme heat, thereby protecting the treated fabric or other combustible cellulosic material, such as cotton, straw, paper, bagasse, rayon and the like.

Cellulosic textile products are impregnated or coated with the above-described water-soluble hydrolyzed product by immersing the said textile materials in previously prepared, aqueous solutions of the hydrolyzed product. Aqueous solutions are preferred but other solvents may also be used. The concentration of the solutions may vary over a wide range depending upon the desired "add-on" which is to be obtained. In general, solutions containing from 5% to 50% by weight of the hydrolyzed product may be employed to obtain an add-on in the range of from 5% to 50% by weight relative to the weight of the base material. Fabrics which are to withstand washing are preferably treated to obtain an add-on of 20% to 25% by weight. In the treatment of rayon it has also been found that dimensional stabilization is greatly improved as a result of the deposition of the said water-soluble hydrolyzed material. After impregnation of the textile fabric and in order to produce a wash-fast, fire-retardant fabric the impregnated fabric is dried and then subjected to a temperature of at least 100° but below 200° C. However, if it is not necessary to produce a wash-fast product the heating step may be omitted.

In accordance with this invention, a fire-retardant composition is provided in which the essential constituent is the above-described hydrolyzed phosphorus-nitrogen-containing component. This material may also be formulated in combination with various organic resinous materials, such as the aminoplast resins and intermediate condensation products thereof. When a resinous component is employed it may be applied in the range of 0.5% to 25% by weight, calculated as final add-on of the final material. The present invention contemplates combination compositions employing amine-aldehyde, aminoaldehyde, iminealdehyde and iminoaldehyde condensation products. A typical example of resins of this class is a urea-formaldehyde resin. Aminoplast resins are discussed in Modern Plastics, 17, 433 (1939). Other aminoplasts are described in C. Ellis, Chemistry of Synthetic Resins, chapter 25 (Reinhold Publishing Company, 1939), and R. Nauth, Chemistry and Technology of Plastics, chapter 3 (Reinhold Publishing Company, 1947). Further examples are the formaldehyde condensation products with urea, melamine, thiourea-guanidine, cyanamide, dicyandiamide, aniline, para-toluene, sulfonamide and also the corresponding acetaldehyde and furfural condensation products in this same relationship. Such resinous compositions may employ high or low degrees of methylation

(or the corresponding acetyl or furfural substitution) such as from 1 to 6 methylol radicals per mole of the acceptor compound in the case of melamine. The use of alkylated modifications of such resins is likewise contemplated, particularly in the butylated modifications, such as are conventional in urea-formaldehyde and melamine-formaldehyde resins. Mixtures of such resins or the addition of other types of resins may also be employed.

In addition to the synthetic type of resins as set forth above, it is also possible to utilize nitrogen-containing resinous materials derived from natural sources such as casein. The casein compositions, insolubilized by formaldehyde, are of particular utility for this purpose. Polyamide resins which may be brought into solution or dispersion may also be introduced into the compositions of the present invention.

In the application of the above combination compositions including essential water-soluble hydrolyzed product described above, the dry components such as a water-insoluble resin may be suspended in water with the aid of dispersing agents and the suspension including the water-soluble hydrolyzed product may thus be applied to fibrous materials in known manner. The hydrolyzed product in combination with the organic resinous constituent apparently adheres to, is impregnated upon, or is adsorbed by cellulosic base materials which are to be treated, thereby reducing the burning tendency of the otherwise combustible cellulosic material.

In combinations utilizing an organic resinous material dissolved or dispersed in water, together with the hydrolyzed compositions described above, it has been found that the latter constituent should be present in the range of from 0.5% to 25% by weight based upon the dry materials, a preferred range or composition for fabrics subject to washing being from 20% to 25% by weight.

The following examples illustrate the invention.

Example 1

A 40% solution of the hydrolyzed water-soluble derivative of the water-insoluble product of phosphorus oxychloride and anhydrous ammonia was applied to cotton cloth to give a 100% increase in weight in the wet state. The cloth was then dried at 105° C. and then cured at 150° C. for 10 minutes. After washing the treated cloth showed a high degree of flame-resistance.

Example 2

A solution was prepared from 25 g. of the above-described hydrolyzed water-soluble material together with 50 g. of methylolated melamine and 90 g. of water as a solvent. The solution was padded on cotton cloth, after which it was dried and then cured at 160° C. It was found that even after washing the fabric an add-on of 30% to 35% remained. The treated cloth was shown to be fire-resistant as determined by the ASTM test. In addition the thus-treated material was found to retain its effectiveness in resisting the propagation of fire even

after 36 washings performed at a temperature of 120° F.

The details of the testing procedure utilized in testing the flameproofing qualities of the present compositions are shown in the book by R. W. Little entitled *Flameproofing Fabric Materials* (Reinhold Publishing Company, 1947).

Example 3

Pieces of filter paper were impregnated with a solution containing 2.5 g. of the water-soluble hydrolyzed derivative of the water-insoluble reaction product of phosphorus oxychloride and anhydrous ammonia, said solution also containing 10 g. of methylolated melamine and 50 g. of water. After drying and curing at 150° C. for 10 minutes, the samples were tested and found to be flameproofed. On exposure to a high humidity (90%) at 50° C. in a closed cabinet for 24 hours, there was practically no increase of weight, indicating that the treated material was not hygroscopic. It was also found that soaking a piece of the treated paper in water for 30 minutes did not reduce the fire-retardant qualities.

In the application of the water-soluble hydrolyzed derivative of the water-insoluble reaction product of phosphorus oxychloride and anhydrous ammonia as coating compositions on combustible materials to render them fire-resistant, it is also contemplated that other chemical components may be used in combination therewith. For example, other fire-retardant chemicals such as antimony oxide may also be applied either as a separate operation of simultaneously with the present materials. In such a combined treatment the present hydrolyzed material is of particular utility in repressing the catalytic tendency of the metal oxides to exhibit the characteristic afterglow.

What is claimed is:

A process for the treatment of cellulosic textile products which comprises applying to a cellulosic textile product a previously-prepared water-soluble hydrolysis product of the water-insoluble reaction product of phosphorus oxychloride and anhydrous ammonia having been formed at a temperature in the range of from 155° C. to 250° C., said water-soluble hydrolysis product exhibiting a pH within the range of from 7.0 to 7.5 in aqueous solution and having a molecular weight in the range of from 200-250, and thereafter heating said treated cellulosic product to at least 100° C., but below 200° C., said treated cellulosic product containing from 5% to 50% by weight of the said hydrolysis product wherein the said hydrolysis product is combined with the said cellulosic textile product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,163,085	Cupery	June 20, 1939
2,424,831	Klaber	July 29, 1947
2,582,181	Truhlar	Jan. 8, 1952
2,596,496	Marling et al.	May 13, 1952
2,596,935	Malowan et al.	May 13, 1952

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,949,385

August 16, 1960

John E. Malowan et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 29, for "of" read -- or --.

Signed and sealed this 18th day of June 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents