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2,811,469

FABRIC FLAMEPROOFING PROCESS

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This invention relates to the flameproofing of fabrics. Although much work has been done in attempting to flameproof fabrics such as textiles including cellulosic fibers, no satisfactory and simple method has been heretofore proposed that would last for any appreciable length of time and that would not affect the appearance and nature of the fabric. By the methods disclosed and claimed herein it is now possible to flameproof fabric by a simple process that is highly effective and results in a flameproof fabric that is resistant to washing and that is relatively unchanged in its physical qualities and texture.

The methods and materials of this invention permit imparting excellent flame resistance to textiles by a single treatment using a single treating solution. The fabric so treated is rendered flameproof even for repeated washings and its other qualities are in no way impaired. The tensile strength is even increased in most instances.

This simple process is accomplished by treating the cloth with a solution of a polymer of a dialkenyl monochloromethanephosphonate and thereafter curing the impregnated material at moderate temperatures.

Compounds which are suitable for flameproofing textiles by my new method are the partial polymers of di beta, gamma unsaturated alkenyl esters of monochloromethanephosphonic acid such as the allyl, methallyl and crotyl esters. The preferred compounds are diallyl chloromethanephosphonate and dimethallyl chloromethane phosphonate. The diallyl ester is described and claimed in the copending application of Toy and Rattenbury, Serial No. 302,835, filed August 5, 1952, now U. S. Patent No. 2,714,100. Briefly, the esters may be prepared by the reaction of a di beta, gamma unsaturated alkenyl alcohol and chloromethanephosphorus oxydichloride in the presence of a tertiary amine under suitable reaction conditions as set out for the diallyl ester in the above copending application. The pure distilled product of such a reaction is the preferred starting material for this invention. In certain instances where a slightly lesser degree of flame resistance would be acceptable it is also possible to use the crude undistilled product for the process of this invention.

In one method of practicing the process of my invention a 50% solution of a di beta, gamma unsaturated alkenyl ester of chloromethanephosphonic acid is mixed with a small percentage of a polymerization catalyst such as benzoyl peroxide and slowly heated until the viscosity has become approximately two to four and preferably three times, the original value. This viscosity change which is in effect a measure of polymerization, obviously depends on the amount of solvent present in the original solution. For a 50% solution a viscosity change of 3 represents the removal of approximately one of the two unsaturations present in a dialkenyl ester. This percentage of partial polymerization has been found to be most satisfactory for this invention.

The resulting partial polymer solution is then precipitated in a suitable solvent such as hexane which serves to separate the soluble monomer from the insoluble par-

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tially polymerized material. The precipitated polymer may then be dried and ground to a powder. Approximately a twenty per cent solution of this powder is then made using a suitable volatile solvent such as a 30/70 methanol/ethylene dichloride solution. The cloth to be treated is then immersed in this solution for a few minutes to allow good penetration following which the cloth is wrung out and cured by heating at approximately 100° C. for one half hour. The resulting fabric has excellent flame resistant qualities which remain even after several washings. The strength of the cloth is unimpaired and the "hand" is still satisfactory.

The actual flame resistance of this type of fabric is customarily tested according to the method described as the vertical flame resistance test in the Supplement to Federal Specifications for Textiles; General Specifications, Test Methods, CCC-T-191a. In this method a 2½ inch by 10 inch strip of the treated cloth is suspended vertically and ignited at the bottom with a Bunsen burner. Flame resistance is measured by the burning time of the cloth, total char length of the burn, and amount of afterglow. A flameproofing process is generally held to be satisfactory if the burning time is less than 12 seconds, char length less than 6 inches and afterglow negligible. As will be shown later, the methods of this invention easily produce fabric meeting these specifications.

The following examples are included as illustrative of the method of my invention.

Example 1

A solution of 50 gm. of distilled diallyl chloromethanephosphonate and 50 gm. of Chlorex, a trade name for B.B' dichloroethyl ether, was placed in a 500 ml. three necked flask equipped with agitator, thermometer, suitable heating means and equipment for providing a nitrogen atmosphere. The solution was heated to 100° C. and a relative viscosity determined by noting the time required for discharge of 5 ml. of the solution from a standard pipette, in this case 6.5 seconds. This time will hereinafter be designated as the efflux time. One gram of benzoyl peroxide was then added and the heating continued for 45 minutes during which time the efflux time rose to 21.2 seconds or approximately three times the original value after which it was cooled to room temperature. The resulting prepolymer solution was poured into 1500 ml. of hexane which served to precipitate the polymerized material from the hexane-soluble monomer. The precipitate was further washed by grinding in a mortar with a liter of hexane. The powdered product was filtered and air dried resulting in a 21.2 gm. of fine white powder which represented 42.4 percent of the original charged liquid monomer. 20 gm. of this powder was dissolved in 80 ml. of 30/70 methanol/ethylene dichloride solution to form a clear light yellow solution suitable for treating cloth. A 20 by 2½ inch strip of muslin was immersed in this solution for 5 minutes so as to become thoroughly impregnated after which the excess was removed by passing through a wringer. The process was completed by curing the cloth for one half hour at 100° C. At the end of this time the cloth was found to have acquired an "add on" of 26.4% of its original weight. One half of this cloth, when subjected to the flame test, had a burning time of 8.6 seconds and a narrow char length of 5¼ inches. The second half of the cloth was washed for 15 minutes in 200 ml. of a 0.5% soap solution at 140° F. and then dried. It lost 4.36% of its original weight. Upon ignition it burned for 11 seconds giving a char length of 4 inches.

Example 2

Following the same procedure shown in Example 1, 50 gm. of distilled diallyl chloromethanephosphonate was

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converted into 21.7 gm. of white, powdered prepolymer. Using this powder and a 30/70 methanol/ethylene dichloride solution, five solutions were prepared containing from 10.7% to 22% of the powder. 2½ by 20 inch strips of muslin were immersed in these solutions and cured for one half hour at 100° C. following the procedure used in Example 1. The impregnated samples were cut in half and tested both before and after washing, giving the following data.

Sample	A	B	C	D	E
Percent "Add on"-----	28.2	24.2	20.8	17.6	15.7
Burning time, unwashed, sec.-----	8.0	8.6	8.0	9.2	10.4
Char length, unwashed, inches-----	6¼	5¾	6¼	5¾	6¾
Weight loss on washing, percent-----	3.1	2.18	2.61	2.36	2.2
Burning time, washed, sec.-----	10.4	-----	9.2	13.9	19.2
Char length, washed, inches-----	6¼	5	5¾	10	10

These data show that this process will give adequate protection over a wide range in the percentage "add on." For cloth which will be subjected to washing the lower limit producing satisfactory results should preferably be approximately 20% "add on" although protection is still afforded at lower levels. The loss on washing shown in the above data occurs only on the first washing with subsequent washings producing no detrimental effect on the qualities of the cloth.

Example 3

A solution of 50 gm. of distilled dimethylalyl chloromethanephosphonate and 50 gm. of Chlorex was placed in a 500 ml. flask with auxiliaries as were used in Example 1. The solution was heated to 100° C. under a nitrogen atmosphere and the efflux time found to be 5.3 seconds. One gram of benzoyl peroxide was added and the efflux rose to 6.1 seconds in 50 minutes, an additional half gram brought the efflux time to 11.5 seconds in 2½ hours so a final 0.25 gram of benzoyl peroxide was added after which the efflux time slowly rose to 16 seconds at the end of 3½ hours total time.

The solution was cooled to room temperature. Following the procedure of Example 1 the solution was precipitated in 1500 ml. of hexane and further worked with 900 ml. of hexane to give 28.6 gm. of free-flowing white powder. This represents a 57.2% conversion from the original monomer. 20 gm. of this powder was dissolved in 80 ml. of 30/70 methanol/ethylene dichloride solution and a 20 by 2½ inch strip of muslin was immersed therein for 5 minutes. The cloth was then wrung out and cured for ½ hour at 100° C. after which it showed a gain in weight or "add on" of 30.4%. The cloth was tested as described in Example 1 and found to have a burning time of 11 seconds and a char length of 8¾ inches.

Example 4

50 gm. of undistilled diallyl chloromethanephosphonate having an index of refraction $ND_{25}^{25}=1.4687$, was added to 50 gm. of Chlorex and placed in a 500 ml. flask as in Example 1. Under a nitrogen atmosphere it was heated to 100° C. and the efflux time found to be 5.9 seconds. 1 gm. of benzoyl peroxide was added and the efflux time rose to 8.9 seconds in 2 hours and 10 minutes so another 0.5 gm. of benzoyl peroxide was added which raised the efflux to 19.3 seconds at the end of 2½ hours. The solution was cooled to 15° C. and poured into 1500 ml. of hexane and then powdered, using an additional 1550 ml. hexane. 23.3 gm. of yellow powder resulted indicating a conversion of 46.6%. A solution of 22.8 gm. of this powder and 80 ml. of 30/70 methanol/ethylene chloride was prepared for flameproofing fabric. A 20 by 2½ inch strip of muslin prepared as in Example 1 gave a burning time of 12 seconds and a char length of 6¼ inches for a 29.7% "add on."

Chlorex is the preferred solvent for the polymerizing step since it appears to promote a more homogeneous polymer, but ethylene dichloride, benzene or other similar

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solvents may be used. It has been found that efflux times for a 50% solution from 2 to 4 times the initial value give the best results although there is a danger of gelling as 4 is approached, and below 2 there may not be sufficient polymerization to produce satisfactory permanence on the cloth. The final efflux time is a function of amount of catalyst, temperature and time of heating. The higher the temperature and percentage of catalyst, the shorter the heating time. The catalyst quantities preferably vary from 2 to 3½ percent of the polymer weight. Temperatures from 70 to 110° C. would be satisfactory although we prefer to use a temperature of 100° C. Heating time is thus dependent on the desired efflux time. Air, oxygen, hydrogen peroxide, and the like are also suitable as catalysts. The inert atmosphere is used only to produce consistent results with catalysts other than air or oxygen. Hexane is the preferred precipitating agent but petroleum ether or benzene may also be used, or any other solvent which shows a solubility differential for monomer and polymer.

For the fabric treating the methanol/ethylene dichloride solution has proved most satisfactory. The methanol in particular seems to help the process. Chloroform may replace the ethylene dichloride. Solution strengths may range from 10 to 40% depending on the desired "add on." The amount of "add on" should be at least 10% and preferably about 10 to 35% while the preferred range is about 15 to 30%. A curing temperature of 100° for ½ hour has been used in the illustrated examples, but 80 to 110° C. is the preferred temperature range with the time varying accordingly.

The term "add on" used herein means the amount of polymer attached on the fabric and is expressed as percentage by weight of the untreated fabric.

The term "flameproof" used herein means that the treated material is at least resistant to burning and preferably will not support combustion when an applied flame is removed.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations should be understood therefrom as modifications will be obvious to those skilled in the art.

I claim:

1. The method of producing a flexible flameproofed cellulosic fabric which comprises partially polymerizing a di-(beta gamma unsaturated) alkenyl monochloromethanephosphonate in a suitable organic solvent, precipitating the partial polymer in a selective solvent for the unpolymerized ester, separating the polymer and dissolving it in a suitable organic solvent, applying such solution to a cellulosic fabric, removing the excess solution, evaporating off the solvent, and curing the treated fabric at a temperature sufficient to cause further polymerization and attachment of the polymer to the fibres of the fabric.

2. The method of claim 1 wherein the initial solvent is B,B'-dichloroethyl ether, the precipitating solvent is hexane, and the final solvent for the partial polymer is a mixture of methanol and ethylene dichloride.

3. The method of claim 1 wherein the initial mixture is polymerized by heating the solution with a peroxide catalyst to increase the viscosity 3 to 4 times before precipitating the partial polymer.

4. The method of producing flexible flameproofed cellulosic fabrics which comprises partially polymerizing diallyl monochloromethanephosphonate in a suitable organic solvent, precipitating the partial polymer in a selective solvent for the unpolymerized ester, separating the polymer and dissolving it in a suitable organic solvent, applying such solution to a cellulosic fabric, removing the excess solution, evaporating off the solvent, and curing the treated fabric at a temperature sufficient to cause further polymerization and attachment of the polymer to the fibers of the fabric.

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