3,667,999

FLAME RETARDANT CELLULOSIC MATERIALS

Francis Raymond Stoveken, Scotch Plains, and Warren Clifford Mayer, Somerville, N.J., assignors to Johnson & Johnson

No Drawing. Filed Apr. 15, 1969, Ser. No. 816,414
Int. Cl. C09k 3/28; C09d 5/18; D21h 1/28
U.S. Cl. 117—137 6 Claims

ABSTRACT OF THE DISCLOSURE

Flame retardant materials having excellent tensile strength, good tear resistance and elongation, improved drape and softness comprising a cellulosic base structure, a self cross-linked polymeric acrylic resin, ammonium bromide, and a weakly basic, water-soluble aliphatic organic, nitrogenous compound containing an amino group; and methods of making the same by simplified single-bath procedures.

The invention relates to flame retardant materials and to methods of making the same. More specifically, the present invention relates to flame retardant cellulosic structures, such as paper and paper products, having excellent tensile strength, improved tear resistance, enhanced elongation, especially in the cross direction, and a fabric-like drape and softness of hand; and made by simplified, economical one-bath methods.

There has been and there continues to be a growing demand for suitable single use, disposable fabric products. This is particularly true in the medical and surgical fields and especially in modern hospitals where disposable drapes, caps, masks, gowns, bed sheets, pillow cases, and the like have acquired wide acceptance. Similarly, disposable aprons, towels, frocks, etc., are in ever increasing demand by food handling and processing establishments. Even the clothing industry today is looking for inexpensive disposable men's work clothes and ladies dresses as a practical and fashionable item. And the house furnishings industry is not to be overlooked in its demand for suitable disposable curtains and drapes, table covers, etc. Such products exist as single ply paper structures or as multiple ply paper structures, or as laminated products in which these structures are adhered to each other or to other sheet-like or fabric-like materials, which may be strengthened by films, strands, gauze, scrim, netting, plastic networks, or other reinforcing materials.

To satisfy the demand and need for disposable products, it is readily apparent that they must be made of inexpensive materials to warrant but a single use. The first approach to making disposable fibrous products was to substitute nonwoven fabrics for the woven fabrics from which reusable products has been made in the past. However, while this was a step in the right direction, nonwoven fabrics are still relatively expensive and in many instances have not reached full acceptance for disposable products because of the expense involved.

Substituting paper and paper-like products for woven and nonwoven fabrics is ideal for the making of economical and inexpensive disposable products, but paper, in general, has had several serious drawbacks from the standpoint of physical characteristics. Paper and paper products, such as those made from wood pulp, are of cellulosic origin and thus present a serious and formidable flammability problem. Also, they normally lack the tensile strength and tear resistance of more conventional woven fabrics and normally do not possess a fabric-like drape or softness of hand.

There have been many efforts made in the past to improve paper and paper products so as to reduce their flammability characteristics, or to improve their tensile strength, elongation characteristics, and tear resistance, or to enhance their drape and softness of hand. It has been possible hitherto to improve paper and paper products individually in one or more of these categories but normally such improvement take place at the expense or loss in properties in one or more of the other categories.

It is therefore a principal object of the present invention to treat paper and paper products in such a way as to reduce their undesirable flammability characteristics, increase their tensile strength, elongation characteristics, and tear resistance, and enhance their drape and softness of hand.

It is also a principal object of the present invention to improve these properties of paper and paper products by simplified, economical methods and techniques.

We have found that such objects may be attained by treating paper and paper products in a single impregnating or saturating bath containing a specific formulation of components which are compatible with each other and which are capable of creating the desired properties and characteristics without creating any adverse interfering effects or undesirable properties and characteristics. These components which must be present in critical proportions in the impregnating bath and also in the final product comprise (1) a cross-linked polymeric acrylic resin, (2) ammonium bromide, and (3) a weakly basic, water-soluble, aliphatic organic, nitrogenous compound containing an amino or lower alkyl substituted amino group. Such compounds include, for example, urea, derivatives of urea such as methyl urea, ethyl urea, 1,1-dimethyl urea, 1,3-diethyl urea, thiourea, derivatives of thiourea such as 1-methyl thiourea,, 1,3-diethyl thiourea, 1,3-dimethyl thiourea, aminourea (semi-carbazide), diaminourea (carbazide), and imino urea (guanidine) and dicyandiamide (1-cyano guanidine).

It is to be appreciated that these components are preferably employed in a single-bath impregnating or saturating process. Such is easier, more economical, more convenient, and more efficient. However, if desired, or where special circumstances require it, the components may be separately applied to the base cellulosic structure in a plurality of impregnating baths. Such, however, is less economical, less convenient, and less efficient and is resorted to only of necessity.

The cross-linking polymeric acrylic resins saturate and impregnate the paper and paper products and considerably increase the tensile strength, improve the tear resistance and elongation, and enhance their drape and softness of hand. Particularly suitable for this purpose, for example, are ethyl acrylate polymers, methyl acrylate polymers, ethyl hexyl acrylate polymers, butyl acrylate polymers, ethyl acrylate-methyl methacrylate copolymers, ethyl hexyl acrylate-methyl methacrylate copolymers, butyl acrylate-methyl methacrylate copolymers, ethyl acrylate-polyvinyl acetate copolymers, and ethyl hexyl acrylate-polyvinyl acetate copolymers.

The polymeric acrylic resin is normally applied to the paper or paper product in the form of an aqueous emulsion or latex and should be included in the impregnating bath in such amounts as to provide a concentration of polymeric acrylic resin solids in the range of from about 3% by weight up to about 30% by weight of the total impregnating bath. Within the preferred embodiments of the present invention, however, a range of from about 7% by weight to about 13% by weight of the polymeric acrylic resin solids in the impregnating bath is found more desirable.

Flame retardancy, which includes the reduction of the burning rate or the prevention of flaming combustion

completely, or the reduction of after-flame or after-glow, is imparted to the paper or paper product by a selective combination having specific proportions of (1) a suitable water-soluble, inorganic salt, namely, ammonium bromide and (2) a suitable weakly basic, water-soluble organic, nitrogenous, amino-containing compound such as urea, derivatives of urea such as methyl urea, ethyl urea, 1,1-dimethyl urea, 1,3-diethyl urea, thiourea, derivatives of thiourea such as 1-methyl thiourea, 1,3-diethyl thiourea, 1,3-dimethyl thiourea, aminourea (semi-carbazide), diaminourea (carbazide), iminourea (guanidine), and dicyandiamide (1-cyano guanidine). Such a combination has been found not to interfere in any way with the drape or softness of hand of the paper or paper product, or to develop any adverse properties and characteristics, and additionally not to interfere in any way with the stability of the acrylic resin emulsion. At the same time, the ammonium bromide-amino-containing compound combination imparts the desired flame retardancy properties and characteristics and actually and unexpectedly enhances the drape and softness of hand of the resulting paper or paper product. It is also observed that the action of the ammonium bromide and amino-containing compound do not interfere in any way with each other and that they actually complement and cooperate with each other and with the acrylate resin in many ways.

The ammonium bromide is normally added to the impregnating bath in such amounts as to provide a concentration of from about 4% by weight up to about 20% by weight, based on the total weight of the bath. Within the preferred embodiments of the present invention, however, a range of from about 5% by weight to about 9% by weight of the ammonium bromide is found more desirable in the impregnating bath.

The amino-containing compound is normally added to the impregnating bath in such amounts as to provide a concentration of from about 1% by weight up to about 20% by weight, based on the weight of the bath. Within the preferred embodiments of the present invention, however, a range of from about 3% by weight to about 6% by weight of the amino-containing compound is found more desirable in the impregnating bath.

The polymeric acrylic resin emulsion containing the added ammonium bromide and amino-containing compound may be applied to the paper or paper product by substantially any known coating or impregnating method or technique. If desired, the paper or paper product may be withdrawn from a source of supply such as a supply roll or the like and guided into the impregnation bath, being immersed completely therein to take up the desired amount of wet treating agent. Or, if desired, the paper or paper product may be guided between the nip of an upper rotable pressure roll and a lower rotable immersion roll which is positioned partially in the impregnation bath from which it picks up the wet treating agent and transfers it to the paper or paper product at the nip with the upper pressure roll.

The amount of wet pick-up of the aqueous treating agent by the paper or paper product may be varied within relatively wide limites and is normally in the range of from about 75% by weight to about 250% by weight, based on the weight of the paper or paper product being treated. Within the preferred embodiments of the present invention, however, wet pick-up ranges of the aqueous treating agent of generally from about 175% by weight to about 225% by weight, based on the weight of the paper product, are found more desirable.

Paper or paper products do exist, however, particularly in the heavier basis weight types, wherein it is desirable not to pick up large quantities of the aqueous treating agent inasmuch as such creates problems subsequently in the removal of the large quantities of water during drying. In such cases, it is more desirable to employ impregnating baths containing a higher concentration of components and to have a lower wet pick-up on the order of only about 75% by weight to about 150% by weight of the paper or paper product.

It is to be appreciated that other materials may be included in the impregnating bath in order to impart to the paper or paper product specified properties and characteristics and special effects. Such other materials include opacifiers, absorbency control agents such as water repellents, fillers, humectants, dyes or pigments, cellulosic plasticizers, or emollients, perfumes, etc.

The treated paper or paper product may be dried in any desired apparatus such as a conventional air-heated oven or drying cans capable of being heated to sufficiently elevated temperatures to dry the paper or paper product. Normally, temperatures in the range of from about 240° F. to about 330° F. are used, depending upon the speed of the paper or paper product through the drying zone or over the drying cans.

After drying, the finished treated paper on paper product contains from about 35% by weight to about 75% by weight of the base cellulosic material; from about 2% by weight to about 25% of the polymeric acrylic resin, from about 7% by weight to about 15% by weight of ammonium bromide, and from about 1% by weight to about 25% by weight of the amine. If desired, up to about 20% by weight of additives, as defined herein, may also be included.

The paper or paper products being treated in accordance with the principles of the present invention may include basically any type of paper or paper product intended for packaging and shipping, printing and writing, building and construction, or of use in the medical and surgical fields, the food handling and processing industry, the clothing or home furnishings industries, or any other application wherein the preparation, processing, handling, storage, use or disposal of such products involves a flame retardancy problem. Such products exist as single ply paper structures or as multiple ply paper structures, or as laminated products in which these structures are adhered to each other or to other sheet-like or fabric-like materials, which may be strengthened by films, strands, gauze, scrim, netting, plastic networks, or other reinforcing materials.

Although the present invention is being described primarily with particular reference to single use or disposable paper or paper products, such is not to be construed as limitative of the broader aspects thereof. Naturally, it must be kept in mind that water soluble flame retardant treating agents are used in the preparation of the product and that exterior exposure to rainfall, immersion, wet or dry cleaning, or laundering may diminish their flame retardant effectiveness. However, uses of an interior nature are quite possible, wherein exposure to moisture or water is not as severe. For such specific uses, the products may be considered substantially permanently flame retardant and may be expected to retain their properties throughout their entire useful life. This, of course, is further enhanced by the fact that the ammonium bromide is non-hydroscopic and is relatively unaffected by varying humidity conditions.

The invention will also be described in greater particularity in the following examples with reference to creped tissue paper, either single ply or multiple plies, in the basis weight of from about 7 pounds to about 75 pounds per 3000 square feet and having stretch levels in the range of from about 5% to about 50%. The invention also finds excellent applicability to laminated tissue structures comprising one or a plurality of layers of creped cellulosic tissue, each layer having a basis weight of from about 7 pounds to about 35 pounds per 3000 square feet and which may be strengthened or reinforced by films, strands, gauze, scrim, netting, plastic networks, and the like, having an equivalent basis weight of from about 2 pounds to about 20 pounds per 3000 square feet. The total basis weights of such laminated structures, after adherence by adhesive, is normally in the range of from

about 15 pounds per 3000 square feet up to about 150 pounds or more per 3000 square feet. It is to be noted that such creped tissue paper and such laminated structures are used to illustrate the application of the principles of the present invention and that such is not to be construed as limitative of the broader aspects of the present invention.

EXAMPLE I

Single ply creped cellulose tissue having a basis weight of about 18 pounds per 3000 square feet is immersed at room temperature in an aqueous impregnating bath containing ammonium bromide, urea, and a self-cross linking vinyl acetate-ethyl acrylate-N-methylol acrylamid terpolymer latex (X-Link Resyn 2873, National Starch & Chemical Corp.). Sufficient amounts of these materials and sufficient water is included in the bath so that.

(1) the polymeric acrylic resin solids are present in an amount equal to about 20% by weight of the impregnating bath,
(2) the ammonium bromide is present in an amount equal to about 12% by weight of the impregnating bath, and
(3) the urea is present in an amount equal to about 10% by weight of the impregnating bath. The creped tissue picks up approximately 100% by weight of the wet treating agent. Drying and curing takes place in a heated oven at temperatures in the range of from about 260° F. to about 325° F.

The dried paper product contains 70.4% by weight of the base cellulosic creped tissue, 14.0% by weight of the polymeric acrylic resin, 8.6% by weight of the ammonium bromide, and 7.0% by weight of the urea. All materials in this and subsequent examples are dried and then oven-aged at 240° F. for 10 minutes prior to testing.

The material is tested in a flame retardancy vertical char test (TAPPI T–461 os–68) and the char length is determined to be only 2.5 inches which is below the necessary passing value of 5.5 inches and well below the desired value of 4.5 inches. There is no appreciable after glow. The test comprises suspending a 2¾" x 8¼" sample of the material with the long dimension hanging vertically. A Bunsen or Tirrill gas burner having a 1½" flame with the air supply closed is placed immediately below the sample with the top of the burner tube ¾" from the bottom edge of the sample. The test flame is applied for 12" and withdrawn. The char length is measured. The "after flame" is the time in seconds required for the sample to stop flaming. The "after glow" is the time in seconds required for the sample to stop glowing.

The material also passes the flame retardancy tests as described in ASTM D–777 and AATCC Spec. No. 34–1952 which are generally similar. The treated paper has outstanding textile-like drape and softness as determined subjectively by a panel of 6 laboratory technicians. The tensile strength in the machine direction (M.D.) is increased from 1.07 pounds to 3.54 pounds per inch width. In the cross direction (C.D.), it is increased from 0.38 pound to 0.80 pound per inch width. The wet tensile strength in the machine direction is increased from 0.26 pound to 2.46 pounds per inch width. The wet tensile strength is increased from 0.082 pound to 0.795 pound per inch width in the cross direction. The elongation in the machine direction is increased from 21.8% to 30.3%. The elongation in the cross direction is increased from 4.3% to 9.8%.

The permeability of the creped cellulose tissue has not been reduced materially by the flame retardant treatment; the voids in the tissue remain unfilled. The creped cellulose tissue handles very easily on converting equipment and it can be readily subjected to cutting, folding, printing and like operations. It is well suited for conversion into hospital pillow cases and is found to be flame retardant, soft and strong, and is tough in the sense that it possesses excellent energy-absorbing ability, that is, it is capable of absorbing applied loads without rupturing.

EXAMPLE II

The procedures of Example I are followed substantially as set forth therein except that the aqueous impregnating bath contains 20% by weight of polymeric acrylic resin solids, 16% by weight of ammonium bromide, and 1% by weight of urea. The finished, dried product contains 73% by weight of the base creped cellulose tissue, 15% by weight of the polymeric acrylic resin, 11% by weight of ammonium bromide and 1% by weight of urea. The flame retardancy vertical char length is 3.5 inches.

The treated product has excellent textile-like draft and softness as determined subjectively by a panel of 6 laboratory technicians. The dry tensile strength in the machine direction is increased from 1.07 pounds to 3.57 pounds per inch width. In the cross direction, the dry tensile strength is increased from 0.38 pound to 1.12 pounds per inch width. The wet tensile strength in the machine direction is increased from 0.26 pound to 2.68 pounds per inch width. It is increased from 0.082 pound to 0.825 pound per inch width in the cross direction. The elongation in the machine direction is increased from 21.8% to 26.5%. The elongation in the cross direction is increased from 4.3% to 8.3%. The other properties and characteristics are improved, comparably to those noted in Example I.

EXAMPLE III

The procedures of Example I are followed substantially as set forth therein except that the aqueous impregnating bath contains 20% by weight of polymeric acrylic resin solids, 16% by weight of ammonium bromide, and 5% by weight of urea. The finished, dried product contains 71.0% by weight of cellulosic fiber, 14.2% by weight of the polymeric acrylic resin, 11.3% by weight of ammonium bromide, and 3.5 percent by weight of urea. The flame retardancy vertical char length is 3.4 inches. The treated product has excellent textile-like drape and softness as determined subjectively by a panel of 6 laboratory technicians. The dry tensile strength in the machine direction is increased from 1.07 pounds to 3.52 pounds per inch width. In the cross direction, the dry tensile strength is increased from 0.38 pound to 1.15 pounds per inch width. The wet tensile strength in the machine direction is increased from 0.26 pound to 2.59 pounds per inch width. It is increased from 0.082 pound to 0.760 pound per inch width in the cross direction. The elongation in the machine direction is increased from 21.8% to 26.2%. The elongation in the cross direction is increased from 4.3% to 9.2%. The other properties and characteristics of the finished product are comparable to those obtained for the product of Example I.

EXAMPLE IV

The procedures of Example I are followed substantially as set forth therein except that the aqueous impregnating bath contains 20% by weight of polymeric acrylic resin solids, 16% by weight of ammonium bromide, and 10% by weight of urea. The finished, dried product contains 68.5% by weight of cellulose fiber, 13.7% by weight of the polymeric acrylic resin, 10.9% by weight of the ammonium bromide, and 6.9% by weight of urea. The flame retardancy vertical char length is 2.9 inches. The treated product has excellent textile-like drape and softness as determined subjectively by a panel of 6 laboratory technicians. The dry tensile strength in the machine direction is increased from 1.07 pounds to 3.95 pounds per inch width. In the cross direction, the dry tensile strength is increased from 0.38 pound to 0.93 pound per inch width. The wet tensile strength in the machine direction is increased from 0.26 pound to 2.72 pounds per inch width. It is increased from 0.082 pound to 0.643 pound per inch width in the cross direction. The elongation in the machine direction is increased from 21.8% to 27.5%. The elongation in the cross direction is increased from

4.3% to 9.7%. The other properties and characteristics of the finished product are comparable to those obtained for the product of Example I.

EXAMPLE V

The procedures of Example I are followed substantially as set forth therein except that the aqueous impregnating bath has the following initial composition:

	Weight, pounds	Solids	
		Pounds	Percent
Water	1,125		
Opacifier (67%)	262	176	6.6
Ammonium bromide	264	264	9.8
Urea	158	158	5.9
Humectant (96%)	91	87	3.1
X-Link Resyn 2873 (45%), National Starch & Chemical Corp.	780	351	13.1
Ammonium hydroxide	4		
Total	2,684		38.5

Five samples are impregnated with the flame retardant composition. The first two samples have a wet pick-up of approximately 250% by weight of the samples. The solids content of the bath is then reduced approximately 35% by the addition of 720 pounds of water to a bath weighing 1380 pounds. The subsequent wet pick-up is maintained at approximately 250% by weight of the sample. After drying, the compositions of these samples are determined and are set forth in the following table:

Treated samples	Fiber content	Opacifier	Ammonium bromide	Urea	Humectant	X-Link Resyn 2873
I	49.8	8.5	12.8	7.7	4.2	17.0
II	50.0	8.5	12.7	7.6	4.2	17.0
III	63.7	6.2	9.3	5.5	3.0	12.3
IV	60.3	6.8	10.1	6.0	3.3	13.5
V	59.2	7.0	10.4	6.2	3.4	13.8

The five samples are accelerated-aged in an oven at 240° F. for ten minutes and are then tested for their flame retardancy according to the TAPPI T-461 os-68 Flame Resistance Test and all passed. There was no ignition. Other properties of the five samples are determined and are set forth in the following table:

Treated samples	Dry tensile		Wet tensile		Elongation, C.D.	Internal tear (grams), M.D.
	M.D.	C.D.	M.D.	C.D.		
I	3.60	0.80	2.57	0.59	16.5	41
II	3.72	0.80	2.58	0.59	16.7	31
III	3.31	0.73	2.19	0.58	11.8	38
IV	3.14	0.61	2.48	0.48	13.7	40
V	2.79	0.73	1.97	0.54	13.2	34

These properties are to be compared to the properties of untreated samples set forth in the following table:

Untreated control	Dry tensile		Wet tensile		Elongation, C.D.	Internal tear, M.D. (grams)
	M.D.	C.D.	M.D.	C.D.		
A	1.17	0.38	0.29	0.096	4.5	24
B	1.03	0.42	0.24	0.081	4.6	30
C	1.03	0.35	0.25	0.079	4.0	20

These three untreated samples did not pass the ASTM-D-1230 Flame Resistance Test.

The marked improvement of the treated samples over the untreated samples is noted for all properties.

EXAMPLE VI

The procedures of Example I are followed substantially as set forth therein with the sole exception that the self cross-linking vinyl acetate-ethyl acrylate terpolymer latex is X-Link Resyn 2833 (National Starch and Chemical Corp.) containing a higher proportion of the ethyl acrylate component. The composition of the treating bath is as follows:

	Pounds	Solids	
		Pounds	Percent
Water	1,135		
Ammonium bromide	174	174	9.0
Urea	100	100	5.1
Humectant (96%)	57	55	2.8
X-Link Resyn 2833 (45%), National Starch & Chemical Corp.	484	218	11.2
Total	1,950		28.1

The pick-up level is maintained at approximately 255% by weight of the sample. After drying, the composition of the tissue sample is determined and is set forth in the following table:

	Percent
Cellulosic fiber	58.6
Ammonium bromide	13.2
Urea	7.6
Humectant	4.1
X-Link Resyn 2833, National Starch and Chemical Corp.	16.5
	100.0

The sample is oven-aged at 240° F. for ten minutes and is then tested for its flame retardancy according to the TAPPI T-461 os-68 Flame Resistance Test. There was no ignition. The treated sample has excellent textile-like drape and softness as determined subjectively by a panel of 6 laboratory technicians. The dry tensile strength in the machine direction is increased from 1.07 pounds to 2.97 pounds per inch width. In the cross direction, the dry tensile strength is increased from 0.38 pound to 0.67 pound per inch width. The wet tensile strength in the machine direction is increased from 0.26 pound to 175 pounds per inch width. The wet tensile strength in the cross direction is increased from 0.082 pound to 0.42 pound per inch width. The elongation in the cross direction is increased from 4.3% to 16.0%, the internal tear resistance in the machine direction is improved from 24 grams to 31 grams. Other properties of the finished product are comparable to those obtained for the product of Example I.

EXAMPLE VII

The procedures of Example VI are followed substantially as set forth except that 2 samples of a 2-ply tissue are used. Each sample has a total basis weight of 23.3 pounds per 3000 square feet.

After drying the composition of each sample is determined and is set forth in the following table:

Cellulosic fiber, percent	57.0	59.4
Ammonium bromide, percent	13.7	12.9
Urea, percent	7.9	7.4
Humectant, percent	4.3	4.1
X-Link Resyn 2833, percent, National Starch & Chemical Corp.	17.1	16.2
Total	100.0	100.0

The samples are oven-aged at 240° F. for ten minutes and tested for flame retardancy according to the TAPPI T-461 os-68 Flame Resistance Test. There is no ignition.

The finished product has excellent textile-drape and softness as determined subjectively by a panel of 6 laboratory technicians. The dry tensile strength in the machine direction is increased from 1.12 and 1.28 pounds per ply per inch width to 5.01 and 4.95 pounds per inch width. The dry tensile strength in the cross direction is increased from 0.61 and 0.58 pound per ply per inch width to 1.59 and 1.65 pounds per inch width.

The wet tensile strength in the machine direction is increased from 0.21 pound per ply per inch width to 3.00 and 2.50 pounds per inch width. The wet tensile strength in the cross direction is increased from 0.077 and 0.081 pound per ply per inch width to 0.85 and 0.73 pound per inch width. The elongation in the cross direction is increased from 3.9% and 4.3% to 16.0% and 15.5%. The internal resistance in the machine direction is improved from 24 and 23 grams to 54 and 43 grams. Other properties and characteristics are similarly improved.

EXAMPLE VIII

The procedures of Example I are followed substantially as set forth therein except that the cellulosic material comprises a three-layer reinforced laminated structure comprising: outer layers of creped cellulose tissue (each having a basis weight of 18 pounds per 3000 square); a central layer of 8 x 8 gauze (having an equivalent basis weight of 7 pounds per 3000 square feet); and an adhesive bonding the layers into a strengthened three-layer laminated structure having a basis weight of 50 pounds per 3000 square feet.

A different composition for the impregnating bath is used for the laminated structure and comprises:

	Percent in bath
Ammonium bromide	8.85
Urea	2.94
X-Link Rhoplex RC–518 Rhom and Haas	1.76
Boric acid	0.59
Total	14.14

Rhoplex RC–518 (Rhom and Haas) is a self cross-linking copolymer of ethyl acrylate and methyl methacrylate.

The wet pick up from the impregnating bath is approximately 140% by weight, based on the weight of the cellulosic product. The dry-add on of solids is approximately 20% by weight, based on the weight of the cellulosic product. This is equal to a dry-add on of 12.5% by weight of ammonium bromide, 4.2% by weight of urea, and 2.5% by weight of acrylic resin. The resulting product passes TAPPI and ASTM Flame Retardancy Tests. All other physical properties and characteristics are improved comparably.

EXAMPLE IX

The procedures of Example I are followed substantially as set forth therein except that the urea is replaced by decreased amounts of approximately 5% of dicyandiamide in the impregnating bath.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

EXAMPLE X

The procedures of Example I are followed substantially as set forth therein except that the urea is replaced by decreased amounts of approximately 5% of aminourea (semi-carbazide) in the impregnating bath.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

EXAMPLE XI

The procedures of Example I are followed substantially as set forth therein except that the urea is replaced by equivalent amounts of thiourea.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

EXAMPLE XII

The procedures of Example I are followed substantially set forth therein except that the self-cross linking acrylate resin is replaced by an equivalent amount of a copolymer ethyl hexyl acrylate and methyl methacrylate.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

EXAMPLE XIII

The procedures of Example I are followed substantially set forth therein except that the self-cross linking acrylate resin is replaced by an equivalent amount of a copolymer of butyl acrylate and methyl methacrylate.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

EXAMPLE XIV

The procedures of Example I are followed substantially set forth therein except that the self-cross linking acrylate resin is replaced by a self-cross linking vinyl acetate ethyl hexyl acrylate co-polymer.

The resultant products are flame retardant and have textile-like drape and softness of hand as determined subjectively by a panel of six laboratory technicians. The products have physical properties and characteristics comparable to those obtained for the products of Example I.

Although the preceding examples disclose the use of specific materials in specific proportions, the same are used for illustrative purposes and are not to be construed as limitative of the broader aspects of the present invention, except as defined by the appended claims.

What is claimed is:

1. A method of treating cellulosic papers and paper products to render them flame retardant and to provide them with improved tear resistance and tensile strength and enhanced drape and softness which comprises impregnating the cellulosic papers and paper products with an aqueous treating bath comprising from about 3% by weight to about 30% by weight of a self cross-linking polymeric acrylic resin, from about 4% by weight to about 20% by weight of ammonium bromide, and from about 1% by weight to about 20% by weight of a weakly basic, water-soluble, aliphatic organic nitrogenous compound containing an amino group and drying said impregnated cellulosic papers and paper products to remove substantially all of the water therefrom.

2. A method as defined in claim **1** wherein amino-containing compound is urea.

3. A method as defined in claim **1** wherein the amino-containing compound is dicyandiamide.

4. Flame retardant cellulosic papers and paper products having improved tensile strength, tear resistance, enhanced drape and softness, comprising from about 35% by weight to about 75% by weight of the base cellulosic paper, from about 2% by weight to about 25% by weight of a self cross-linked polymeric acrylic resin, from about 7% by weight to about 15% by weight of ammonium bromide, and from about 1% by weight to about 25% by weight of a weakly basic, water-soluble, ali-

phatic organic nitrogenous compound containing an amino group.

5. Flame retardant cellulosic papers and paper products as defined in claim 4 wherein the amino-containing material is urea.

6. Flame retardant cellulosic papers and paper products as defined in claim 4 wherein the amino-containing material is dicyandiamide.

References Cited

UNITED STATES PATENTS

2,097,509	11/1937	Boller	117—137
2,415,112	2/1947	Seymour et al.	117—137
2,415,113	2/1947	Seymour et al.	117—137
2,668,294	2/1954	Gilpin	2—114
2,917,476	12/1959	Peterson et al.	117—137 X
3,179,955	4/1965	Wade	2—243
3,253,881	5/1966	Donahue	106—15 X
3,276,906	10/1966	Nielsen	117—136
3,231,533	1/1966	Garrett	117—155 X
3,476,581	11/1969	Weitzel et al.	117—139.5 X

FOREIGN PATENTS

668,028	8/1963	Canada	117—155

WILLIAM D. MARTIN, Primary Examiner

H. J. GWINNELL, Assistant Examiner

U.S. Cl. X.R.

117—139.5 A, 143 A, 155 UA; 106—15 FP

PC-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,667,999 Dated June 6,1972

Inventor(s) Francis R. Stoveken and Warren C. Mayer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 3, line 67, " of the paper product " should read ---- of the paper or paper product ----.

In Column 7, line 62, Under Wet Tensile C.D., " 0.096" should read ---- 0.086 ----.

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents