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TREATMENT OF CELLULOSIC MATERIAL WITH APO-THIOUREA FLAME RESISTANCE AND THE RESULTING MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method for rendering cellulosic textiles durably flame retardant, even after repeated laundering, comprising treating the textiles with an aqueous solution containing a mixture of thiourea and tris(1-aziridinyl) phosphine oxide (APO).

This invention relates to an improved composition and method for the treatment of cellulose and/or cellulosic-containing materials. More particularly, the present invention relates to the treatment of cellulose-based or cellulose-containing woven and non-woven textiles (such as cotton and rayon), paper, wood, cardboard, rope and jute with a mixture containing tris(1-aziridinyl)phosphine oxide and at least one thiourea compound.

The use of tris(1-aziridinyl)phosphine oxide (APO) in combination with urea for the production of flame resistant textiles is disclosed, for example, in U.S. Patent 2,859,134 to Reeves et al. A process for fixing pigments on fibrous materials using a mixture of urea precondensation products and polyfunctional ethylenimine compounds is disclosed in U.S. Patent 2,961,349 to Bartl et al. One of the disadvantages of such processes, however, is that comparatively large amounts of expensive APO are required in order to obtain good flame retardant properties. While a good finish is obtained when the active ingredients of the treating bath consist of urea and APO, the durability of the finished textile to laundering is low and the treating chemicals are removed after several laundering cycles. Furthermore, odoriferous volatile products of undetermined composition are formed during the curing step when a mixture consisting of urea and APO is employed in the treating composition.

It has now been found that the amounts of APO required to achieve satisfactory flame-retardance for various cellulosic materials (especially woven and non-woven textiles) can be reduced considerably by using mixtures of thiourea (and/or substituted thiourea compounds) along with APO as the major components of the treating composition.

In the case of cellulosic textiles, the finished cellulosic-containing fabric has better fiber strength and retains its finish much longer than can be achieved with other APO-containing compositions. Another advantage of the invention is that dye shade changes in fabrics either do not occur with APO-thiourea treating compositions, or else occur uniformly over the fabric during treatment.

According to the present invention, a mixture of a thiourea compound and APO is incorporated into a treating bath and a cellulosic-containing material is impregnated with the bath composition. The impregnated material is then cured to form a flame-resistant product.

In a specific embodiment of the present invention, a

mixture containing a thiourea compound and APO in a mole ratio of from about .3:1 to 3:1 (preferably from about .5:1 to 2:1, thiourea:APO) is dissolved or dispersed in a solvent such as water to form a treating bath in which the concentration of the combined thiourea-APO composition is from 15 percent to 50 percent by weight based upon the total weight of the treating bath. Although a catalyst is not necessary to accomplish polymerization of the treating materials on and within the fibers which are to be treated, a conventional catalyst (for example, $Zn(BF_4)_2$, an organic acid such as acetic acid, perfluoroacetic acid, citric acid, oxalic acid or other known APO polymerization agent) may be incorporated into the bath in catalytic amounts (usually no more than about 5 percent by weight, and preferably no more than 3 percent). The cellulosic material to be treated is then contacted with this bath composition to form a product of any desired degree of impregnation, and the impregnated product is then cured by any suitable method. Heat curing is the preferred method, but curing can be carried out at ambient room temperatures over extended time periods (several weeks). Curing is probably accomplished by the reaction of the thiourea compounds and aziridinyl phosphine oxide to give polymers containing phosphorus, nitrogen and sulfur which are bound to the cellulosic materials by reaction of the aziridinyl rings with the cellulosic hydroxyl groups, or other reactive substituents.

If the cellulosic material which is to be treated is a textile, other known conventional fabric treating agents such as fabric softeners, wetting agents and emulsifiers may be incorporated into the treating bath. Amounts of up to a total of about 10–15 percent by (dry) weight (based on the total weight of the bath) of such treating agents may be employed. Typical fabric softening agents which may be incorporated into such a treating bath include quaternary ammonium salts such as the dimethyl benzylamine quaternary formed by combination with the reaction product of a polyethoxylated nonylphenol and epichlorohydrin, emulsified polyethylene and emulsified stearamide. Typical non-ionic wetting agents include polyoxyalkylene polyethers and hydroxy-containing polyethers such as are obtained by the reaction of alkylated phenols with 8–15 moles of ethylene oxide. In addition, other flame-proofing ingredients (for example, lower alkyl ammonium phosphates such as methyl ammonium phosphate, ethyl ammonium phosphate, etc.) may be incorporated into the treating composition. Amounts of urea of up to about 5 percent by weight may be incorporated into the treating bath without the production of undesirable fumes.

Water is the preferred carrier for the treating mixtures, although other solvents may be used if desired. The compositions may be heated to form a prepolymer prior to deposition on the cellulosic material. Typical treating bath concentrations using water as the carrier and/or solvent are summarized in Table 1 (all percentages are based upon the total weight of the bath). In addition to the ingredients listed in Table 1, a fabric softener and wetting agent was used in each bath composition. The fabric softener used was "Moropol–700" softener (containing 30 percent by weight of emulsified polyethylene). The concentration used was from 3.0 to 5.0 percent by weight based on the total weight of the bath. The wetting agent was "Dowfax 9N9" non-ionic surfactant. The concentra-

tion used was from 0.1 to 0.5 percent by weight based upon the total weight of the bath.

TABLE 1

APO (Conc. in Percent by Wt. Based on Total Wt. of Treating Composition)	Thiourea Compound (Percent by Wt. in Parentheses)	Catalyst (Percent by Wt. in Parentheses)
10–15	$H_2N-\overset{\overset{S}{\|\|}}{C}-NH_2$ (5–15)	$Zn(BF_4)_2$ (1.0–2.5)
15–25	$H_2N-\overset{\overset{S}{\|\|}}{C}-NH_2$ (10–13)	$Zn(BF_4)_2$ (1.0–2.5)
15–25	$H_3C-\overset{H}{N}-\overset{\overset{S}{\|\|}}{C}-NH_2$ (10–20)	$Zn(BF_4)_2$ (1.0–2.5)
15–30	$H_2N-\overset{\overset{S}{\|\|}}{C}-\overset{H}{N}-CH_2OH$ (10–20)	$Zn(BF_4)_2$ (1.0–2.5)
10–25	$C_2H_5-\overset{H}{N}-\overset{\overset{S}{\|\|}}{C}-\overset{H}{N}-C_2H_5$ (10–25)	No catalyst
15–30	$HOCH_2-\overset{H}{N}-\overset{\overset{S}{\|\|}}{C}-\overset{H}{N}-CH_2OH$ (10–25)	$Zn(BF_4)_2$ (1.0–2.5)

The treating bath is generally held at a temperature of from about 32° to 100° F. during the impregnation of the material to be treated.

When substituted thiourea compounds are employed, it is preferable to use N-lower alkyl (1-4 carbon atoms, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec.-butyl, tert.-butyl, i-butyl) or N-alkylol substituted thiourea compounds of the formula

$$R_1-\overset{1}{\overset{H}{N}}-\overset{2}{\overset{\overset{S}{\|}}{C}}-\overset{3}{\overset{H}{N}}-R_2$$

wherein each of R_1 and R_2 is a group of the formula

$$-\left(CH_2\right)_x-H \quad \text{or} \quad -\left(CH_2\right)_y-OH$$

x is an integer of from 0 to 4 and y is an integer of from 1 to 2. Thus, when x is 2 and y is 2, compounds such as 1-ethyl-3-ethylol thiourea, 1,3-diethyl thiourea and 1,3-diethylol thiourea are represented by the proper choice of the substituents R_1 and R_2. Other examples include 1,3-dimethyl thiourea and 1-methyl-3-n-propyl thiourea.

Any cellulose-containing material (especially textiles, paper and wood) may be treated with the bath compositions of the invention by merely impregnating the material with a treating bath (solution, mixture or dispersion) at ambient temperature containing APO and a thiourea compound, followed by curing the impregnated material at temperatures of from about 200° to 350° F. for from about 1 to 2 minutes to ½ hour (higher temperatures requiring less time). The material may be dried prior to the curing step. In ordinary commercial mill operation, the textile material to be treated is dipped in the bath once or twice followed by a squeezing or wringing operation to remove excess bath solution. The impregnated fabric is then dried and cured. The treated fabric contains from 5 to 20 percent of APO based upon the dry weight of the fabric and from 5 to 15 percent of the thiourea compound. Typical fabrics (either woven or non-woven) which may be efficiently rendered flame retardant according to the present invention include cotton, viscose rayon, rayon acetate, cotton blend fabrics, as well as other cellulose-based natural and synthetic textiles. Wood specimens which are treated with compositions containing APO and thiourea char when placed in a Bunsen burner flame but do not burn when the flame is removed. When wood is treated according to the invention, it is not necessary to impregnate the fibers deeply. Only an amount of APO-thiourea mixture sufficient to inhibit the burning of the surface of the wood is used.

The following examples are submitted for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any way.

Examples I–XVI.—General Procedure

A bath was prepared containing APO and a thiourea compound in a mole ratio of approximately 1:1, so that the solids content (based upon the total weight of the bath) of the APO-thiourea mixture was about 35 percent. The fabrics used were broadcloth, sateen and twill with an untreated weight per square yard of 3½ ounces, 8 ounces and 9 ounces, respectively. The fabrics were padded through the treating bath once and pressed once with rollers to remove excess bath fluid. The wet fabric was dried at about 240° F. for about 2 minutes and then cured for two minutes at 325° F. The treated fabric was then given a standard "after wash" in an automatic home laundry washer (ten gallons of water at 150° F., ½ cup of a commercial alkylbenzene sulfonate detergent, ten minute wash cycle, followed by one spray rinse and one deep rinse). The fabrics were rated according to the "hand" and to the flame retardance (AATCC Standard Test 34–1952, "Vertical Char" test). No conditioning was given to the fabrics before testing for the vertical char, except the conditioning existing in the laboratory at the time of the test. These conditions were (1) temperature: approximately 70°–75° F. and (2) relative humidity: approximately 30–40 percent.

The fabrics were given a series of four durability washes and the vertical char test was then repeated after each boil cycle. A durability wash consists of the following treatment: The fabric is washed for 45 minutes at 200°–212° F. in an agitator-type washing machine with 100 grams of soda ash (Na_2CO_3), 100 grams of "Ivory Flakes" neutral soap and 10 grams of "Tide" detergent in 88 pounds of water for every 4 pounds of fabric. The washed fabric is then given a 15 minute rinse in water at 160° F.

The results are summarized in Table 2.

For a fabric with a weight of from 2.0 to 6.0 ounces per square yard, the maximum permissible average char length in warp or filling direction is 5½ inches and the maximum length of char for any one sample is 6½ inches. Similarly, for fabrics (such as twill or sateen) with a weight of from 6.0 to 9.5 ounces per square yard, the maximum permissible average char length in warp or filling direction is 4½ inches and the maximum length of char for any one specimen is 5½ inches. Fabric irregularities produce some high values.

The following standard tests were used throughout the examples:

The vertical char test (AATCC Test No. 34–1952) is carried out using strips of cloth 10 inches long by 2¾ inches wide held vertically in a standard apparatus while a preadjusted flame is applied to the bottom ¾ inch of the fabric for a fixed standard time. Average values of three samples are taken.

The Elmendorf tear test (ASTM D–1424–56T) measures the tearing force required by a piece of fabric of standard size using a swinging pendulum to tear the fabric. Measurements are taken on both the warp and fill fibers.

Breaking strength is measured with a Scott tester using the grab method by placing a piece of fabric of standard size between two parallel jaws and applying a load (ASTM D39–49, Section 10).

TABLE 2

Example No.	Thiourea Compound	Mole Ratio Thiourea Compound:APO	Percent Total Solids (APO+Thiourea Compd.)×100÷APO+Thiourea Compd.+Remainder of Bath	Fabric Type	(Dry Wt. of APO+Thiourea Compd.)×100÷Dry Fabric (Percent Total Add-on)
I	$(NH_2)_2CS$	1:1	35.0	BBC	21.9
II	$(NH_2)_2CS$	1:1	35.0	OD	26.5
III	$(NH_2)_2CS$	1:1	38.0	BBC	23.9
IV	$(NH_2)_2CS$	1:1	38.0	OD	28.3
V	$(NH_2)_2CS$	1:1	35.0	BBC	22.0
VI	$(NH_2)_2CS$	1:1	35.0	OD	24.9
VII	$(NH_2)_2CS$	1.5:1	35.0	BBC	23.4
VIII	$(NH_2)_2CS$	1.5:1	35.0	OD	25.9
IX	$(NH_2)_2CS$	1:1	34.4	WBC	21.5
X	$(NH_2)_2CS$	1:1	34.4	T	23.0
XI	$(NH_2)_2CS$	1.5:1	34.4	WBC	20.7
XII	$(NH_2)_2CS$	1.5:1	34.4	T	22.1
XIII	$(HOCH_2N)_2C=S$	1.06:1	35.7	BBC	23.6
XIV	$(HOCH_2N)_2C=S$	1.06:1	35.7	OD	28.2
XV	$(HOCH_2N)\overset{\overset{S}{\|}}{C}-NH_2$	1.25:1	35.0	BBC	20.3
XVI	$(HOCH_2N)\overset{\overset{S}{\|}}{C}-NH_2$	1.25:1	35.0	OD	26.2

TABLE 2—Continued

Example Number	Char Length (inches), Average of Three Runs, Maximums in Parentheses—Number of Durability Washes				
	0	1	2	3	4
I	4⅜ (4½)	4¼ (4¼)	5⅛ (6¾)	4⅞ (5)	4⅜ (4⅝)
II	3⅜ (3½)	3⅜ (3⅝)	3⅜ (3⅝)	3½ (3⅝)	3⅞ (3⅞)
III	3¾ (4)	4⅛ (4¼)	4⅛ (4⅜)	4½ (4¾)	4¾ (5¼)
IV	3⅛ (3½)	3⅛ (3¼)	3¾ (4¼)	3¾ (3¾)	3⅜ (3½)
V	4½ (5⅜)	4½	3¾	4⅛	5
VI	3½ (3½)	3½	3¾	3½	4⅛
VII	4 (6¾)	5½	5½	6¾	6¾
VIII	3¾	3⅜	3⅜	4⅜	4
IX	3⅞ (4)	6¾ (7⅛)	5½ (6)	4⅜ (4½)	4¼ (5)
X	3½ (3⅝)	4⅜ (4½)	3⅜ (3⅝)	3½ (3½)	4½ (4¾)
XI	4⅜ (4⅜)	6 (7)	4½ (4½)	4⅝ (4⅞)	4 (4½)
XII	3⅜ (3½)	3¾ (3⅞)	3½ (3¾)	3⅜ (3⅜)	3½ (3¾)
XIII	3¾ (4)	4¾ (4¾)	4⅛ (4¼)	4⅝ (4⅝)	4¼ (4¾)
XIV	3¼ (3½)	3¾ (3⅞)	3¾ (4⅛)	3 (3½)	3½ (3⅞)
XV	4⅝ (4⅝)	7⅛ (9)	4¾ (4⅞)	7⅛ (8¼)	5¼ (5½)
XVI	3⅛ (3⅜)	3⅝ (3⅞)	3⅜ (3⅜)	3⅜ (3½)	3⅝ (4)

WBC=white broadcloth (3½ oz. per sq. yard).
BBC=beige broadcloth (3½ oz. per sq. yard).
OD=olive drab sateen (8 oz. per sq. yard).
T=twill (9 oz. per sq. yard).
Maxima omitted from the table were not recorded.

The tear strengths and breaking strengths (both warp and fill) of the treated fabrics were excellent even after 4 durability washes.

Example XVII

The following ingredients were combined to form an aqueous bath solution (all percentages by weight based on the total weight of the bath solution).

Ingredient:	Percent
APO	21.40
Thiourea	12.90
Catalyst $[Zn(BF_4)_2]$	2.14
Fabric softener (polyethylene-type)	1.50
"Dowfax 9N9" non-ionic wetting agent	0.20
Total solids	38.14
Remainder water.	

Samples of white broadcloth and brown nine ounce twill were padded through the bath to a 50 percent wet pick-up

$$\left(\frac{\text{Wt. of solution on cloth}}{\text{Dry wt. of cloth}}\times 100\right)$$

which corresponds to about 22.8 grams of solid add-on per 100 grams of dry, untreated cloth. The fabrics were dried at about 210° F. for about 2 minutes and cured at 325° F. for 2¼ minutes. The treated fabrics were then given an afterwash (as in Examples I–XVI). The dried fabrics were then given successive vertical char tests after each of the four durability wash cycles. The following char lengths were obtained:

Number of Durability Washes	0	1	2	3	4
Length of char (inches) of broadcloth	4¼	4⅞	4½	4½	4
Length of char (inches) of 8 oz. twill	3⅜	3¾	3¾	3⅜	3½

Example XVIII

In a manner similar to that used in the preceding examples, a bath consisting of the following ingredients was prepared:

Ingredient:	Grams
(1) 80 percent APO solution in CH_3CH_2OH	108
(2) Diethylthiourea	99
$[CH_3CH_2\overset{\overset{H}{\|}}{N}-\overset{\overset{S}{\|}}{C}-\overset{\overset{H}{\|}}{N}CH_2CH_3]$	
(3) "Moropol–700" fabric softener (an emulsified polyethylene containing 30 percent by weight solids)	25
(4) Reaction product of nonylphenol and ethylene oxide in mole ratio of about 1:9, respectively ("Dowfax 9N9" non-ionic wetting agent)	1
(5) Water	267
Total	500

White broadcloth (3½ ounces per square yard) was dipped in the bath, squeezed in a roller, dried 2 minutes at 240° F. and cured for 2 minutes at 325° F. The wet pick-up was 64.5 percent, corresponding to a total dry solids pick-up of

$$(64.5)\left(\frac{185}{500}\right)\sim 23.8$$

grams per 100 grams of dry fabric. The fabric was given an afterwash as in the preceding example and dried. The char length of the fabric by the AATCC (American Association of Textile Chemists and Colorists) vertical char test 34–1952 was 5⅜ inches.

Example XIX

In a mill comparison of APO-thiourea and APO-urea mixtures with identical fabric softener, catalyst and non-ionic wetting agent, smoke-like fumes were formed with the APO-urea mixture during the curing step. The venting system would not remove the fumes as they were formed. No fumes were obtained with the APO-thiourea mixture.

Example XX

A bath composition consisting of the following ingredients was prepared by simply mixing the components.

Ingredient:	Grams
80 percent APO in ethyl alcohol	216
Thiourea	117
Water	1150
Total	1483

Red cedar shingles (approximate dimensions: 7" x 16" x ¼") were dipped in the freshly-prepared bath for 30 minutes, drained and weighed to determine wet pick-up. The average wet pick-up (6 samples) was 20 percent. The drained specimens were cured for 30 minutes at 300° F. in an oven. The treated specimens charred when placed in a luminous open flame (Bunsen burner), but would not burn when the flame was removed.

Example XXI

A bath containing 31 percent by weight of an APO-thiourea mixture (mole ratio of thiourea to APO of 1.5:1) was prepared as follows.

Ingredient:	Pounds
(1) 80 percent APO in ethyl alcohol	240
(2) Thiourea	126
(3) "Fabritone 23" fabric softener (an emulsified stearamide)	45
(4) "Dowfax 9N9" wetting agent	3
(5) Ice	50
(6) Water sufficient to bring the total volume to 115 gallons	571
Total	1035

The temperature of the bath was about 70° F. when initially prepared. The starting temperature of the water was about 100° F. and ice was used to cool the bath to 70° F. A sample of 3000 yards of Type 140 muslin (42 inches wide, mint green casing for pillowcases, approximately 3 ounces per square yard) was padded through the treating bath to an estimated wet pick-up of 75 percent. The fabric was pressed with rollers to remove excess fluid. The running speed was 75 yards per minute. Drying was accomplished with infrared preheaters and a tenter frame heated to 240° F. (A tenter frame is a conveyor equipped with parallel clips which keep the wet fabric taut while the fabric is moved through a drying oven.) The fabric was cured at 330°–335° F. in a 150 yard curing oven. The fabric was then washed in a small amount of wetting agent, rinsed and dried. The treated fabric had excellent flame retardant characteristics as measured by AATCC Test No. 34–1952.

Example XXII

A bath composed of the following ingredients was prepared at room temperature.

Ingredient:	Concentration (percent by wt.)
APO	21.1
Thiourea	13.9
"Polymul CS–41" fabric softener	4.5
"Triton X–100" non-ionic wetting agent	0.2
Remainder water	60.3
Total	100.0

Unfinished broadcloth was treated in accordance with the procedure of Examples I–XVI. The wet pick-up was about 65 percent. The percent dry add-on per 100 grams of dry fabric was 13.6 grams for the APO and 9.0 grams for the thiourea. The breaking strength (as measured according to ASTM D–39–49, Section 10) and tear strength (as measured according to ASTM D–1424–56T) were as follows:

	Unfinished Control	Finished Fabric
Breaking strength (lbs.):		
Warp	98	79
Fill	54	31.5
Tear strength (gms.):		
Warp	670	905
Fill	550	630

This data indicates that no appreciable decrease in breaking strength occurs as the result of treatment, while the tear strength actually increases somewhat. In addition, the treated fabric had good flame retardance after four durability washes and after 50 home launderings. Similar results were obtained using a bath composed of 21.0 percent APO, 13.6 percent thiourea, 0.64 percent $Zn(BF_4)_2$, 3.9 percent "Polymul CS–41" fabric softener and 0.2 percent "Triton X–100" wetting agent, with the remainder of the bath composed of water (all percentages by weight).

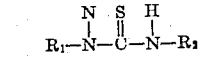
As used herein, the term "cellulosic" is meant to include materials which contain cellulose as well as materials which are based upon cellulose derivatives. Thus, viscose rayon (based upon the reaction of the hydroxyl groups of cellulose with carbon disulfide in the presence of NaOH to give xanthates), oxidized cellulose and rayon acetate are typical examples of cellulosic materials.

I claim as my invention:

1. Method of treating cellulosic material which comprises contacting said material with a treating bath containing from 10 to 50% by weight of a mixture of

(1) tris(1-aziridinyl)phosphine oxide, and

(2) a thiourea compound of the formula



wherein each of R_1 and R_2 is selected from the group consisting of

(a) $-(CH_2)_xH$ and

(b) $-(CH_2)_yOH$

wherein x is an integer of from 0 to 4 and y is an integer of from 1 to 2, to form an impregnated material and curing said impregnated material, wherein the mole ratio of (2):(1) is from 0.3:1 to 3.0:1.

2. The method of claim 1 wherein the cellulosic material is a cellulose-containing fabric.

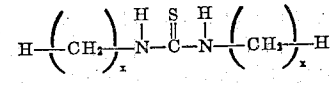
3. The method of claim 1 wherein the cellulosic material is wood.

4. A method of treating a cellulose-containing fabric which comprises:

(1) contacting said fabric with an aqueous treating bath containing from 15 to 50 percent by weight of a mixture of

(a) tris(1-aziridinyl)phosphine oxide, and

(b) a compound of the formula



wherein x is an integer of from 0 to 2 and wherein the mole ratio of $(b):(a)$ is from 0.5:1 to 2.0:1, to form an impregnated fabric, and

(2) curing said impregnated fabric at a temperature of from about 200° to 350° F.

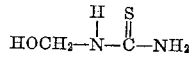
5. The method of claim 4 wherein the impregnated fabric has a wet pick-up of from 30 to 120 grams of treating bath per 100 grams of dry fabric.

6. The method of claim 4 wherein the cellulose-containing fabric is a cotton textile.

7. A method of treating a cellulose-containing fabric which comprises:

(1) contacting said fabric with an aqueous treating bath containing from 15 to 50 percent by weight of a mixture of

(a) tris(1-aziridinyl)phosphine oxide, and
(b) the compound



wherein the mole ratio of (*b*):(*a*) is from 0.5:1 to 2.0:1 to form an impregnated fabric, and

(2) curing said impregnated fabric at a temperature of from about 200° to 350° F.

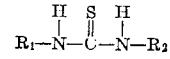
8. A method of treating a cellulose-based textile which comprises contacting said textile with a treating bath containing from 10 to 50 percent by weight of a mixture of N,N'-dimethylol thiourea and tris(1-aziridinyl)phosphine oxide in a mole ratio of from 0.5:1 to 2.0:1, respectively, to form an impregnated textile and curing said impregnated textile at a temperature of from 200° to 350° F. to produce a flame retardant product.

9. A method of flame-proofing wood which comprises contacting the wood with a treating bath containing from 10 to 50 percent by weight of a mixture of thiourea and tris(1-aziridinyl)phosphine oxide in a mole ratio of from 0.5:1 to 2.0:1, respectively, to form an impregnated wood product and curing said impregnated wood product at a temperature of from 200° to 350° F.

10. A treating bath for flame-proofing cellulose-containing material which comprises an aqueous solution of from 10 to 50 percent by weight of a mixture of

(1) tris(1-aziridinyl)phosphine oxide, and

(2) a compound of the formula



wherein each of R_1 and R_2 is selected from the group consisting of

(a) $-(CH_2)_xH$ and
(b) $-(CH_2)_yOH$

wherein x is an integer of from 0 to 4 and y is an integer of from 1 to 2 and wherein the mole ratio of (2):(1) is from 0.3:1 to 3.0:1.

11. A flame-retardant cellulosic material produced according to the process of claim **1**.

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