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FLAME RESISTANT FABRIC MATERIAL

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This invention relates, generally, to improvements in the art of imparting fire resistance to cellulosic fibers and fabrics, as well as other relatively inflammable fibers and fabrics, while simultaneously rendering the fibers and fabrics thus processed, resistant to the action of weathering and attack by bacteria and fungoid agencies, usually described under the collective title of mildew, and the invention relates, more particularly, to a novel fire resistant processed product, and to the process of preparing the same and the material with which the processing is effected. This application is a continuation-in-part of applicant's co-pending application Serial No. 457,226, filed September 3, 1942, for Flameproofing of textiles and method of making the same.

The material to be treated of most common occurrence and commercial importance is cotton duck, cotton sheeting, cotton camouflage and other types of netting, and the various types of cotton clothing fabric such as drills and twills and poplins. At present commercially acceptable grades of fire resistance must meet the requirements of Federal specification CCC-D-746, February 1939, for duck, cotton, fire, water and weather resistance, and as amended by supplementary specification (tentative) 242. Processed material that will substantially comply with the requirements of the above specified specifications may be considered as "fireproofed" within the meaning of this invention.

Material processed as "fireproof" which will meet the requirements of specifications 746 and 242, noted above, has hitherto been prepared by the application of a fire resistant paint formula in which ground pigments of various types are suspended in a halogenated organic material which serves as a base and as a carrier for the essential pigments. These pigment solids are preferably mixed or ground with the halogenated carrier material (almost universally a chlorinated compound), and then deposited in and on the fabric, the chlorinated material serving as a base or carrier, usually known as a vehicle.

While the fire resistance produced by the application of this fire resistant paint meets the requirements of the aforesaid specifications, a very heavy loading of the fabric is an indispensable prerequisite, the heavy loading producing the defect of tackiness at normal temperatures and objectionable stiffness when subjected to the usual winter temperature of the temperate zone, which stiffness is accentuated greatly when subjected to arctic temperatures.

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While the degree of stiffness may be materially modified by the addition of relatively large amounts of plasticizing media, the addition of plasticizing media greatly increases the degree of tackiness. Another objection, vital in many cases, lies in the tendency of the soft fire resistant paint to "crock" or rub off, soiling any article with which it may come in contact, a defect which renders fabrics processed with such fire resistant paints unavailable for clothing, chair or seat covers, and affects adversely their usefulness for tentage and awning purposes, largely for the reason that they will soil any fabric which comes in contact with them, and having a soft tacky surface such processed fabrics attract dirt and grime and quickly become unsightly, although still retaining their fire resisting characteristics.

The present invention does not make use of a fire resisting paint composition, but instead employs materials that are introduced into the fabric, fiber or structure to be fire proofed in the form of solutions, which are then insolubilized on and within the fibers of the cellulosic structure. These materials may be introduced into the fabric either in the form of aqueous solutions of the salts of the metals and compounds to be employed, or, where feasible in solutions of the desired compounds in aliphatic, aromatic or chlorinated hydrocarbons, the hydrocarbon in this latter case being first removed by evaporation, and the residual metallic compound being then insolubilized (as to water) by means of appropriate precipitants, usually compounds of the alkali metals, or ammonia, such as the carbonates and hydroxides of the alkali metals.

The principal object of the present invention is to provide a novel fire resistant textile fabric or similar material with the use of a minimum amount of loading, i. e., reducing the effective loading from 40 to 60 percent of loading ordinarily required in the case of fire resistant textile fabric heretofore known.

Another object of the present invention is to provide a novel fire resistant textile fabric or similar material which will not crock nor will the fire resistant material rub off as in the case of paint-coated fabrics heretofore commonly used, whereby the material of this invention is adaptable for use for clothing, awnings, furniture, etc.

Another object of the present invention is to provide a novel fire resistant textile fabric or similar material that is not tacky and is further not stiff at low temperatures but possesses a de-

gree of flexibility approximating that of the untreated fabric.

A still further object of the present invention is to provide a flame resistant fabric or similar material preferably employing antimony trioxide as the flame resistant ingredient thereof and also preferably employing an organic compound for preventing the propagation of a sort of creeping combustion through the fabric or material.

It has long been known that the chlorides of the antimony group, antimony, bismuth and vanadium, possess the power of conferring fire resistance to normally inflammable structures, such as, for instance, cellulose, but because of its relative cheapness, antimony is the only one of the group that can be considered of commercial importance. The chemical characteristics of antimony chloride, and antimony salts in general, are such that no successful or practical application of this quality has thus far been possible. Antimony chloride cannot be dissolved in water without immediate decomposition into insoluble antimony oxychloride and hydrochloric acid, the formula being

$$SbCl_3+H_2O\rightarrow SbOCl+2HCl$$

If it were possible to impregnate a cellulosic fabric with antimony chloride, the latter would decompose as soon as it came in contact with water, with the formation of antimony oxychloride and hydrochloric acid, and the latter (hydrochloric acid) would immediately destroy the fabric. On the other hand, while an aqueous impregnation of a cellulosic fabric is impossible in view of the chemical characteristics of the element antimony, antimony chloride is quite soluble in alcohol and most hydrocarbon solvents, aliphatic, aromatic or chlorinated carbons, such as carbon tetrachloride. However, while the fabric can be impregnated with a solution of antimony chloride in hydrocarbon solvents such as gasoline, toluene, Varsol, etc., the antimony chloride thus impregnated immediately decomposes upon removal or evaporation of the hydrocarbon solvents, setting free hydrochloric acid which, in turn, at once destroys the fabric.

Applicant has discovered that if the fabric to be fireproofed by means of antimony chloride is first impregnated with a carbonate or acetate or other weak salt of a metal of the alkali group, such impregnating compound, while soluble in water, being substantially insoluble in alcohol or hydrocarbon solvents or, in any event, insoluble in the medium in which the antimony chloride has been dissolved, and the fabric thus impregnated with such protective compound be thoroughly dried, it will now be possible to safely impregnate the fabric thus prepared with a solution of antimony chloride in a hydrocarbon solvent, aliphatic or aromatic as the case may be; and it will be found that the antimony chloride, even after the complete expulsion of the hydrocarbon solvent, will have no damaging or deleterious effect on the strength of the fabric thus impregnated. Any evolution of hydrochloric acid resulting from the possible hydrolysis of the antimony chloride is at once neutralized by the carbonate with which the fabric has been impregnated. At this stage, the fabric to be made fire resistant possesses an impregnation of carbonate of an alkali and also antimony chloride, the solvent having meanwhile been removed.

The impregnated and dried fabric thus prepared and, as stated, carrying an impregnation of carbonate of an alkali metal, e. g., sodium carbonate and antimony chloride, is next passed through a solution of sodium carbonate, preferably warm, which solution immediately decomposes the impregnated antimony chloride with the formation of antimony oxide.

The compounds of the antimony group [antimony, bismuth, vanadium and the rare columbium (niobium) and tantalum], especially the respective oxides and halogen compounds and the chlorides of these metals, show marked flame inhibiting characteristics. Because of the cost, the only important member of this series in a commercial sense is antimony, although bismuth might have commercial possibilities under certain conditions as a flame-proofing agent. Antimony may, therefore, be selected as a commercially practicable type, but representative of the mentioned group.

While antimony tri-chloride is an excellent flame inhibitor, a cellulosic structure impregnated with antimony chloride is neither practical nor commercially valuable because of the instability of the antimony tri-chloride in the presence of water, especially in view of the fact that water is an invariable constituent of all cellulosic structures, the usual content being from 7 to 10 per cent of the entire fabric, and in many cases the water content is still higher than the amount noted. Under these circumstances when a cellulosic fabric is impregnated with a solution of antimony chloride in an organic solvent and the latter is evaporated, leaving the fabric impregnated with antimony trichloride, the antimony chloride is immediately decomposed by the water content of the cellulosic fabric, with, as above stated, the formation of insoluble antimony oxychloride and hydrochloric acid, which acid immediately attacks the cellulose with destructive effects.

Antimony trichloride in the presence of a water soluble carbonate of the alkali metals or ammonia is immediately decomposed with the formation of insoluble antimony oxide, an excellent flame inhibitor, together with sodium chloride and the evolution of carbon dioxide, as follows:

$$2SbCl_3+3Na_2CO_3\rightarrow Sb_2O_3+6NaCl+3CO_2$$

Antimony trioxide is inert insofar as the fabric may be concerned.

If the fabric destined to be impregnated with antimony trichloride is soaked in an aqueous solution of a water soluble carbonate, which carbonate is insoluble, or but sparingly soluble in an organic solvent, such as those already mentioned; and this carbonate impregnated fabric then dried by appropriate means, such processed fabric can then be safely impregnated with an organic solution of antimony trichloride. Under these conditions there is no danger from hydrochloric acid. Should any water be present, it will at once dissolve a portion of the sodium carbonate with which the fabric has been processed, and this solution of sodium carbonate, present, at best, only in small quantities if at all, will at once decompose its chemical equivalent of antimony trichloride with the formation of the corresponding quantity of insoluble antimony trioxide and the innocuous accompanying products of the reaction, sodium chloride and carbon dioxide.

The sequence of steps which constitute the invention are as follows, antimony trichloride or other halogen compound of antimony being taken as a type of the group to which antimony belongs.

First, the fabric is impregnated with sodium

carbonate solution (aqueous) or other equivalent carbonate.

Second, the fabric is dried. (Usually on cans.)

Third, the dried fabric is impregnated with a solution of antimony trichloride in an organic solvent.

Fourth, the fabric impregnated with antimony trichloride is dried, the organic solvent being volatilized.

Fifth, the dried fabric impregnated with antimony trichloride is now passed through a warm solution of sodium carbonate, which solution in addition to dissolving the sodium carbonate already incorporated with the fabric (first step), decomposes the antimony trichloride present as a result of the third and fourth steps, forming insoluble antimony trioxide, sodium chloride and carbon dioxide.

Sixth, the thus processed fabric is now washed with water, which treatment removes the residual sodium carbonate, sodium chloride, and after drying, nothing remains but a fabric impregnated with antimony oxide which is now flame proofed. The fabric will not now support flame, but combustion can still be propagated through the fabric, but without flame effect.

The following will serve as an example of a working process.

First, the fabric or cellulosic structure to be fireproofed is padded (that is, passed through a dye bath and squeezed through rollers or "nips") with a hot solution of sodium carbonate (or equivalent carbonate); temperature near boiling, sodium carbonate being 10 per cent of the whole.

Second, the fabric is dried on cans.

Third, the dried, thus processed fabric is impregnated with a 15 per cent solution of antimony chloride in an organic solvent, which may be a petroleum or coal tar solvent or alcohol.

Fourth, the antimony impregnated fabric is dried on cans.

Fifth, the dried fabric (fourth step) is padded with a 10 per cent solution of sodium carbonate, warm but not hot.

Sixth, the processed fabric is washed and dried.

The processed fabric has now been flameproofed, but the treatment herein proposed does not prevent the propagation of flameless combustion through the fabric upon the application of the necessary degree of heat. Thus, the fabric will "glow," and the zone of combustion will creep, although actual flaming is no longer possible. The prevention of "glowing" or the propagation of a creeping area of flameless combustion requires an additional treatment.

Certain organic compounds, principal among which may be named chlorinated paraffin, tricresyl phosphate, triphenyl phosphate, polymers of vinyl resin and various phenolic compounds will prevent the propagation of a zone of creeping combustion but will not, in themselves, prevent flame propagation. A combination of the two media will result in the production of a "fireproofed" fabric which will not only not support flame propagation but creeping or "glowing" propagation of a zone of combustion as well.

These compounds may be added to the fabric processed as above by means of a separate and distinct operation, or they may be incorporated with the solution of antimony chloride in organic solvents. In the former case the fabric, processed as above described, is passed through a solution of chlorinated paraffin, tricresyl phosphate, triphenyl phosphate, separately or a combination of one or more of these ingredients,

after which the solvent may be removed by evaporation. On the other hand, the simultaneous application of the flame and "glow" inhibiting compounds would be effected as follows:

First, the fabric is incorporated with a carbonate of the alkali metals.

Second, the fabric is dried.

Third, the dried fabric is impregnated with a solution of antimony trichloride (15%) and chlorinated paraffin (20%) with the inclusion of tricresyl phosphate (6%) in an aromatic or aliphatic hydrocarbon solvent, the usual proportion of this solvent being 50 per cent of the whole mixture, although this proportion is susceptible of variation according to circumstances.

Fourth, the fabric is now dried with the evaporation of the solvent as an incident. The dried fabric will now contain the sodium carbonate base, antimony chloride and the glow resistant hydrocarbon compounds, such as chlorinated paraffin, tricresyl phosphate, or whatever media may have been selected.

Fifth, the dried fabric now containing carbonate of soda (base), antimony chloride, glow resisting hydrocarbon compounds is now passed through a warm, though preferably not hot, 10 per cent solution of sodium carbonate, squeezed through rolls and washed and dried over cans, or other methods of drying. This procedure has the effect of removing all carbonate of soda while converting the antimony chloride into antimony oxide, while the glow inhibiting hydrocarbons are not changed.

What is claimed is:

1. The method of producing a fire resistant textile fabric comprising impregnating a fabric with sodium carbonate solution, drying the fabric, impregnating the dried fabric with a solution of antimony trichloride in an organic solvent, the presence of residual sodium carbonate in the fabric preventing any hydrochloric acid resulting from hydrolysis of the antimony trichloride from attacking the fabric, drying the thus impregnated fabric, passing the fabric through a warm solution of sodium carbonate thereby precipitating insoluble antimony trioxide throughout the interstices of the fabric, washing the fabric with water to remove residual sodium carbonate, drying the fabric, thereafter passing the fabric through a solution of chlorinated paraffin and then again drying the fabric.

2. The method of producing a fire resistant textile fabric comprising impregnating the fabric with a carbonate of an alkali metal, drying the fabric, impregnating the dried fabric with a solution of antimony trichloride and chlorinated paraffin in an organic solvent, drying the fabric, and passing the same through a warm solution of sodium carbonate, squeezing, washing, and drying the fabric.

3. The method of producing a fire resistant fabric material comprising impregnating the material with an aqueous solution of an alkali metal carbonate, drying the material, impregnating the dried material with an organic solution of antimony trichloride, the presence of residual sodium carbonate in the fabric preventing any hydrochloric acid resulting from hydrolysis of the antimony trichloride from attacking the fabric, again drying the material, passing the dried material through an aqueous solution of an alkali carbonate, washing the material to remove residual alkali carbonate, drying the material and passing the same through a solution of chlorinated paraffin capable of rendering the fabric

resistant to creeping combustion and again drying the fabric.

4. The method of producing a fire resistant textile fabric comprising impregnating the fabric with a carbonate of an alkali metal, drying the fabric, impregnating the dried fabric with a solution of antimony trichloride and a solution of an organic compound of the group consisting of chlorinated paraffin, tricresyl phosphate and triphenyl phosphate, drying this fabric, passing the same through an alkali carbonate solution, and washing the fabric to remove residual alkali carbonate.

5. The method of producing a fire resistant textile fabric comprising impregnating fabric with a sodium carbonate solution, drying the fabric, impregnating the dried fabric with a solution of antimony trichloride in an organic solvent, drying the thus impregnated fabric, passing the fabric through a warm solution of sodium carbonate, washing the fabric with water to remove residual sodium carbonate and drying the fabric, said fabric being impregnated with chlorinated paraffin subsequent to the initial impregnation with sodium carbonate.

6. The method of producing a fire resistant textile fabric comprising impregnating the fabric with a hot solution of sodium carbonate, drying the fabric, impregnating the fabric with a solution of antimony trichloride in an organic solvent, drying the fabric and passing the fabric through a solution of hot sodium carbonate, thereby precipitating insoluble antimony trioxide throughout the interstices of the fabric to render the same flameproof and then washing and drying the fabric.

7. The method of producing a fire resistant fabric comprising passing the fabric through a hot solution of sodium carbonate of approximately 10% concentration, drying the fabric, impregnating the fabric with a solution of antimony trichloride of a strength of approximately 15% in an organic solvent, drying the impregnated fabric, passing the fabric through a hot solution of sodium carbonate of the strength of approximately 10%, washing and drying the fabric and passing the fabric through a solution of chlorinated paraffin and again drying the fabric.

8. A method of employing antimony trichloride in the impregnation of an organic, especially cellulosic fabric by which the normally destructive action of the antimony trichloride on the fabric is inhibited, comprising the initial impregnation of the fabric with a solution of a carbonate of an alkali metal, drying the fabric thus impregnated, impregnating the fabric thus dried with a solution of antimony trichloride in an organic solvent, again drying the fabric and converting the antimony trichloride to antimony oxide by passing the dried fabric through a solution of a carbonate of an alkali metal, washing the thus treated fabric and then again drying the same.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,388,828	Arent	Aug. 23, 1921
2,044,176	McCulloch	June 16, 1936
2,299,612	Clayton	Oct. 20, 1942
2,036,862	Dreyfus	Apr. 7, 1936

OTHER REFERENCES

American Dyestuffs Reporter, July 5, 1943, vol. 32, No. 14, pages 297 to 301.