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FLAMEPROOFING OF TEXTILES

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The widespread public interest in the flameproofing of textiles, as evidenced by the numerous requests for information on the subject, prompted the preparation of this circular. Consisting of information compiled from various sources, it includes a review of the principles of flameproofing, a brief history of the researches, formulas for various processes, an outline of the most important testing methods, and a list of publications on the subject.

I. PRINCIPLES OF FLAMEPROOFING

Textile flameproofing is concerned chiefly with cotton and other fibers of vegetable origin. Such fibers are composed of cellulose, which is readily combustible. Wool and other fibers of animal origin are less flammable, largely because the protein constituents decompose on heating to liberate non-flammable nitrogenous gases.

Complete fireproofing of textiles -- making them fully resistant to charring and decomposition even at high temperatures -- has not yet been achieved, and is probably not possible. The most that can be expected of a flameproofed fabric is that it will resist ignition by a match or similar small sources of heat, or that, if once ignited, it will not continue flaming upon removal of the source of ignition, since after a fire is well started, even a well-treated material will add fuel to the flame. Such flameproofing may be accomplished by impregnating the cloth with solutions of various chemicals, either singly or mixed.

Salts suitable for textile flameproofing may be grouped as follows, according to the way in which they are supposed to protect the fabric: Group 1. - Salts, such as certain ammonium compounds, which on heating give off non-flammable gases to dilute the flammable gases from the decomposing textile. Group 2. - Salts which produce a glaze over the fiber surface, cutting off the oxygen supply, examples being ammonium phosphate, and borax-boric acid mixtures. Group 3. - Salts having a mechanical action in that they load the fabric, rendering it less susceptible to ignition and less able to perpetuate its own kindling temperature, an example of which is stannic oxide. Some salts may fall within more than one group.

Freeman (1)[1] states that chemicals of the second group are the most effective flameproofing agents. Regarding water of crystallization, he considers important the amount of heat required to be absorbed before this water can be given up; but he minimizes its effect when converted into steam, as a diluent for flammable gases.

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[1] Numbers in parentheses indicate references listed at end of paper.

In the choice of a flameproofing agent, several factors, the importance of which is dependent upon the intended use of the fabric must be considered. Some chemicals discolor the cloth or injure it when it is ironed; others weaken it, or make it unduly harsh or heavy. Chemicals which absorb moisture from the air may promote the growth of mildew and accumulation of dirt. Chemicals which give off moisture to the air, thus causing dusting or discoloration, also are undesirable. Crystalline compounds deposited from concentrated solutions may mar the appearance of the fabric. Most chemicals deposited in a fabric will be worn away or dusted out with handling. Some chemicals cost too much, or are poisonous. If the material must stand wetting or laundering, the flameproofing agent must not wash out.

In their efforts to find a flameproofing agent having the optimum of desirable properties, many experimenters have prepared mixtures of fire-retardant chemicals. One such mixture contains ammonium sulfate, ammonium carbonate, borax, and boric acid. The ammonium salts on heating liberate non-flammable gases, while the borax and boric acid fuse to glaze the surface of the fibers. Often an expensive chemical is mixed with other chemicals which may be somewhat less effective as flameproofers but are less costly.

The relatively insoluble compounds are fixed in the cloth by successive dippings in solutions which interact chemically and precipitate the flameproofing agent on and within the fibers. Soluble flameproofing agents are generally applied from water solution by steeping, brushing, or spraying, followed by drying. In the case of certain fabrics, the method of application may have considerable effect upon the success of the treatment. For example, the application of a cold solution with a brush may be unsatisfactory for treating theater scenery, since the sizing may prevent rapid absorption of the solution. Hot treatments are generally to be preferred for most materials. Dipping the fabric insures more complete penetration than brushing or spraying. A number of successive applications are often made before effective protection is achieved.

II. RESEARCHES

The subject of fireproofing has been one of great interest since ancient times. It is said that the Romans attempted to fireproof their houses and war vessels by dipping the wood in a bath of vinegar and clay. An early mention of textile flameproofing occurs in a paper published in 1638 by Nikolas Sabbattini, who urged reforms in the construction and furnishing of Italian theaters from the standpoint of fire prevention, and recommended that the color used in painting theaters and scenery should be mixed with clay or gypsum.

In 1735 Jonathan Wild, of England, was granted a patent dealing with a flameproofing mixture composed of alum, ferrous sulfate, and borax. Wild's work was followed by other investigations; and the subsequent history of textile flameproofing contains the names of many experimenters, of whom only a few can receive mention here.

Gay-Lussac (2) in 1821 published the results of an investigation suggested by Louis XVIII, in which he determined the flameproofness imparted by numerous salts when deposited on linen and hemp cloth in the amounts of 10 and 20 percent. He found that ammonium phosphate, equal parts of ammonium chloride and ammonium phosphate, and equal parts of ammonium chloride and borax, were effective.

A worthy contribution was made by Versmann and Oppenheim (3), who in 1859 reported to the British Association for the Advancement of Science the results of a study of 40 chemicals in their protective action on muslin. Their work was conducted on a commercial scale as well as in the laboratory. They found that only five of the salts and mixtures tried had practical value: Ammonium phosphate, sodium-ammonium phosphate, ammonium phosphate and ammonium chloride mixture, ammonium sulfate, and sodium tungstate.

At the instigation of Freeman (1), Whipple and Fay did considerable work on flameproofing theater scenery. Ammonium phosphate was found to be the most effective of many salts tried; it was, however, conducive to the growth of mold and mildew. Reporting the results, Freeman states emphatically that although many substances were found that would make gauze and canvas proof against ignition by small flames, "nothing was found that would prevent the instant burning with a rush of flame when the test was made with a strong blaze on closely hung sheets of canvas". In later work on scenery, Kling and Florentin (4) of the Paris Municipal Laboratory found a solution of borax and boric acid in a 6:5 ratio to be the most suitable of many agents tried.

Ramsbottom and Snoad (5), working at the Royal Aircraft Establishment with cotton fabric, corroborated the effectiveness of a borax-boric-acid mixture, but preferred a 7:3 ratio to the proportions of Kling and Florentin.

Perkin (6), seeking a permanent process for cotton flannelettes and other highly flammable cotton goods, found the best treatment to be stannic oxide precipitated on the fibers by a method given in Section III. Flannelettes treated by this method retained their flameproof qualities after being laundered 20 times.

III. FORMULAS AND PROCESSES

Numerous formulas for the flameproofing of textiles are to be found in the literature and patents. Although they include a variety of substances, most of these formulas depend for their fire-retarding effect upon ammonium salts, phosphates, borates, stannic oxide, or sodium tungstate, or mixtures thereof.

A few representative formulas are given below. Only the first of these, the Perkin process, may be said to be truly water-resistant. Some of the other formulas specify the use of insoluble salts, but these are more or less subject to removal by the mechanical action of water as in washing.

Type numbers given with the formulas have the following significance:

Type 1. - Insoluble salts, resistant to the mechanical action of water.

Type 2. - Insoluble salts, not fully resistant to the mechanical action of water.

Type 3. - Soluble salts.

Measurements are by weight unless otherwise indicated. One gallon of water weighs about 8.3 lb. at 20°C (68°F).

1. Perkin Process (6) (Type 1)

Solution A --
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$ . . . . . 41.8 parts
Water . . . . . 100 "

Solution B --
Ammonium sulfate, $(NH_4)_2SO_4$ . . . . . 15.0 parts
Water . . . . . 100 "

The cloth is thoroughly washed to remove oils, waxes, or other substances which might reduce its absorptive power; it is then acidified with acetic or other weak organic acid, washed, dried, and immersed and agitated in Solution A, then squeezed and dried again. It is next run through Solution B, squeezed, dried, and washed in cold water to remove the sodium sulfate formed by the interaction of the salts in the two solutions. If desired by the finisher, the sodium sulfate may be left in the cloth.

The goods must be heavily squeezed after passing through the solutions, since the pressure seems to increase the affinity of the cloth for the stannic oxide formed, with the consequent deposition of more of the latter.

The process has been used for flannelettes and other light cotton goods. Perkin states that the stannic oxide is not removed by any amount of washing with soap and hot water; the treatment does not injure delicate colors, and is not harmful to the skin; the stannic oxide gives the cloth a softer and fuller feel than that of the original flannelette; and the material is considerably strengthened by the process.

2. Textile World (7)(Type 2)

Solution A --
Sodium aluminate, $NaAlO_2$ . . . . . 14.1 parts
Water . . . . . 100 "

Solution B --
Ammonium sulfate, $(NH_4)_2SO_4$ . . . . . 12.0 parts
Ammonium phosphate, dibasic, $(NH_4)_2HPO_4$ . . . . . 12.0 "
Water . . . . . 100 "

The goods are saturated in the cold Solution A, let stand wet in roll form for several hours, and dried without rinsing. The treatment is fixed in Solution B. For some goods and uses, a little clay suspended in the bath is recommended. The finish is harsh, but the treatment stands weather, is fairly effective, and is cheap. It is used for heavy cotton goods.

3. Matthews (8) (Type 3)

Ammonium phosphate, dibasic, $(NH_4)_2HPO_4$	7.5	parts
Ammonium chloride, NH_4Cl	5.0	"
Ammonium sulfate, $(NH_4)_2SO_4$	5.0	"
Water	100	"

Either the cloth may be impregnated directly with this solution, or the starch sizing may be made up with it. It has been used for curtains; Matthews recommends it for cotton fabrics in general.

4. Ramsbottom and Snoad (5) (Type 3)

Borax, $Na_2B_4O_7 \cdot 10H_2O$	7.0	parts
Boric acid, H_3BO_3	3.0	"
Water	100	"

The amount of water may be varied, and should depend upon the absorptive capacity of the fabric to be treated. This mixture, when present on light cotton fabrics to the amount of 6 percent of the weight of the untreated fabric, is said to be effective in retarding flame. Fabrics so treated retain their flexibility and softness. They do not become dusty, feel damp, or lose their strength under ordinary conditions of use. The materials are non-poisonous and do not promote the growth of destructive micro-organisms. Brosnan recommends the solution in 7 percent strength for rayon and sheer fabric.

5. Kling and Florentin (4) (Type 3)

Borax, $Na_2B_4O_7 \cdot 10H_2O$	6.0	parts
Boric acid, H_3BO_3	5.0	"
Water	100	"

The fabric is steeped in a warm solution until thoroughly impregnated, then dried. Heavy applications by spray or brush are usually reasonably effective. Such applications may have to be repeated two or three times with drying between applications to get the desired degree of flameproofing. The treatment has been used for many kinds of fabrics, including theater scenery; Grove-Palmer recommends it for rayon. As in the case of most of the other formulas listed, care must be taken in ironing to avoid discoloration by heat.

6. Chesneau (15) (Type 3)

Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$	20.6 parts
Sodium phosphate, dibasic, $Na_2HPO_4 \cdot 12H_2O$	0.6 "
Water	100 "

Sodium tungstate has been used for flameproofing theater scenery in Paris, London, and elsewhere. The addition of the sodium phosphate is recommended by Chesneau to prevent crystallization, resulting from the formation of an acid sodium tungstate.

7. National Bureau of Standards (Type 3)

Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$	24.0 parts
Ammonium phosphate, dibasic, $(NH_4)_2HPO_4$	6.0 "
Water	100 "

This formula was developed for use on airplane fabrics. Results of further work on airplane fabric treatments were published by the Bureau of Standards in 1935 (16).

8. Matthews (8) (Type 2)

Solution A --	
Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$	3.2 parts
Zinc sulfate, $ZnSO_4 \cdot 7H_2O$	2.4 "
Water	100 "
Solution B --	
Alum, $KAl(SO_4)_2 \cdot 12H_2O$	6.0 parts
Water	100 "

The goods are immersed and agitated in the boiling solution A and allowed to remain therein overnight. Next morning they are treated again with the hot solution and dried. They are then run through solution B and dried without rinsing. This recipe has been used for awnings.

9. Matthews (8) (Type 3)

Starch (or flour, sago, dextrin, etc.)	22.0 parts
Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$	11.0 "
Borax, $Na_2B_4O_7 \cdot 10H_2O$	7.0 "
Water	As desired

This mixture is used for sizing.

10. Martin (8) (Type 3)

Ammonium sulfate, $(NH_4)_2SO_4$	8.0 parts
Ammonium carbonate, $(NH_4)_2CO_3 \cdot H_2O$	2.5 "
Borax, $Na_2B_4O_7 \cdot 10H_2O$	8.0 "
Boric acid, H_3BO_3	3.0 "
Starch	2.0 "
Dextrin	0.4 "
Water	100 "

The amount of water may be varied as desired. The mixture is applied at 86° to 100°F. It is useful for many purposes, particularly for laces, curtains, and aprons.

IV. TESTS AND TESTING METHODS

For the most part, the various experimenters seem to have devised their own methods of testing the relative effectiveness of the flameproofing treatments investigated. None of the methods developed has received general recognition as a standard procedure.

Whipple and Fay (1) used ignition tubes with small pieces of the treated cloths to determine whether combustible gases were evolved at different temperatures. They later devised a portable lamp for testing treated fabrics in the form of strips 8 in. long by 1 in. wide. J. R. Freeman (1) suspended six strips of treated fabric, about 3 in. wide by 24 in. long, in an asbestos-lined joint of stove pipe 5 in. in diameter by 24 in. long with 3/4 in. spacing between strips. He found that the strips burned regardless of the kind of treatment used.

Ramsbottom and Snoad (5) have thoroughly investigated the subject of tests and testing procedure. They used cotton fabric weighing 4 oz. per sq. yd., having 110 warp yarns and 100 filling yarns per inch. The flame tests were made on strips 1 in. wide by 18 in. long held vertically in a box perforated at top and bottom. A flame 1 in. long from an orifice 0.02 in. in diameter was played across the lower end of the strip until it was burning evenly, whereupon the flame was withdrawn. The rate of flaming was determined by observation of the time required for the fire to travel over a 12-inch length between marks 3 in. and 15 in. from the lower end.

Three methods, which have been used at the National Bureau of Standards to determine the relative flammability of various treated and untreated fabrics, are the Match-Flame Ignition Test, the Horizontal Rate-of-Burning Test, and the Vertical Rate-of-Burning Test.

Match-Flame Ignition Test. - This test is employed qualitatively to determine whether an untreated fabric should be classed as hazardous or slow-burning, or whether a supposedly treated fabric contains an effective amount of the flameproofing agent. It is described as follows:

A specimen 2 in. wide is suspended vertically with the long edge in a horizontal direction. Lighted safety matches are applied to the lower edge, and the susceptibility to ignition is determined.

A similar match-flame test is used by inspectors of the District of Columbia Fire Marshal's Office to determine whether theater scenery and curtains have been effectively flameproofed. To be acceptable, a fabric must not burst into flame when the burning match is held along a vertical edge.

Horizontal Rate-of-Burning Test. - A specimen about 2-3/4 in. wide and 15 to 30 in. long is cut from the sample and placed with its surface horizontal between two parallel clamps 2 in. apart, supported on a steel frame. The specimen is ignited at one end with a small flame from a Bunsen burner and allowed to burn freely over the entire length in the still air of the laboratory. The time for the flame front to travel over a definite length is measured, from which the rate of burning in inches per minute is calculated.

The Horizontal Rate-of-Burning Test is employed chiefly to compare the rates of burning of untreated fabrics. Test results can be reproduced within a variation of about 10 percent. It is not a severe test, and therefore will generally not give useful results in the case of fabrics treated with a flameproofing agent.

Vertical Rate-of-Burning Test. - This test is similar to that devised by Ramsbottom and Snoad. It is more severe than the Horizontal Rate-of-Burning Test, and affords a simple and speedy means of determining the flameproofness of a fabric. The results have a somewhat wider range of variation than in the horizontal test.

A specimen 2 in. wide by 12-1/2 in. long is clamped in a vertical position with the lower end free, and with 1/2 in. of the upper end in the clamp, so that a 12 in. length is exposed. To protect the specimen from drafts, the apparatus is inclosed in a sheet metal shield 14 in. wide, 12 in. deep, and 30 in. high, open at the top, and provided with a vertical sliding glass front. Sufficient room is left at the bottom of the front to allow manipulation of the gas burner used in igniting the specimen.

The specimen is suspended 3/4 in. above the top of the gas burner -- which has a tube of 3/8 in. inside diameter -- and is ignited by a luminous flame 1-1/2 in. long. The flame is applied for 6 sec. (in the case of an untreated fabric) or 12 sec. (in the case of a treated fabric).

A record is made of the time from the application of the burner flame until flaming, if any, ceases, and the rate of burning in inches per minute is calculated on the basis of the length of specimen which has been charred. A successfully treated fabric should not flame at all after the test burner has been removed.

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