SBD,MWS,SHI
III-6

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
Washington

Letter
Circular
LC 818
(Supersedes
LC 467)

February 21, 1946

FLAMEPROOFING OF TEXTILES

CONTENTS

Page

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. It includes condensed sections on (I) the principles, (II) the history of flameproofing, (III) types of treatments, (IV) formulas for various processes, (V) tests and testing methods, and (VI) a brief list of publications on the subject.

I. PRINCIPLES OF FLAMEPROOFING

Textile flameproofing is concerned chiefly with cotton, rayon, and other fibers of vegetable origin. Such fibers are composed of cellulose which, when heated, decomposes into readily combustible gaseous and tarry products. Wool and other fibers of animal origin are less flammable, largely because the protein constituents decompose on heating to liberate nonflammable nitrogenous gases. The recently developed, truly synthetic fibers, nylon and Vinyon, are also less flammable than cotton or rayon and do not present a serious fire hazard, although they melt at relatively low temperatures.

Glass fibers are incombustible, and the amount of oil and coatings used in the finished cloth is generally not large enough to introduce a fire hazard.

Complete fireproofing of combustible textiles -- making them fully resistant to burning, charring, and decomposition at high surrounding 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 source of heat, or that, if once ignited, it will not continue burning upon removal of the source of ignition. Such flameproofing may be accomplished by impregnating or coating the cloth with preparations of various chemicals, either singly or mixed.

1. Function of Flameproofing Chemicals

There are several types of action by which the compounds are believed to flameproof the fabric. They may be listed as follows:

(a) Modification of the cellulose molecule chemically by the flameproofing agent either before or at the time of combustion, one effect of which is alteration in the decomposition products formed, i.e. less of the very flammable tarry products, and more of the nonvolatile charred residue.

(b) The production of a flux or foam from the fireproofing agent by the heat of the fire, thus coating the fibers of the fabric and retarding combustion.

(c) The evolution of noncombustible gases or vapors on decomposition of the flameproofing agent which dilute the combustible gases from the cellulose decomposition or tend to blanket the fabric and exert a smothering influence on the flame.

(d) The physical weighting of the fabric with noncombustible material, thus rendering it less susceptible to ignition and less able to perpetuate its own kindling temperature.

Many of the flameproofing compounds may combine two or more types of action, and most investigators at present believe that a chemical modification of the cellulose probably represents the major result of the more effective treatments. In view of the small amount of a good flameproofing agent required for effective protection, it is scarcely plausible that either (c) or (d) can account entirely for the results obtained. The formation of a glaze (b) could more readily be accepted as a complete explanation of the action of such compounds as borax and boric acid, but there is indication that they also modify the cellulose in their action. Thus, Ramsbottom and Snoad (1)[1] in an extensive study using borax, boric acid, and mixtures of the two, conclude that they modify the action of heat on the fabric, lowering the temperature at which blackening of the fabric occurs and causing a reduction in the amount and the degree of flammability of the volatile combustibles produced. Their study indicated, in general, that efficient flameproofers increase the destructive action of heat on cellulose, lowering the blackening temperature of the fabric. Many of the ammonium salts of inorganic acids are efficient fire retardants and upon being heated evolve ammonia gas which may aid in reduction of flame propagation, but the acid and its reaction on the fabric may play the dominant part. Work recently carried out for the Quartermaster Corps of the United States Army also indicates that even small amounts of fire retardants modify the action of heat on cellulose, increasing the production of char, water, and nonflammable gas, and substantially reducing that of volatile tarry matter.

2. Glow-Proofing

The satisfactory flameproofing of a fabric does not always prevent the occurrence of afterglow, that is, the continued slow burning of the fabric by glow even though it does not flame after ignition. If this afterglow is confined to the already charred areas it is not usually serious, but when it spreads extensively into the undamaged fabric it is a continued hazard and may completely consume the fabric. Good glow-proofers appear to function either by coating the fibers, thus cutting off a sufficient air supply, or by chemically altering the course of the oxidation reaction. Among the effective glowproofers may be mentioned ammonium phosphate, and the urea phosphates which, on heating, yield phosphorus pentoxide and in the presence of free carbon

---

[1] Figures in parenthesis indicate the literature references given in Section VI, page 22.

appear to react chemically to control afterglow. Boric acid and such compounds as zinc borate, which yield boric oxide on heating, also function as effective glowproofers, and recently some organic compounds have been found efficient.

II. HISTORICAL NOTES

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 fire-retardant properties 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 the protective action on muslin of 40 chemicals. 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 (4), Whipple and Fay did considerable work on flameproofing theater scenery. Ammonium phosphate was found to be the most effective of many salts tried but was 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 (5) 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 (1), 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 IV.

The development of a commercial method of producing sulfamic acid (7) led to the use of ammonium sulfamate as a new and effective flameproofer (8), which has been made the basis of a proprietary product on the market.

Other investigators have aimed to combine the desirable properties of borates and phosphates without use of ammonium salts, which sometimes produce a progressive and destructive acidity by gradual loss of ammonia. A satisfactory flameproofer in the form of a complex boro-phosphate resin (9) has been developed and made the basis of another proprietary product.

In the recent emergency the armed services became deeply interested in the problem of flameproofing textiles and considerable work has been carried out on the fundamental principles of flameproofing as well as its practical applications. The Chemical Warfare Service Development Laboratory at Massachusetts Institute of Technology (10) has developed a water-resistant formula using antimony oxide in a vinylite binder which is described in Section IV. The National Research Council Laboratories at Columbia University have carried out extensive investigations in the field. The water-soluble formula which they have recently recommended to the Army Quartermaster Corps for general clothing use also appears in Section IV. They consider this formula as satisfactory as any of the water-soluble group with respect to both flameproofing and glowproofing.

The work of Dr. Martin Leatherman (11) is representative of the basic development of the present fire and weather resistant finishes for cotton duck. Dr. Leatherman's early work was concerned with improvements in the Perkin process, particularly in preventing afterglow by applying an overcoat of chlorinated resin or rubber to the treated fabric. These materials were known to have slow-burning properties. He found that the flameproofing oxides (the stannic oxide of the Perkin process and numerous others) can be mixed with the chlorinated resin or oil with retention of the flame and weather resistant properties, thus eliminating the more complicated two-bath method of impregnation.

Interest in the flameproofing field is still very active and a number of laboratories are working on new or improved formulas. Commercial flameproofing of fabrics at the time of manufacture is feasible only when the treatment has a reasonable degree of permanence to laundering or water leaching. The present fire and weather resistant finishes for canvas and duck meet this requirement fairly well and factory treatment is common. However, flameproofing will not be of general interest to commercial finishers of fine fabrics until permanent treatments are developed which are effective in weightings compatible with the uses of such fabrics. Some promise along this line is found in the field of oil-in-water and water-in-oil emulsions, and in treatments which will decidedly modify the cellulose molecule. Interest is also centered in the possibility of treating fibers before spinning to produce a permanently flameproofed material which will require no further treatment after fabrication.

III. TYPES OF TREATMENTS

Three general types of fire-retardant treatments are in use at present. One combines weatherproofing with fireproofing and is commonly applied to canvas and duck intended for tentage, awnings, and similar outdoor purposes. The other two are either partially or completely removed by laundering or water leaching and are applicable for clothing, decorations, and general indoor purposes.

1. Fire and Weather Resistant Finishes (Type 1, Section IV)

The requirements of the armed forces have given considerable impetus to the recent development of improved finishes for heavy fabrics intended for outdoor exposure, combining flame and weather resistance. For the most part, the present finishes of this type are designed to meet requirements similar to those of Federal Specification CCC-D-746 for Fire, Water, and Weather Resistant Cotton Duck (12).

Since these finishes are designed to withstand outdoor exposure, flame tests after weathering, as well as on the freshly treated fabric, are essential in judging the effectiveness of a treatment. Accelerated weathering tests have been developed which attempt to produce in a short time the effects of longer natural exposures. In the development of specification requirements, the National Bureau of Standards carried out an investigation of the correlation between the effects of natural exposure and those of an accelerated weathering machine, in which the material is exposed to the radiation from a carbon arc and to periodic applications of water spray. Tests were also made of the effects of water spray alone upon well-treated awning material, with results indicating that rainfall alone is not of primary importance in weathering as it affects flammability, but that the greatest deterioration is probably due to sunlight, and the shock of interspersed sunlight and rainfall. Thus, artificial rainfall applied intermittently over a 40-hour period, equivalent in amount to about 12 years of natural rainfall in Washington, D. C., produced little loss in flameproof properties. On the other hand, natural weathering in Washington, D. C., for six months and one year, and artificial weathering (carbon arc and water spray exposure) for 15 and 30 days had a much greater effect. The accelerated weathering can only approximate a speed-up of the natural weathering process. It is apparent that the great variations in climate mean a corresponding variation in the actual weathering a fabric may be required to withstand.

2. Flameproofing Treatments Suitable for Clothing and Indoor Purposes

Several processes that deposit a water-insoluble compound in the fabric have been developed which will withstand a number of launderings, but none of them is entirely satisfactory for general use (Type 2, Section IV). Their application is often difficult and complicated and is best carried out in a commercial finishing plant. The antimony oxide-Vinylite process (No. 2 in Section IV), one of the most recent of such developments, gives promise of being suitable for work clothing and perhaps such materials as upholstery and carpeting, but it so stiffens the fabric that a fairly severe softening process is necessary, and its value for very fine materials is doubtful.

A number of the flameproofers suitable for the finer fabrics, such as ammonium salts, borates, phosphates, silicates, etc. (Type 3, Section IV), have been known and used for curtains and interior decorations for many years. A few, such as ammonium and urea sulfamates, borophosphate resins, and alkyl and aryl phosphates and borates, are of more recent introduction. 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 growth of mildew and accumulation of dirt. Those which give off moisture to the air and cause dusting or discoloration, are also undesirable. Crystalline compounds deposited from concentrated solutions may mar the appearance of the fabric. Some chemicals cost too much or are toxic. Nevertheless, in general, it is not difficult to select a formula suitable for the desired purpose.

(a) Permanence

The problem of permanence has not been completely solved for any of the treatments suitable for fine fabrics. All of the usual water soluble chemicals are removed by laundering or water leaching and the treatment must be renewed after each laundering. Most chemicals will be worn away or dusted out of the fabric with continued use or handling. In some recent wear tests made with workmen's clothing that had been flameproofed with a borax-boric acid treatment, the flameproofing treatment remained entirely effective after two weeks of severe wear. After one month's use some parts of the garments showed a considerable loss in flameproofing but reasonable efficiency was retained in most areas.

Some chemicals, boric acid in particular, are slightly volatile and are slowly dissipated over a long period of time. As a result of indoor sunlight aging tests made at the Bureau of Standards, it was concluded that good water-soluble treatments will give protection of indoor decorations for periods from 6 months to 2 years if the materials are not laundered. The period of retention depends both upon the flameproofing treatment used and the fabric treated. A lightweight white muslin deteriorated more rapidly than a heavier black velveteen.

Therefore, most of the treatments cannot be depended upon to give protection indefinitely without renewal.

Better success has been realized in the development of treatments resistive to dry cleaning solvents since the chemicals in general use are less soluble in such solvents than in water. It should be remembered, however, that present commercial dry cleaning procedures employ water-dissolved soaps which may remove a considerable part of flameproofing agents not affected by dry cleaning solvents alone. A number of proprietary products justifiably claimed to be resistant to pure dry cleaning solvents would not resist the regular dry cleaning process on this account.

(b) Method of Application

Soluble flameproofing agents are generally applied from water solution by immersion, brushing, or spraying, followed by drying. The method of application may have considerable effect on the success of the treatment. Hot solutions will generally give better penetration, but in some cases their use is undesirable. Borax and boric acid, for instance, can be most readily dissolved in hot water, but it is advisable to cool the solution to approximately room temperature before application, as the hot solution appears to have a greater tendering effect upon the fabric. Dipping the material insures more complete penetration than brushing or spraying. With the latter methods a number of successive applications, with drying between them, may be required before effective protection is achieved. For best results all sizing or dressing should be washed out of the fabric before treatment. Where this is not feasible, the addition of a small amount (about 0.1 to 0.2 percent by weight) of an effective wetting agent to the treating solution will aid wetting and penetration into closely woven or heavily sized materials.

A more uniform distribution of the salts will be maintained if the articles can be dried in horizontal position. Drying in vertical position permits a certain amount of drainage of the solution, particularly from upper areas, depending on the wetness of the wrung articles. If horizontal drying is not feasible, it will be advisable to slightly increase the weighting applied in order to allow for some drainage. Materials treated with water-soluble compounds should not be sprinkled and rolled before ironing since an unsightly spotting from the chemicals may result. Dampening should be done with a steam cloth or similar arrangement at the time of ironing. Care should be exercised to avoid discoloration from a very hot iron.

(c) Required Loadings

The weighting with flameproofing treatments necessary for adequate protection will vary with the fabric treated, lighter weight fabrics requiring somewhat heavier loadings. In general, the water-soluble chemicals should be applied in weightings of from 8 to 15 percent, that is, the weight of fabric after treating and drying should be this much greater than that of the original dry fabric. In the immersion method the material is soaked in the solution until thoroughly saturated (about 15 to 20 min). If the wet fabric is wrung out by hand, it will usually weigh approximately 100 percent more than the original dry fabric, and the chemicals left in the material after drying will approximate their percentage concentration in the treating solution. However, if a mechanical wringer is used, more of the solution is likely to be extracted and a more concentrated solution may be necessary to obtain the desired weighting of salts in the fabric. The concentrations suggested of the water-soluble chemicals (Type 3) of Sec. IV are, in general, suitable for hand wringing, and the quantity of water used should be varied to suit the method of application and type of fabric treated. If the concentration of solution desired exceeds the limit of solubility of the chemical, the wringer pressure may be reduced so that a less concentrated solution will provide the required weighting of salts in the fabric. The following table of solubilities of some of the most commonly used salts will indicate the concentrations which can be obtained.

Table 1. Solubilities of Flameproofing Chemicals

Solubilities -- in parts by weight of salt per 100 parts of water

	32°F	68°F	86°F	158°F	212°F
Ammonium chloride, NH_4Cl	29.7	37.3	41.6	59.9	76.0
Ammonium sulfate $(NH_4)_2SO_4$	70.7	75.7	78.1	91.7	103.3
Diammonium phosphate $(NH_4)_2HPO_4$	43.6	59.4		93.8	
Ammonium carbonate $(NH_4)_2CO_3$	55.7				
Boric acid, H_3BO_3	2.6	4.9	6.6	18.5	39.4
Borax, $Na_2B_4O_7.10H_2O$	2.1	4.9	7.6	35.3	75.7
Sodium tungstate, $Na_2WO_4.2H_2O$	41.0	82.2			109.5
Di-sodium phosphate $Na_2HPO_4.12H_2O$		4.2	60.5		
Alum, $KAl\ (SO_4)_2.12H_2O$	5.6	10.8	15.2	65.9	
Lead acetate $Pb(C_2H_3O_2)_2.3H_2O$	23.0	51.7	81.2		
Zinc sulfate, $ZnSO_4.7H_2O$	74.6	96.6	110.5		

(d) Application in Commercial Laundry Equipments

Treatment with flameproofing solutions in commercial laundry operations requires certain precautions if the desired results are to be obtained. The temperature of the solution and operating temperatures of the equipment need, in general, to be lower than for the regular laundry process. Particular attention must be given to regulation of the extraction procedure and to the concentration of the flameproofing solution in order to insure the proper final weighting of chemicals in the fabric.

The articles to be flameproofed should first be laundered with the usual number of suds and rinses, and extracted. When highly soluble flameproofing chemicals are used, the articles may be passed directly from the extractor to the flameproofing solution, since the solution concentration can easily be increased to compensate both for the water remaining in the fabric before treatment and for the loss of solution from the fabric during the subsequent extraction. If less soluble chemicals, such as borax and boric acid, are used, it may be advisable to dry the articles before the flameproofing treatment, as the concentration of these compounds in solution is limited. Increased solubility of such chemicals may be obtained by heating the solution, but this is limited by the danger of tendering the fabric at high temperatures. Dilution of the flameproofing solution by introducing the materials damp instead of dry may be minimized by increasing the proportion of solution to goods to be treated.

Treatment may be accomplished by immersion and soaking for 15 minutes in a tank of the flameproofing solution or by agitation for about 5 minutes in a wheel or washer containing the solution. If the articles have been dried before the flameproofing treatment, the solution should be used in a concentration about twice the desired final weighting of chemicals, to allow for removal of the solution during extraction. A 15 minute extraction in the usual equipment leaves moisture in the fabric to the extent of about 50 percent of its dry weight; that is, 150 lbs of the damp, extracted materials will weigh approximately 100 lbs when dried. Hence, if a final weighting of 10 percent of the flameproofing chemicals is required in the fabric, the treating solution should be used in a concentration of about 20 percent so that, after extraction, a 10 percent weighting will remain. If the materials are only extracted and not dried before the flameproofing treatment, a somewhat more concentrated solution will be required depending on the amount of treating solution used in relation to the quantity of materials treated and the water remaining in the fabric before treatment. The articles may be taken from the flameproofing solution, extracted and finished in the usual manner. The extractor and other equipment in which the flameproofing solution is used should be equipped to permit recovery of the solution which may be used repeatedly, assuming clean and fast-colored fabrics.

Possible damage to treated materials in the tumbler will depend upon the type of fabric, the treating solution used, and the temperature and time of the tumbler operation. More information on these factors is needed. If the goods can be passed directly from the extractor to the mangle for finishing such possible effects are avoided but consideration should be given to proper mangle temperatures.

In treating curtains, velour or velveteen draperies and the like, some laundries prefer a procedure which is longer but more suitable for certain fabrics. The flameproofing solution is used in a concentration about equal to the final weighting of chemicals desired, and extraction is reduced to a time that leaves about 100 percent moisture in the fabric. The articles are then hung up to dry. For special work this method may offer definite advantages and avoids possible damage from heating in the tumbler.

IV. PROCESSES AND FORMULAS

The flameproofing processes for textiles given below are grouped into three main divisions as outlined in the preceding section.

No formulas covered by patents or based on patented proprietary compounds are included except that some of the processes coming under the general description of Type 1 may be patented. Formulas are stated in terms of parts by weight and, also, where water is the solvent, in avoirdupois weight of chemicals and volume of water in U. S. gallons. Smaller or larger volumes can of course be prepared by decreasing or increasing all constituents, including the solvent, in the same proportion.

1. Processes Combining Fireproofing and Weatherproofing, Type 1

No. 1. Finishes meeting requirements of Federal Specification CCC-D-746 and similar specifications.

The essential components of the treating compounds may be described in general as follows:

(a) An organic binder, such as chlorinated paraffin, chlorinated rubber, or vinyl resins as a film-forming material which acts as a water repellent and also affords some degree of fireproofing. With the addition of proper plasticizers, such as tricresyl phosphate or alkyd resins, this binder counteracts much of the stiffening effect of the inorganic ingredients on the fabric.

(b) Inorganic flameproofing agents such as oxides, borates and others.

(c) Pigments, fillers, stabilizers, and other materials such as mildew-proofing agents which add specific desirable properties. Pigments not only give color, but, being opaque, they also serve to protect the finish from the action of sunlight which appears to decompose the chlorinated paraffin to a certain extent with the formation of hydrochloric acid. The finish may be further stabilized by the inclusion of basic compounds such as calcium carbonate, magnesium carbonate and aluminum stearate, to absorb and counteract the hydrochloric acid which has a tendering effect on the fabric. The protection afforded by these materials is important not only to preserve the finish in its proper condition over a period of use, but also to increase the durability of the treated fabric.

(d) An organic solvent in which the other ingredients are dissolved or suspended during application The solvent must be volatile and evaporate entirely in the drying. Water-in-oil emulsions have also been successfully used for impregnation.

The fabric is impregnated most effectively in a processing plant but compounds which will give comparable protection when brushed or sprayed on untreated canvas, or when used to renew the treatment after a period of use and exposure, are available.

Manufacturers usually advise renewal after one year's exposure and at varying intervals thereafter, depending on conditions of use and exposure. These treatments afford considerable protection to the fabric from the effects of weather, microorganisms, and handling, and may extend materially the useful life of the fabric.

A considerable degree of permanence has been achieved in these finishes, but the weightings necessary for effective protection are high, from 40 to 60 percent of the weight of the cloth. They are not suitable for use on fine fabrics, for so heavy a loading alters the characteristics of the fabric more than is compatible with use for clothing and decorative purposes. The numerous compounds effective in lighter weightings are not suitable for outdoor exposure since they are either water-soluble and removed by leaching, or, when insoluble, sufficiently permanent impregnation to withstand any extended period of outdoor exposure has not yet been achieved. If treatments can be developed that effect a basic and permanent change in the cellulose molecule these limitations may be overcome in whole or part. Attempts have been made to bind on water-soluble flameproofers with an over-coat of resin, but the results have not been promising.

2. Water-Resistant Finishes, Type 2

The degree of resistance to water leaching will depend on the details of application and loading as well as the chemicals used. Full resistance in this respect cannot be premised for any of them. Some information on the attainable degree thereof, if known, is given under the respective treatments.

No. 2. Chemical Warfare Service Process (10) Type 2

Antimony oxide, Sb_2O_3	120 parts
Vinylite VYHH (vinyl chloride-acetate copolymer)	60 parts
Methyl ethyl ketone	420 parts

(This amount of methyl ethyl ketone is suggested for trial, but it should be varied as necessary to produce a 35 percent pickup of the Sb_2O_3-Vinylite fraction on the cloth.)

Where the white color of antimony oxide is objectionable, part of it may be replaced by suitable coloring pigments matching the color of the untreated fabric. Improvement in glowproofing will be effected if 27 parts of zinc borate are added.

The Vinylite is dissolved in one half the required methyl ethyl ketone and the antimony oxide added with agitation. If equipment is available, the mix is put through a paint mill to produce a more stable dispersion. Before use, sufficient methyl ethyl ketone is added to give a suitable viscosity and pickup.

All sizing and soil must be removed from the cloth by thorough washing and rinsing before treatment. The dry cloth is passed through the impregnating mix and put through squeeze rolls to remove the excess. The setting of the squeeze rolls may be varied to help adjust the pickup to the desired amount. The cloth is carefully dried, then softened by treating for 30 to 60 minutes on a scouring machine using a 0.2 percent solution of soap or other suitable detergent at 120° to 212°F, depending upon the type of material. It is then rinsed, dried, and may be further softened by treatment on a sanding or sueding machine.

Duck treated by this process has been through 12 commercial launderings with a loss of treatment of less than 10 percent of an original pickup of 40.4 percent and with no apparent loss in flameproofing. The treated fabric is also unaffected by Stoddard or similar dry cleaning solvents, but will not withstand cleaning with chlorinated solvents. This treatment is recommended for cotton, wool and wool-rayon fabrics.

There has been some indication that antimony oxide has a toxic effect upon certain individuals and it is possible that fabrics carrying this treatment and worn next to the skin may be found irritant in some cases.

No. 3. Perkin Process (6) Type 2

Solution A --

Sodium stannate, $Na_2SnO_3.3H_2O$	41.8 parts	11 lb 13 oz
Water	100 parts	12 gal

Solution B --

Ammonium sulfate $(NH_4)_2SO_4$	15.0 parts	15 lb
Water	100 parts	12 gal

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 may have to be repeated or more concentrated solutions used, preferably the former, in order to obtain the required loading of tin oxide which should approximate 20 percent.

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

The treatment, particularly in the lighter loadings, may not prevent propagation of glow. While originally indicated as withstanding as many as 20 washings without loss in effectiveness, recent work has shown a large loss with only a few regular washings in present-day laundry equipment, each involving several suds and rinses of relatively long duration.

The difficulty experienced by many investigators in obtaining an effective application of this process may be due in part to the absorption of alkali by the stannic oxide. Leatherman (11) recommends the use of ferric sulfate or chloride instead of ammonium sulfate as the precipitating agent in order to maintain an acid solution.

3. Water-Soluble Treatments, Type 3

No. 4. Kling and Florentin (5) Type 3

Borax, $Na_2B_4O_7 \cdot 10H_2O$	6.0 parts	6 lb
Boric acid, H_3BO_3	5.0 parts	5 lb
Water	100 parts	12 gal

The fabric is steeped in a cool 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 (13) 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.

The treatment is effective in weightings of from 8 to 12 percent depending upon the type of fabric. Hand wringing from a solution of the concentration suggested above gives a weighting of 10 to 12 percent after drying.

No. 5. Ramsbottom and Snoad (1) Type 3

Borax, $Na_2B_4O_7.10H_2O$	7.0 parts	7 lb
Boric acid, H_3BO_3	3.0 parts	3 lb
Water	100 parts	12 gal

The amount of water may be varied, and should depend upon the absorptive capacity of the fabric to be treated. In general, loadings from 8 to 10 percent of the weight of the dry cloth will be found effective. Hand wringing from the above solution will give approximately these weightings. 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 microorganisms. It has been found to flameproof airplane cloth as over-coated with acetate (14). Brosnan (15) recommends the solution in 7 percent strength for rayon and sheer fabrics.

No. 6. Army Quartermaster Corps - Type 3

Borax, $Na_2B_4O_7.10H_2O$	7 parts	7 lb
Boric acid, H_3BO_3	3 parts	3 lb
Diammonium phosphate $(NH_4)_2HPO_4$	5 parts	5 lb
Water	110 parts	13-1/5 gal

This formula gives very satisfactory results both in flameproofing and glow proofing. It will be found effective in weightings of 7 to 15 percent depending upon the fabric treated. Hand wringing from the above solution gives weightings of about 10 to 12 percent.

No. 7. Matthews (16) Type 3

Ammonium phosphate, dibasic $(NH_4)_2HPO_4$	7.5 parts	7-1/2 lb
Ammonium chloride NH_4Cl	5.0 parts	5 lb
Ammonium sulfate $(NH_4)_2SO_4$	5.0 parts	5 lb
Water	100 parts	12 gal

No. 10. National Bureau of Standards - Type 3

Sodium tungstate, $Na_2WO_4.2H_2O$	24.0 parts	24 lb
Ammonium phosphate, dibasic $(NH_4)_2HPO_4$ ...	6.0 parts	6 lb
Water	100 parts	12 gal

Hand wringing from the above concentration produces a loading of about 30 or 31 percent. It is very effective in preventing flaming, but there is some afterglow.

No. 11. Matthews (16) Type 3

Starch (or flour, sago, dextrin, etc.)	22.0 parts	22 lb
Sodium tungstate, $Na_2WO_4.2H_2O$	11.0 parts	11 lb
Borax, $Na_2B_4O_7.10H_2O$	7.0 parts	7 lb
Water	as desired	

This formula is used for sizing. Although the tungstate and borax afford some fire-retardant effect, their proportion relative to the amount of starch is so low that adequate flame protection is not provided.

V. TESTS AND TESTING METHODS

Through the years of development of flameproofing treatments, various methods of testing and comparing the effectiveness of such treatments have been devised by different experimenters. In the earlier work on test methods, particular recognition should be accorded the work of Whipple and Fay (4), J. R. Freeman (4), and Ramsbottom and Snoad (1) who thoroughly investigated the subject of tests and testing procedure. In 1938 the National Bureau of Standards (18) made a comparative study of a number of testing procedures, including the National Bureau of Standards vertical flame test, the Underwriters' Laboratories flammability test, the Freeman stove pipe test, the Whipple-Fay burning test, the British Standards Institution test, and a fold test. As space does not permit a full discussion of the various testing methods developed, descriptions in this circular will be limited to those in present use at the National Bureau of Standards.

1. Vertical Flame Test

This test is similar to one devised earlier by Ramsbottom and Snoad. It is fairly severe and is the performance test required by Federal Specification CCC-D-746 for Duck, Cotton; Fire, Water and Weather Resistant (12) and is suitable for flameproofed textiles, in general.

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. The ammonium chloride and, to less extent, the ammonium phosphate are hygroscopic and the use of the formula for materials other than those in dry locations may not be advisable. The treatment is effective in weightings of 10 to 18 percent depending upon the type of fabric treated. Hand wringing from a solution of the above concentration gives weighting of about 16 to 18 percent.

No. 8. Martin (16) Type 3

Ammonium sulfate $(NH_4)_2SO_4$	8.0 parts	8 lb
Ammonium carbonate $(NH_4)_2CO_3.H_2O$	2.5 parts	2-1/2 lb
Borax, $Na_2B_4O_7.10H_2O$	8.0 parts	8 lb
Boric acid, H_3BO_3	3.0 parts	3 lb
Starch	2.0 parts	2 lb
Dextrin	0.4 parts	6-1/2 oz
Water	100 parts	12 gal

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. It is effective in loadings of 14 to 28 percent depending upon the fabric. Hand wringing from the above concentration deposits a loading of about 28 percent.

No. 9. Chesneau (17) Type 3

Sodium tungstate, $Na_2WO_4.2H_2O$	20.6 parts	20 lb 9-1/2 oz
Sodium phosphate, dibasic, $Na_2HPO_4.12H_2O$	0.6 parts	9-1/2 oz
Water	100 parts	12 gal

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. Hand wringing from the suggested concentration gives a weighting of about 23 percent. The treatment is effective in preventing flaming, but afterglow continues for a considerable time, and may seriously extend the char.

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. The lower end of the specimen is 3/4 in above the top of a Bunsen or Tirrill gas burner which has a tube of 3/8 in inside diameter. A 1-1/2 in luminous flame is used for ignition and is applied to the center of the lower end of the specimen for 12 sec. To protect the sample from drafts, the apparatus is enclosed in a sheet metal shield 14 in wide, 12 in deep, and 30 in high, open at the top, and provided with a door containing a glass inset for observation of the burning specimen. A metal bar, secured to the base of the burner and extending outside the cabinet through a slot in one side, permits manipulation of the burner without opening the door. In this way the burner is moved under the specimen for the ignition period only, and the flame is left burning continuously throughout a series of tests.

A record is made of the time the specimen continues flaming after the igniting flame is removed, the time of glow after flaming has ceased, and the char length. The char length is defined as the distance from the end of the specimen which was exposed to the fire to the end of a tear made lengthwise through the center of the charred area in the following way. A hook is inserted in the specimen at one side of the charred area 1/4 in in from the adjacent outside edge. A weight, which with the hook is equal to approximately 10 percent of that required to tear the unburned cloth, is attached to the hook, and a tearing force is applied to the specimen gently by grasping the corner at the other side of the char and raising the specimen and the weight clear of the support.

The following indicates satisfactory performance of flameproofed material:

No specimen shall continue flaming for more than 2 seconds after the igniting flame is withdrawn. The average length of char of 10 specimens shall not be more than 3-1/2 in, and the maximum length of char for any one of the 10 specimens shall not be more than 4-1/2 in. For very thin fabrics, however, these requirements are perhaps somewhat severe. While the flame spread is greatest for the specimen in vertical position as in this test, it is not as severe as a multiple vertical strip or fold test but gives a greater difference in results between well-treated and poorly-treated fabrics.

Although fairly consistent results have been obtained with this equipment, the following modifications have been applied recently to enable closer control of test conditions:

Making the specimen wider and securing the vertical edges in a light sheet metal clamp to give an exposed width of 2 in centered over the flame;

Connecting the gas supply line for the burner to a gas chamber to reduce fluctuations in the flame; and

For the same purpose, applying top closure to the shield or box around the burner with a baffled vent placed therein above the burner location.

2. Clamp Field Test

This test (19) was designed for field use and gives results comparable to those of the vertical laboratory flame test described above. It may be applied to any horizontal edge or slit in the fabric (or any edge which can be placed in a horizontal position for testing) without the necessity of cutting out samples or, in general, of removing the material from its position.

The clamp is made of duplicate rectangular pieces of sheet metal about 1/16 in thick, with an area 2 in wide by 5 in deep cut out from the center of one end, leaving U-shaped plates. The two plates are clamped together by spring type paper clips, 1-1/4 in wide, at the ends of the U prongs. The clamp is used with the U in an inverted position, the cloth being slipped between the plates until the horizontal edge of the cloth is even with the ends of the U prongs. Thus, an area of cloth, 2 in by 5 in is exposed, held in a vertical position and firmly clamped in a metal shield which prevents flame from spreading beyond the exposed area. A paraffin candle of 3/4 in diameter is used as the source of ignition and is carried in a holder hinged to one side of the clamp in such manner that it may be swung away from the fabric for adjustment. When used for ignition, the candle holder swings against a stop when the center of the candle is directly under the 2 in wide exposed lower edge of the specimen. Before use, the tapered portion of the candle is allowed to burn away until a normal constant flame is obtained. It is then adjusted in the holder so that the top of the wick will be 1/10 in below the edge of the fabric when in position. For ignition, the flame is applied to the edge of the fabric for 12 seconds.

A satisfactorily flameproofed fabric will meet the following requirements. It will not continue flaming more than 2 seconds after the igniting flame is removed. The average length of char in three tests will not be more than 2-1/2 in. By length of char is meant the distance from the edge of the fabric to the end of a tear through the charred area, made by hand with enough force to tear through the charred or scorched portion but not sufficient to break undamaged threads.

Vertical flame tests, such as those described above, are too severe for satisfactory application to fabrics which have not been flameproofed, since nearly all untreated fabrics burn so rapidly that little differentiation is possible. For the comparison of rates-of-burning of such untreated fabrics, the National Bureau of Standards has developed the following horizontal test.

3. Horizontal Rate-of-Burning Test

A specimen 4-1/2 in wide and 12-1/2 in long is cut from the cloth and slipped into a steel frame which clamps each long edge of the specimen, leaving a center strip 2 in wide and 12-1/2 in long taut and exposed. Marking wires attached to the frame but clear of the specimen cross it at 1-1/2 in from the end which is to be ignited and 1 in from the other end, which leaves a specimen length of 10 in between wires (fig. 1). The frame is supported horizontally in a metal cabinet, 8 in wide, 15 in long, and 14 in high inside, to protect the burning sample from drafts. Ten 3/4 in holes near the sides in the raised bottom and a 1/2-in free space all around under the cover provide ventilation. The front and spaces in the top are glazed to enable observation of the sample.

The sample frame is inserted through a slot in one end of the cabinet and slides on a track until it strikes a stop, when the middle of the end of the specimen will be 3/4 in above the top of a bunsen or Tirrill 3/8 in gas burner tube. A 1-1/2 in long luminous flame, obtained by shutting off the air inlets to the burner, is used for ignition and may be left burning continuously throughout a series of tests. The time required for the flame front to travel the 10 in between the marking wires (a 1-1/2 in length burns before the timing is started) is measured with a stop watch, from which the rate of burning is calculated.

The dimensions of the cabinet and method of inserting and igniting the specimen can be varied somewhat from the above without appreciably changing the results. If matches or candles are used for ignition, the end to be ignited is left protruding until ignition is accomplished, when it is pushed inside. There should be sufficient ventilation for free combustion without direct drafts on the burning sample. A 1-1/2-in length thereof should burn before the significant length is reached over which the burning rate is determined, to obtain a uniform and easily observable start for the flame at the border of this portion of the sample.

The samples should be conditioned at 140°F for about one hour before testing. Unless tested immediately they should be stored under conditions that will prevent undue humidification from atmospheric moisture. Any nap or pile on a fabric should be raised and fluffed before test. The rate of burning is to be given as the average from not less than five tests except that in case there is a spread of more than 40 percent of the average between individual results, ten tests are to be made and the average rate of burning based on the five highest rates from the individual tests.

Most fabrics when subjected to this test burn at a rate well under 15 in per minute. Some fine-napped materials have shown a flash rate (flame flashing through the nap) of 400 in per minute. Light netting and thin coated fabrics give intermediate results.

4. Conditioning of Test Samples

A procedure for conditioning samples before testing, regardless of the test employed, has not been satisfactorily standardized, although it is generally agreed that conditioning is an important factor in performance. For most tests of textiles -- strength, weight, etc. -- the samples are regularly conditioned for at least 24 hours at 70°F and 65 percent relative humidity prior to testing. It is questionable whether as high relative humidity as 65 percent is representative for fire hazard tests since room humidities, particularly during the heating season, are generally much lower. It has been the practice at the National Bureau of Standards to dry the samples in a large ventilated oven at temperatures of 100 to 120°F until equilibrium is reached, after which they are kept in a container conditioned with chemicals to have relative humidity of about 20 percent. The preliminary drying, particularly of samples that have been subjected to accelerated weathering, is important since the humidity jar cannot be depended on to abstract very much moisture from the samples.

VI. REFERENCES

1. Ramsbottom, J. E., and Snoad, A. W., Fireproofing of fabrics. Fabrics Co-ord. Research Comm., Dept. Sci. and Ind. Research (Gt. Brit.). First Report, 52 (1925). Second Report, Appendix I (1930).

2. Gay-Lussac, J. L., Note on the property of salts for making fabrics incombustible. (In French) Ann. Chim. Phys. (2) Vol. 18, 211 (1821).

3. Versmann, F., and Oppenheim, A., On the comparative value of certain salts for rendering fibrous substances non-inflammable. Brit. Assn. Adv. Sci. Rep. 1859, Trans. Sect. Meetings, 86; J. prakt. Chem. Vol. 80, 433; J. Franklin Inst. Vol. 39, 354 (1860).

4. Freeman, J. R., On the safeguarding of life in theatres. Trans. Am. Soc. Mech. Eng. Vol. 27, 71 (1906).

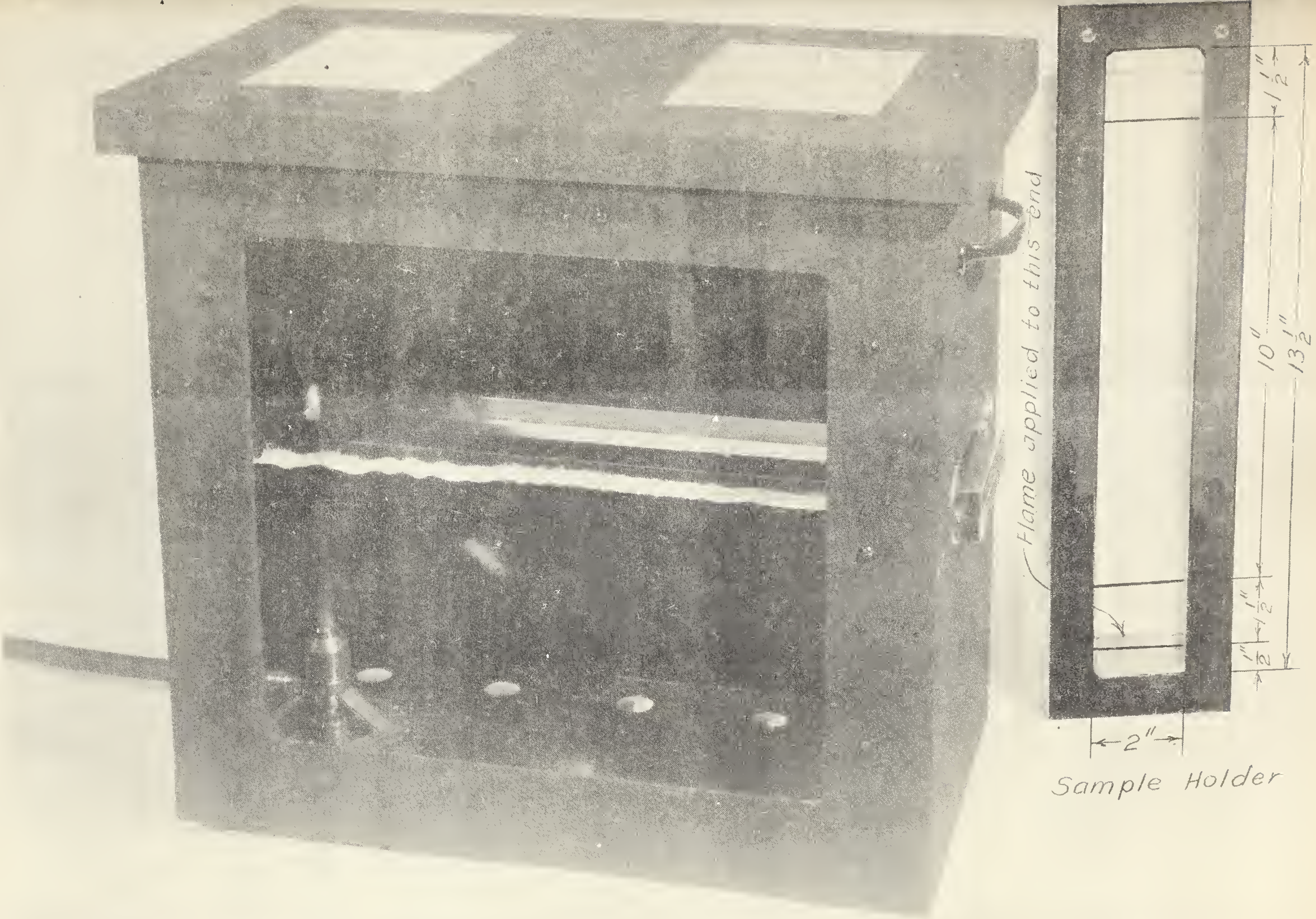

Fig 1 - View of Horizontal Rate-of-Burning Apparatus

5. Kling, A., and Florentin, D., *Protection against fire by fireproofing textiles and wood.* (In French) Génie Civil Vol. 80, 180 (1922); (In English) Quart. Nat. Fire Prot. Assn. Vol. 16, 134 (1922).

6. Perkin, W. H., *The permanent fireproofing of cotton goods.* Proc. Eighth Int. Cong. Applied Chem. Vol. 28, 119 (1912); Quart. Nat. Fire Prot. Assn. Vol. 6, 179 (1912); Nat. Fire Prot. Assn. Educ. Bul. D37 (Boston, 1912).

7. Cupery, M. E., *Sulfamic acid, a new industrial chemical.* Ind. Eng. Chem. Vol. 30, 627-31 (1938).

8. Gordon, W. E., *Fire retardant treatments for textiles.* Am. Dyestuff Reptr. Vol. 30, 305-8 (1941). *Flameproofing textile merchandise*, Rayon Text. Month. Vol. 22, 98-9 (1941).

9. Deutsch, N. L., *New development in flame-proofing of fabrics.* Rayon Text. Month. Vol. 17, 689 (1936).

10. Van Tuyle, R., *Fireproofing cotton and woolen fabrics.* Am. Dyestuff Reptr. Vol. 32, No. 14, 297 (July 5, 1943).

11. Leatherman, M., U. S. patents No. 1,961,108, May 29, 1934; 1,990,292, Feb. 5, 1935; 2,012,686, Aug. 27, 1935; 2,017,805, Oct. 15, 1935; 2,167,278, July 25, 1939; 2,286,744, June 16, 1942.

12. Fed. Spec. CCC-D-746 for duck, cotton; fire, water, and weather resistant (1939). Obtainable at five cents per copy from Superintendent of Documents, Washington 25, D.C.

13. Grove-Palmer, F., *Fire-resisting rayon goods.* Am. Dyestuff Reptr. Vol. 19, 715 (1930).

14. Kline, G. M., *Fire-resistant doped fabric for aircraft.* J. Research NBS Vol. 14, 575 (1935); RP788.

15. Brosnan, W. F., *Fireproofed textiles.* Textile World Vol. 84, 2399 (1934). J. Textile Inst. Vol. 26, A 203 (1935).

16. Matthews, J. M., *Textile fibers.* (John Wiley & Sons, New York 1924). See pp. 568-577.

17. Chesneau, R., *The flameproofing of textiles.* (In French) Bul. Soc. ind. Rouen Vol. 60, 265 (1932); (In English) Dyer Vol. 69, 357, 393 (1933); Text. Colorist Vol. 55, 375, 420 (1933).

18. *Tests of flameproofed textiles by several methods.* Quart. Nat. Fire Prot. Assoc. Vol. 32, 95 (1938).

19. *Field test for flameproofed textiles.* Quart. Nat. Fire Prot. Assoc. Vol. 33, 351 (1939).

20. Travis, H. S., et al., *The impact of wartime requirements on post-war finishing.* Am. Dyestuff Reptr. Vol. 31 No. 25, 634 (1942).

21. Redmond, J. R., *Fire resistant duck.* Am. Dyestuff Reptr. Vol. 32, 375-8 (1943).

22. Akin, E. W., Spencer, L. H., and Macormac, A. R., *Bibliography on flameproofing of textiles.* Am. Dyestuff Reptr. Vol. 29, Nos. 17 and 18, 418-20 Aug. 19, and 445-52 Sept. 2 (1940).

23. *The fireproofing of textiles.* Contains bibliography of patents and literature references. Textile Research Institute, Inc., N. Y. (1943). 15 pages, mimeographed, $1.00 per copy.