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FIREPROOFING REGENERATED CELLULOSE

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This invention relates to the flame-proofing of artificial materials or products of the viscose cellulose type and in a particularly important respect, to the flame-proofing of viscose rayon, e. g. regenerated cellulose fibers manufactured by the viscose process. Considerable effort has been expended over many years to flame-proof various fabrics or the fibers of which they are made, and while a chief object has usually been to attain some measure of permanence in the results of flame-proofing treatment, i. e. permanence against washing or cleaning of the fabric, the art has not generally been very successful in accomplishing that purpose while at the same time preserving the hand and draping qualities of the fabric.

Flame-proofing, as used herein and as understood in the art, means the conditioning of the fabric or its fibers so as to resist or inhibit the propagation of a flame, the conventional tests being to apply a flame to the material, as for a given period of time and the material then being considered flame-resistant if it does not thereafter burn, i. e. propagate flame, of its own accord. It will be understood that some charring may occur, or indeed in many cases some so-called after-glow may be permissible; while an absolutely fire-proof character, as of asbestos fiber, is not required, flame-proofing or flame-resistance is generally understood to connote a reasonably safe resistance to flame propagation by the fabric.

Heretofore conventional flame-proofing procedures have often involved the application of one or another of various metal compounds to the completed textile, and while much effort has been made to impregnate the metal salts or the like in the fibers, most of such finishes, and particularly those which impart the most satisfactory characteristics of flame-proofing, are rather easily removed by water or soap solutions, with the result that the fabric must be re-treated after every time it is washed or cleaned.

While it might be thought that in the case of a synthetic fiber, such as viscose rayon fibers, suitable metal oxides or like compounds could be incorporated in the original viscose solution and thus be embodied directly in the fibers as they are spun and regenerated, and while for purposes other than flame-proofing, some proposals may have been made for the application of certain inorganic compounds to rayon fiber in this manner, experience has heretofore failed to indicate that a satisfactory fiber, suitably and permanently flame-proofed, can be so produced. In some instances, the amount of compounds which could be so applied was found to be apparently ineffective for flame-proofing, while in other cases objectionable impairment of the fiber, e. g. making it weak and brittle, or stiff, was found to occur. Indeed the procedures of regeneration and desulfurization appear to have presented a further obstacle to the hypothetical inclusion of flame-proofing compounds in the fibers, since, according to present evidence, one or another of these procedures is apt to affect the metal compound or its situation in such way that the intended flame-proofing

2

substance is easily leached out, indeed even in these spinning or other baths used in manufacturing the fiber.

The present invention, which involves a number of specific procedures that have been demonstrated to provide satisfactory viscose rayon material having flame-proof properties of a relatively substantial degree of permanence, is believed to involve the more general discovery that by establishing a suitable metal compound in the fiber (for example, preferably by treatment with a soluble metal compound not later than the time that the fiber remains in a wet, i. e. undried, state as on a bobbin upon which it may be wound from the spinning step or in an equivalent unrelaxed state in commercial procedures that do not employ bobbin winding) and by there modifying such compound to an insoluble state, and especially to an enlarged molecular or quasi-molecular structure, the flame-proofing material will be effectively retained by the completed fiber and thus in the ultimate textile or other article fashioned from it. While the theoretical understanding of this concept is supported by considerable experimental evidence such theory is not to be regarded as essential to the specific methods, e. g. in that the procedural operations described below have produced an unquestionably new and more effectively flame-proofed product; nevertheless it seems fairly clear that a new principle is involved, namely the embodiment of insoluble, flame-proofing compounds (e. g. compounds of metals such as antimony, zirconium, tin and others) having molecular characteristics (generally herein considered to be characteristics of size, reference herein to a "molecule" of enlarged dimensions or size being understood to include molecular aggregates held together by secondary bonds or forces) such that these compounds are retained among the micelles or other portions of the regenerated cellulose structure, against escape, on even prolonged leaching or washing, through the interstices of the fiber structure.

As intimated above, the application or introduction of suitable compound material into the cellulose structure should very preferably be accomplished at an early stage in the complete process of fiber manufacture, for instance, at some time before the ultimate fiber has come into such condition as to resist any deep introduction of a suitable metal compound. Present experience has been that for unusually effective results, the addition of the metal compound should not be attempted until after the cellulose has been coagulated and regenerated, and preferably not until after the completion of any desulfurizing treatment that may be used. It will be understood that with an acid spinning bath the cellulose is there regenerated, but that alternatively the viscose can be spun into a coagulating salt bath (e. g. a sulfate bath) and thereafter regenerated in a sulfuric acid bath; the present process, although generally applicable in either case, appears to be more effective in some instances where the two-stage coagulation and regeneration method has been followed. Soluble metal compounds in the bath or baths in which the viscose is coagulated or regenerated do not appear to enter or remain in the filaments, to any effective degree. Thus in the present process the metal compound is applied to the completed fiber, most preferably while it (i. e. the filament) is wet, and while it remains wound on a bobbin or remains otherwise unrelaxed. In such condition, for example as wound on the bobbin, the fiber has not yet shrunk in a substantial manner, it being apparently accurate to define such fiber in an unrelaxed condition.

Thus for example, the initial treatment with a soluble metal compound may be applied to the unrelaxed or equivalently tensioned fiber while the latter is wet or essentially undried but preferably after effecting any chemical treat-

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ment (which may be conventional in the viscose process) of the fiber, the last-mentioned requirement being particularly applicable to the use, in the present process, of compounds of metals which, even though made insoluble in the fiber, might react with the chemical content of a desulfurizing or other bath so as to be converted to a form which could be easily leached out. According to the present invention, one unusually effective way in which to establish an insoluble metal compound deeply embedded, so to speak, within the regenerated cellulose structure, involves incorporation in the latter (for example by direct inclusion in the viscose solution before spinning) of an organic compound, preferably one derived from or analogous to cellulose itself, which is distributed through the lattice of regenerated cellulose and which will react with, or produce a reaction of a subsequently applied soluble metal compound so as to yield, in situ, a desired insoluble compound of the metal, such last-mentioned insoluble compound simultaneously acquiring part or all of the desired molecular characteristics, or at least being capable of acquiring such characteristics upon further treatment, so as eventually to become established in the desired, relatively non-releasable condition.

In all cases, it is preferred that after the treatment of the undried, tensioned or similarly circumstanced fiber with solution of appropriately soluble metal compound, a subsequent treatment be utilized to effectuate production of a molecularly enlarged or molecularly further enlarged insoluble, metal compound within the fiber, particular instances of such second treatment being an apparent polymerization (for example, what appears to be a polymerization of a hydrated metal oxide) or the formation of a complex with another metal compound. For convenience, the attainment of an apparently enlarged condition of the deposited metal compound (as with the further treatments described), whether by actual chemical combination or by formation of a complex or by other aggregation of molecules, is herein described and identified as polymerization.

Pursuant to the invention, compounds of various metals can be incorporated in viscose rayon fibers by procedures of the sort described above and there afford notable success in yielding satisfactory fibers having flame-resistant qualities which may be expected to have considerable permanence in all cases, although with some notable variation among different metals. Such metals, which may be generally classified as having inherent flame-proofing characteristics and which are thus generally contemplated by the invention, include any one or more of elements such as antimony, tin, zirconium, titanium, zinc, vanadium, strontium, tungsten, chromium and molybdenum, and indeed in some cases even tantalum, boron, aluminum, manganese, iron, cobalt, and nickel. As explained below, however, unexpectedly satisfactory results have been obtained with pentavalent antimony and also to a considerable degree with zirconium and very notably with antimony and zirconium together, e. g. as ultimately embodied in what is understood to be a complex compound of these metals. In general, as stated, the procedure involves applying the metal, or each metal, in solution form, for instance as a metal salt such as an antimonate, or a salt of the metal exemplified by zirconium sulfate, zirconyl acetate, ammonium zirconyl carbonate, and the like.

As also stated, a presently preferred operation involves the preliminary inclusion in the fiber, as by original incorporation in the viscose solution of a reactive organic material, which may be a cellulose derivative or similar substance and which is appropriately more reactive than the cellulose per se ultimately regenerated from the viscose. An outstanding example of such cellulose material is carboxy methyl cellulose (i. e. the glycolic acid ether of cellulose), a compound which is soluble in the viscose

solution and is characterized by carboxy, i. e. acid groups. When included in the viscose, carboxy methyl cellulose is then understood to appear in a distributed, embedded form in the regenerated fiber, and thereafter upon application of the metal compound, such as the antimonate, reaction is or may be effected for the desired conversion to an insoluble metal compound, preferably one having at least somewhat difficultly releasable characteristics.

Thus it is understood that upon treating an unrelaxed viscose fiber which contains a minor percentage of carboxy methyl cellulose with an appropriate antimonate, there is produced an insoluble, hydrated antimony oxide, or antimonous acid, which is retained by the regenerated cellulose body. In this (as indeed in other specific procedures described below, using carboxy methyl cellulose, or other cellulose material having carboxyl groups) it is not clear that the reaction produces an actual compound of the metal with any cellulose or cellulose derivative, as by esterification or otherwise; the evidence indicates, nevertheless, that the carboxy methyl cellulose reacts to precipitate the insoluble antimony compound, i. e. a hydrated oxide compound, within the fiber.

As indicated above, various other metal compounds, e. g. soluble compounds thus applicable in water solution (or in dilute acid solution) to the viscose fiber, have been found to precipitate insoluble metal oxides of correspondingly suitable molecular structure, by reaction with or in the presence of carboxy methyl cellulose (which may sometimes herein be identified in abbreviated form as CMC). Examples of such compounds, used in aqueous solution, were sodium tungstate, sodium stannate, antimony pentachloride, and titanium tetrachloride, the respectively produced oxide compounds of tungsten, tin, antimony and titanium being found to give the fibers a flame resistance of considerable durability against leaching in water. Useful results have also been obtained with other metal compounds (used in place of antimonate), such as those of zirconium, e. g. zirconium sulfate and ammonium zirconyl carbonate. All of the compounds mentioned above are not only compounds of metals which in the oxide state will impart flame resistance but are compounds having the further property (in common) of precipitation as oxide (hydrated) of the metal when their solutions are affected by a change in pH. More specifically, it may be noted that the tungsten and tin compounds mentioned above appear to react in a similar fashion to the antimonate, pH values below 7 being similarly appropriate for such compounds; while the chlorides of antimony and titanium seemed to require the CMC of the fiber to be in the state of sodium carboxy methyl cellulose, i. e. alkaline rather than acid. However, whether the reaction in the fiber was simply the production of a hydrated metal oxide (as is believed to be the case with antimonate) or an actual combination with the CMC (either by the CMC forming a coordinate compound with the metal or by formation of the CMC salt of the metal), the result is the establishment of an insoluble metal oxide compound having molecular structure and location tending to retain it well within the cellulose body of the fiber.

Thus in the case of sodium tungstate, for instance, the CMC-containing fiber, in acidified condition, was treated with the tungstate solution, and this procedure (similar to that using antimonate) then appeared to precipitate the desired tungstic acid in the fiber. As stated, effective precipitation with the antimony pentachloride and the titanium tetrachloride were achieved by maintaining Na-CMC in the fibers. Treatment of CMC-containing fiber with a zirconium compound, for example a heated solution of zirconium sulfate, yielded considerable flame resistance of good stability. As in other cases, high concentrations of CMC in the viscose may adversely affect the physical properties of the fiber, but experience has indicated that the CMC content (for purposes of

5

this invention) need not be so high as to have such adverse effect, and may usually be no more than a few per cent; indeed useful results, with zirconium sulfate as with other compounds, were obtained in fibers from viscose having only 0.8% CMC. It was noted that whether the fiber contained free acid CMC or its sodium salt at the time of heating in zirconium sulfate solution, the product exhibited the same degree of flame resistance and stability to leaching; a likely explanation is that the acid CMC formed a coordinate compound with zirconium and the Na-CMC formed a zirconium salt of CMC.

Results of some utility were also achieved with other titanium compounds, such as an organic compound of titanium, with which it was found possible to saturate the fiber, and then to precipitate hydrated titanium oxide by immersion of the fiber in water. Specifically a titanium compound was prepared according to U. S. Patent No. 2,489,651 (Langkammerer, November 29, 1949) and was probably $Ti(OH)_2(OCOCH_3)_2$. This compound is soluble in CH_3OH-H_2O , and was applied in such solution to the unrelaxed fiber; the compound is decomposed (to an insoluble oxide form) by additional water, and hence it was precipitated in the cellulose, presumably as a hydrated titanium oxide, by immersion of the fiber in water. This fiber, however, although initially flame-proof, was somewhat less resistant to leaching than many of the other treated fibers here described.

Although a number of antimony compounds can be employed, very preferably pentavalent compounds and notably compounds (such as antimonates) which are readily precipitated and are then convertible, e. g. by acid reaction or by dehydration, into antimony oxide (as described below), unusually superior results were obtained with a specific antimonate, viz. potassium dihydroxyantimonate $[KSb(OH)_6]$, such compound being herein sometimes conveniently identified in abbreviated form as PDPA. This compound was conveniently used in water solution, say a 6% solution, although it is understood that more concentrated solutions are available and may therefore be used, including for example a commercial syrup of 40% concentration. To apply the antimonate to the fiber, the latter, while still wet and wound tightly on the bobbin or otherwise maintained in tensioned state (the bobbin having a suitably perforated core for better access to both sides of the winding of regenerated viscose filaments), may be simply immersed for an appropriate length of time in the stated solution. For example, immersion in the 6% solution for a short period of time and preferably at somewhat elevated temperature, such as 55° C., has been found quite satisfactory.

As indicated above, a useful feature of the present invention is the incorporation of a reactive cellulose or like substance in the viscose fiber, a particularly preferred instance of such material being carboxy methyl cellulose, either in its normal acid state, or as an alkali metal salt such as the sodium salt. Generally speaking, the function of such substance, which will cooperate to precipitate metal oxides in the fiber, is achieved by a material having a sufficiently high molecular weight in order to be retained by the fiber long enough to enter into a reaction. More particularly, it appears that such material should be an organic compound of a chemical composition and structure similar to cellulose, and of high molecular weight, which will fit into the cellulose structure, i. e. the lattice of regenerated cellulose, and which will have appropriate orientation in conformity with that of the regenerated cellulose, to avoid making the fibers weak and brittle. Examples of compounds of this class are algin, pectins, chitin, and compounds such as CMC (introduced as such or equivalently by partial carboxy methylation of the cellulose before xanthation), as well as the composition resulting from partial carboxy ethylation of the viscose, all of these being or representing sub-

6

stances which contain carboxy groups. As stated, however, CMC (including its sodium or like salts) is unusually effective and convenient, and therefore of itself represents a specific feature of the present process in its preferred and most complete state.

It has also been discovered that correspondingly high molecular weight compounds, preferably cellulosic or similar compounds, which contain or are made to contain *cis* 1,2 diol groups may be effective in reacting with compounds of metals of the character described above, to produce an effectively high molecular weight, metal compound in or with the fiber. Reactive compounds which thus lend themselves to inclusion in viscose for the described function include such substances as alginates, monoglyceryl esters, hemicelluloses (that contain largely rhamnose, mannose, or galactose), gum arabic, and the like, these being high polyhydroxy compounds, chiefly compounds which contain the *cis* 1,2 diol (or glycol) groups. A specific compound of this character which has been found quite effective is the glycerol ether of cellulose, such being the compound understood to be produced by reacting cellulose swollen in monochlorohydrin with alkali. Thus upon preparing such cellulosic material, defined as the glycerol ether of cellulose, which is a compound soluble in dilute alkali (NaOH), and upon adding this soluble cellulose compound to viscose in suitably minor concentration, the resulting spun and regenerated fiber, while undried and wound on the bobbin, was successfully treated with metal compounds such as PDPA, salts of zirconium, and the like, so as to produce a suitably retained metal compound having flame-proofing characteristics. Although there was some evidence of direct reaction between the glycerol ether and the potassium salt of antimonic acid (PDPA), conditions were preferably adjusted so as to provide free antimonic acid in the fiber after its adsorption of PDPA, for the actual reaction with the glycerol ether of cellulose. Specifically, for instance, the procedure was first to treat the fiber with PDPA solution, then to acidify it (e. g. with sulfuric, acetic or other suitable acid) and finally dry the fiber at a high temperature (say 100° C.); in such fashion antimonic acid was present with the glycerol ether at a high temperature, the evidence indicating that a reaction occurred to provide molecular characteristics of the antimony compound (presumably in combination with the glycol grouping), so that a flame-resistant fiber resulted which withstood leaching in water for rather long periods, although not as effectively as the preferred products of the procedures herein described using CMC in the viscose.

While the reactive effect of carboxy or glycol groups has appeared to be significant in the results obtained, an additional or alternative possibility is that the presence of such polar groups tends to increase the capability of the cellulose fiber to swell, perhaps by forcing apart the cellulose chains, and therefore providing greater accessibility for the metal compounds.

It is further to be noted that the carboxy methyl cellulose may be in effect incorporated in the viscose in either of two ways, one being by simple addition to such solution, e. g. after it has been completely formed by carbon disulphide treatment of alkali cellulose but preferably before ripening of the viscose; or alternatively the cellulose, from which viscose is to be made, can first be partially carboxy methylated. The last-mentioned operation may be performed in a known manner, as by treating the cellulose with monochloroacetic acid and alkali, the resultant compound being then xanthated (although with more difficulty than in the case of ordinary alkali cellulose) to yield a viscose which is understood to contain carboxy groups of essentially the same character and relation as the viscose to which CMC is directly added. Hence unless otherwise specified it is to be assumed herein that reference to viscose (or viscose fibers) containing carboxy methyl cellulose means viscose (or fibers spun and re-

generated from it) to which CMC has been added (whether as the acid carboxyl compound or more usually, in the form of a sodium or like salt) and also viscose (or fibers from it) made of cellulose that has been itself partially carboxy methylated.

Indeed it may be that where the CMC is added to a pre-established viscose solution, the CMC itself becomes at least in part xanthated; thus reference herein to viscose fiber containing carboxy methyl cellulose means cellulose fiber structure wherein carboxy methyl groups are attached to cellulose molecular structure throughout the depth of the fiber, whether produced by partial carboxy methylation of the original cellulose (before xanthation) or by adding carboxy methyl cellulose to the viscose solution (i. e. fiber produced from viscose of this or the former type), or otherwise. Such is to be distinguished, however, from fiber having only a surface carboxy methylation; for example, where pure viscose fibers (in completed, dried and unrelaxed state) have been subjected to a carboxy methylation treatment and thereafter treated with antimonate, it is found that no antimony compound is retained by the fiber, at least beyond a brief washing in water. The experiment just described confirms the understanding elsewhere herein expressed, namely that the insoluble antimony or other metal compound should be precipitated deep within the cellulose fiber, very preferably (according to present belief) within the intramolecular spaces of the cellulose (i. e. within the cellulose micelles, or within the more crystalline area), for example where, in the CMC fiber, the carboxy groups presumably reside for effectuation of such precipitation.

In general, the chemical character of the carboxy methyl cellulose-containing viscose, whether made by addition or by original conversion of the cellulose, may be measured or considered as if made by such addition. For most purposes, the effective range of CMC concentration in the viscose is a minor proportion, e. g. from about 10% and preferably from about 6% (by weight) downward. There is some indication that above 25%, and indeed to some extent, above 10 or 15%, the presence of carboxy methyl cellulose may under certain conditions affect the strength and like properties of the fibers. References herein to percentage concentration of CMC or other compounds in the viscose, or even loosely to percent of such in the fiber, mean percentage (by weight) of CMC, or other compound, based on the cellulose content of the viscose. Quite satisfactory results have been obtained with viscoses containing as little as 0.8% CMC (or say, in a range of about 0.3% to 2%) where further treatment of the fiber has been employed, such as the polymerization or other treatments mentioned elsewhere herein, e. g. acid or additional metal compound applications or both, as will be described. It will be understood that however introduced, whether as sodium salt or in free acid state, or equivalently by original, partial carboxy methylation of the cellulose, the CMC content of the extruded viscose normally appears in the form of the alkali metal (i. e. sodium) salt, by reason of the alkaline character of the viscose solution. For most instances of the subsequent metal compound treatment (but with exceptions as elsewhere noted herein), and especially for the treatment with antimonate, the produced fiber should first be acidified as by brief immersion in dilute sulfuric acid, to provide carboxy groups in the acid or free state in the fiber.

As indicated above, effective contribution to the permanent flame-proofing of the fiber, may be achieved with certain further, special treatments following the presently preferred step of immersion in PDPA solution; indeed present evidence indicates that considerable, lasting flame resistance may be obtained by following such course of treatment (initiated by an immersion in PDPA or equivalent metal compound solution), and especially a course of repeated treatments, upon pure viscose fibers (containing no CMC or other special cellulosic material), pro-

vided that the treatment is applied under the conditions such as defined above, namely that the fiber is wound on its original receiving bobbin or is otherwise presented in an unrelaxed condition, i. e. preferably without shrinking and also preferably without drying. Primarily, however, the subsequent treatments have appeared to afford greatest advantage in connection with the original CMC-PDPA reaction, and will be so described.

Thus for instance, after a fiber made from viscose containing 0.8% to 6% or more of CMC and maintained in an undried, unrelaxed condition, had been treated for about 30 minutes in the warm 6% solution of PDPA, such fiber (either dried or undried, but preferably though not necessarily kept under tension) is then immersed in a dilute acid solution, specifically 1% sulfuric acid, preferably at an elevated temperature (e. g. 45°-60° C.), for a suitable period of time, say from 20 to 40 minutes. When finally dried, the thus acid-treated fibers are found to be effectively flame-proof and considerably more resistant to loss of such properties by leaching in water or washing in soap, than the fibers similarly produced but without the acid treatment. Although the actual phenomena are not readily ascertainable, it is believed that while the original reaction between acid-CMC and PDPA establishes miscelles of antimononic acid which are sufficiently large to resist water leaching for a period of many hours, the subsequent acid treatment forms larger micelles of the antimononic acid or antimononic oxide, e. g. in a way that very probably in fact and at least for convenience of description may be herein characterized as a polymerization of the antimony compound. It may also be that the acid treatment modifies the cellulose structure, as by decreasing its pore size, to provide additionally improved retention of the metal compound.

The sulfuric acid treatment, however, exhibits some slight tendency to damage or weaken the fiber. Although such deterioration is not of consequence for many purposes, it was found to be essentially obviated by utilizing, for the polymerization, certain acids selected as inherently less destructive to the cellulose, such acids being found equally suitable and essentially non-deleterious even though somewhat longer times or higher temperatures of treatment are desirable with some of them. Thus any one of a number of acids was found suitable for effecting the polymerization or other modification of the metal compound in the fiber, all of the examples of such acids being at least as non-deleterious as sulfuric acid, and indeed generally (with the possible exception of nitric acid) being essentially entirely non-deleterious as explained above. In each case, the acid should be one in which the metal compound is insoluble; thus none of the acids here named, even in a heated state, appears to dissolve the hydrated oxide of antimony, as distinguished from alpha-hydroxy acids such as glycolic and lactic acids which seem to be capable of reacting with such oxide to yield a soluble compound.

In addition to sulfuric acid, other specific examples of acids suitable for the after-treatment of the present process are acetic acid, formic acid, nitric acid, and hydroxylammonium acid sulfate, in each case used in dilute aqueous solution. Upon utilizing each of these, for instance, for the after-treatment of the precipitated antimony compound in the fiber, in the same manner as the dilute sulfuric acid mentioned above, viscose fibers were obtained that were flame-resistant and that maintained such property even after many days of leaching in water. While examples of these sulfuric or other acid treatments have been described as involving heating the fiber in an acid bath, similar results are attainable by briefly immersing the fiber in acid solution and then removing and moderately heating the fiber.

The mechanism of the apparent polymerization effected by these treatments (with sulfuric or other acid) may in fact be no more than the removal of water from many mols of antimononic acid, resulting in a high mo-

molecular compound, i. e. of large molecular weight or structure. Indeed nonacidic polymerization or aggregation of like effect on the PDPA-treated fibers has been successfully achieved. For example by treating the dried fibers with acetic anhydride at an elevated temperature, such compound being a dehydrating agent, the product was a flame-proof fiber considerably more resistant to loss of its properties in water than the product of the simple CMC-PDPA treatment.

Similar and indeed markedly superior results have been obtained by using another metal compound for the second treatment; for instance, one effective process, more fully described below, has involved following the PDPA treatment of CMC-containing fiber, with a treatment in a solution of a zirconium compound, the fiber preferably remaining unrelaxed during such introduction and precipitation of the second metal compound in the fiber.

While many of the above specific tests respecting the various so-called polymerization treatments were initially performed upon fibers that had been made from viscose solution to which carboxy methyl cellulose had been admixed after preparation of such viscose, it was likewise established by test that similar advantages of the complete treatment (for example, PDPA treatment of the acidulated CMC-containing filaments, followed by the acid or non-acid polymerization) were achieved with fibers containing carboxy methyl cellulose material introduced by partial carboxy methylation of the original cellulose (prior to xanthation). Indeed results appeared to be still better, especially in respect to the durability of flame resistance after leaching and washing operations on the fiber, where the fibers were of the last-mentioned type; perhaps in such case there is a greater concentration or a deeper embedding (or both) of the carboxy groups in the fiber, than can be readily achieved in fibers spun from viscose having admixed CMC.

As explained above, unusual results have been attained with very low initial concentrations of CMC in the fiber, even less than 1%, notably where special successive treatments are then performed. For example, a viscose fiber, while remaining in undried and unrelaxed condition, and containing approximately 0.8% of admixed CMC, was treated with the PDPA and thereafter with dilute sulfuric acid in the manner described above. The contained insoluble antimony compound was moderately resistant to removal, in withstanding several days of leaching. However, by treating the fiber repeatedly with immediately successive applications of PDPA and dilute sulfuric acid, a much more effectively and durably flame-proofed product was obtained. Thus the complete process using only a very small original content of CMC in the fiber, say 0.8%, involved first immersing the fiber in warm PDPA solution, say for 30 minutes, and then directly into warm dilute sulfuric acid (1%) for 30 minutes. After the fiber had dried, but preferably while it still remained wound on the bobbin, the immediately successive treatments in PDPA solution and warm sulfuric acid solution were repeated, the result being a marked improvement in the stability of the flame-resisting compound (the fiber being effectively flame-resistant) to leaching in water. Still further repetition or repetitions of the PDPA and acid treatment were found to increase the properties last-mentioned, particularly the resistance to leaching in water, although as the treatments were repeated, some increasing damage or deterioration of the fiber was observed, probably because of the effect of repeated exposure of the regenerated cellulose to the sulfuric acid, or perhaps because of excess deposit of metal oxide.

It is also to be noted that in these special, successive treatments of soluble metal compound (such as PDPA or other compounds as indicated herein) and acid, described as following the use of a fiber containing not more than a small quantity of CMC, other acids than

sulfuric may be effectively employed, e. g. acids such as specified above for the acid polymerization step, the effect and use of such other acids being likewise as explained above relative to them. Thus, for example in one set of tests, dilute formic acid was employed with considerable success in lieu of sulfuric acid in these procedures involving repeated treatments with antimonate. It may be here noted that in operations of this special type, the successive acid treatments may perhaps be effective to acidify the carboxy group in the CMC, at each such treatment, so that it again becomes capable of reacting with further antimonate to produce more antimonic acid; on the other hand, the direct effect of heating the successive quantities of antimonate in the presence of an acid (such as sulfuric, formic, or other acid applied for treatment) may be the immediate conversion of at least much of the antimonate to antimonic acid in more or less polymerized or molecularly enlarged form.

Another mode of greatly improving the PDPA-treated fiber has been found to involve its treatment with another metal compound which is precipitated to provide enlarged molecular structure of flame-proofing material in the fiber, particularly effective results having been achieved with compounds of zirconium, which appears to achieve complex combinations with other metals such as antimony. Thus CMC-containing fibers, treated with PDPA but not subjected to any subsequent acid or other polymerization treatment of the character described above, were treated with solutions of various soluble zirconium compounds, and found in each case to yield a product having unusually permanent flame-resistant characteristics. Zirconium sulfate (which is rather strongly acidic, as applied in solution, and thus may perhaps in part function somewhat like the sulfuric or other acid treatments) is effective for this after-treatment, while especially useful results have also been obtained with zirconyl acetate solution, and likewise with ammonium zirconyl carbonate solution. It will be noted that the latter compound is slightly alkaline in solution and thus does not behave either as an acid or as a dehydrating agent, i. e. like the agents used in the polymerization treatments described above.

The effect of heating the antimonic acid fiber in ammonium zirconyl carbonate solution was found to result in a highly flame-proof fiber which was unusually resistant to leaching in water and to many washing cycles, i. e. rigorous washing with soap solution at elevated temperature. Furthermore there appeared to be no deterioration of the fiber by the flame-proofing treatment. Indeed successful results, in reaching an antimony-zirconium complex compound (it being believed that such reaction occurs between the applied substances) have been achieved (by the treatments with antimonate and a soluble zirconium compound) where the CMC content of the fiber is relatively very low, for example with the fiber described above that contained only 0.8% CMC. The results last mentioned and other evidence would seem to indicate that effective reaction can apparently take place directly between antimonate in the fiber (e. g. deposited PDPA) and the subsequently applied zirconium compound. It seems particularly desirable that for this subsequent treatment of an antimonate-treated fiber with a zirconium compound (such as ammonium zirconyl carbonate, or zirconyl acetate), the fiber remain in undried, tensioned (i. e. unrelaxed) condition.

Indeed it has been found, more generally, that plural chemical treatments of the sort described herein are effective in imparting significant flame resistance to ordinary, fresh viscose fiber (without CMC or other special ingredient), such treatments being effected in the manner described (e. g. upon the unrelaxed fiber), and being either the repeated additions of antimonate and acid (or other polymerizing agent), or alternatively and most preferably, the treatments with antimonate and a zir-

conium compound, especially ammonium zirconyl carbonate. In the latter case, it appears that since the fiber contains no carboxy or other reactive groups (as described above), the successive antimonate and zirconyl compound treatments may be repeated at least once in order to obtain superior results, especially as to permanence of the flame-resisting property. Evidence also indicates that corresponding apparent formation of enlarged or complex metal compounds (or at least of some retained, flame-proofing material) by treatment of the unrelaxed, pure viscose fiber with other, repeated combinations of solutions (e. g. a solution of another metal compound followed by a polymerizing agent; or other combinations of metals than the specific antimony-zirconium combination, such metals being applied as separate compounds in successive solutions for precipitating reaction in the fiber) can be similarly effective, particularly providing that the metal or metals be selected from the general class delineated hereinabove and that their compounds be adapted for reactions of the described character, to yield insoluble substances of large molecular structure, which may thus be firmly retained within the cellulose body of the rayon fiber.

Among the various specific procedures which have been described above and which all involve treatment whereby successive substances (of which at least one is a soluble metal compound) are incorporated or introduced into the regenerated cellulose fiber (preferably before the fiber shrinks or relaxes) so as to provide by reaction an insoluble metal compound retained by its molecular structure within the cellulose body, the very best results appear at present to have been achieved by the successive introductions of antimonate and zirconium compounds, especially where the cellulose contains a small proportion of carboxy groups. Thus to restate this preferred process somewhat more specifically, the viscose solution is established as containing carboxy methyl cellulose in an amount from say 0.5 to 2% or so (0.8% being found very effective), either by direct inclusion of CMC or alternatively by partial carboxy methylation of the original cellulose to a limited extent such as will provide in the ultimate viscose (i. e. after xanthation) an equivalent concentration of carboxy groups. As indicated above, another way of providing carboxy groups tied to cellulose structure within the filament is by partial carboxy ethylation, which is accomplished upon treatment of the viscose with acrylonitrile, e. g. by adding the latter compound to the viscose solution as it is made.

The viscose filaments or fibers are then spun by known procedure, for simultaneous or successive coagulation and regeneration as explained hereinabove, and when finally withdrawn from such bath or the second of such baths, may be subjected to any necessary after-treatment such as desulfurization. The filaments are kept in a stretched or unrelaxed condition, and preferably prevented from drying to any appreciable extent. While they remain in such condition, for example as wound on a bobbin or like support directly from the spinning bath, the fiber is then treated with antimonate, e. g. an aqueous solution of PDPA, preferably at a somewhat elevated temperature, say in the range of 50 to 75° C. The immersion in warm antimonate is continued for a period of the order of 20 to 40 minutes or more, usually 30 minutes. Although in some cases the fiber can then be dried before further treatment, it is preferably at once, and again without being relaxed, subjected to treatment in a solution of a soluble zirconium compound, preferably at a similarly elevated temperature; as stated, ammonium zirconyl carbonate has been found very suitable, and likewise zirconyl acetate. The fiber is thus immersed in the warm zirconyl salt solution, for a similar period and is ultimately removed and dried. The resulting structure which is understood to contain both antimony and zirconium in combined, insoluble form, has been found to be effectively flame-proof and to retain its flame-resistant

properties over long periods, i. e. after months of leaching in water and after repeated, strenuous washings in hot soap solution. While the precise chemical reactions involved are difficult to ascertain, it seems likely that the antimonate is at least in part first converted to antimonous acid by the carboxyl groups, and the zirconium compound then further reacts to provide further, difficultly removable, insoluble material in the fiber, probably including an enlarged molecular structure of the antimonous acid; the phenomena very likely involve the formation of an insoluble complex metal compound which includes both antimony and zirconium.

Although antimony compounds are at present greatly preferred as the first metal-containing reactant, it has been explained above that soluble compounds of other metals than antimony have been found to react with carboxy methyl cellulose (or to be capable of ultimate precipitating reaction, similar to antimonate, in fibers containing cis 1,2 diol groups) for establishing insoluble, flame-proofing compounds in viscose rayon fibers. Utility is thus contemplated for a considerable number of other metals as stated hereinabove, but particularly good results appear possible with compounds of zirconium, tungsten, tin and titanium or combinations of these with each other or with antimony. Various procedures can be used (for various types of soluble compounds) as indicated, and subsequent polymerization or repetitive treatments may also be advantageously employed. For instance, where sodium tungstate was used to treat an acidified CMC-containing fiber and thereby precipitated an insoluble compound (presumably tungstic acid) in the cellulose, conversion of the molecular structure of the precipitated compound to more lastingly retained state in the fiber was successfully achieved with treatment such as used for like purpose upon antimonous acid, e. g. an acid treatment (say, heating in dilute sulfuric acid) which thus apparently polymerized the tungstic acid or additionally or alternatively reduced the dimensions of the capillary spaces in the fiber.

Turning now to the following specific examples of the procedures of the present invention, it will be understood that in every case the viscose can be made by standard conventional methods, e. g. by the treatment of appropriate cellulose to provide the so-called alkali cellulose which is then xanthated with carbon disulfide, to yield a viscose solution which is finally treated in the usual manner, with the conventional ripening time. The ripened viscose solution is spun through the usual fine orifices into a coagulating or regenerating bath. A conventional acid bath can be used, wherein the filaments are solidified and the viscose is regenerated to cellulose, for example a bath containing about 11% sulfuric acid, 8 to 16% sodium sulfate, 2-3% magnesium sulfate and 2-6% zinc sulfate. Alternatively (and indeed now preferably in Examples I and VI) the viscose can be spun into a salt bath for coagulation (for example, an aqueous solution containing about 21% ammonium sulfate, 3% sodium sulfate and 0.5% sulfuric acid) and then regenerated in an aqueous acid bath, e. g. a 10% sulfuric acid solution. As formed, the filaments are handled in any suitable manner, as by being withdrawn from the bath directly to a perforated core bobbin upon which the fiber is thus wound under tension and upon which the fiber may be retained for the subsequent treatments as set forth. Although not specifically mentioned in the examples below, the fiber is given the usual desulfurizing treatment before subjecting it to PDPA or other subsequent treatment; desulfurizing usually involves immersing the fiber in an aqueous solution of sodium sulfide (about 5%), and then rinsing.

In the various examples utilizing fibers made from a viscose solution to which CMC had been added as a separately prepared ingredient, the latter material was a high viscosity carboxy methyl cellulose (although CMC of medium or low viscosity can be used), and was intro-

13

duced in various quantities equaling from 0.8% to 6% or more (based on the cellulose content) in the final viscose solution, i. e. the solution containing the added CMC. The carboxy methyl cellulose (conveniently in the form of an alkali metal salt, e. g. the sodium salt) was simply added to the viscose solution and the mixture was thoroughly stirred and then filtered through a stainless steel plate filter. In many cases the addition was made to viscose solution as freshly prepared and the ordinary ripening was thereafter allowed to take place; however, tests indicated that results of the present process were essentially the same where the CMC was not added until part or all of the ripening had occurred.

Example I

In this example a fiber (i. e. a winding of fibers or filaments on a bobbin as described above) containing 0.8% of high viscosity CMC was acidified, i. e. by brief immersion in 10% H_2SO_4 solution to insure the presence of free acid carboxy groups. The fiber, thus remaining in unrelaxed or unshrunk condition on the bobbin was then immersed in a 6% aqueous solution of potassium dihydro pyroantimonate for 30 minutes at 55° C., and was thereafter directly immersed (without intermediate washing or drying) in a 20% aqueous solution of a saturated solution of ammonium zirconyl carbonate, for 30 minutes at 55° C. The fiber was then rinsed in water for several minutes and dried at room temperature. When dry, the fiber was unwound from the bobbin and subjected to various tests. Specifically, the treated fiber was tested for flame resistance, e. g. by holding a flame at one end of a length of a group of strands, while the group of strands, in successive tests with different pieces of it, was held at various angles, e. g. horizontal, vertical and intermediate angles. There was no flame propagation by the fiber at any of these positions and afterglow disappeared in less than four seconds following removal of the flame. A quantity of the treated fibers were then immersed in water for over 60 days, dried and tested again for flame resistance in the same manner. Another batch of the treator fiber was also subjected to repeated launderings, i. e. successive washings in hot soap solution and rinsing in hot water, followed by acetic acid sour and cold rinsing, and was then dried and likewise tested. The flame resistance after both leaching and washing, was the same in all cases as observed in the freshly treated fiber, thus indicating a remarkable durability of the flame proofing material.

Example II

In these tests, the fiber, as wound on the bobbin, contained 2% of the carboxy methyl cellulose. It was acidified as before, and then immersed in the 6% solution of PDPA, for 30 minutes at 55° C. It was thereafter dried at 90°–110° C. (while remaining on the bobbin) and thereupon heated in a 1% solution of sulfuric acid for 30 minutes at 55° C. Fiber removed and dried after this stage of the process was found to be effectively flame-resistant, under the same tests as before, and to be well retained against leaching in water. The tests also included a repetition of the procedure of heating in PDPA solution and then in acid solution, i. e. retreating the fiber in the same way after the initial treatments. The fiber resulting from the repeated operation was likewise effectively flame-proof by the same tests, and was found to maintain its flame-resistance even after leaching in water for several months.

These operations were repeated with essentially identical results, but using various other acids instead of sulfuric acid for the acid treatment following the immersion in PDPA solution. Instances of such acids were nitric acid, acetic acid, and formic acid. Likewise the process was performed utilizing acetic anhydride instead of an acid solution, for the step or steps following the PDPA treatment, i. e. for the steps understood to provide a poly-

14

merization of the insoluble antimony compound. With some of the other acids, particularly those of weaker character, a longer heating time was found necessary, e. g. of the order of one hour or so. Satisfactory results were obtained in all of these further tests, i. e. in yielding an effectively flame-resisting fiber, which maintained such properties after long periods of leaching in water, and indeed after repeated laundering tests.

Example III

In this example, the viscose was prepared from partially carboxy methylated cellulose, i. e. as distinguished from viscose to which separately prepared CMC is added. A test quantity of the partially modified cellulose was obtained by treating 30 grams of pure cellulose of a type suitable for making viscose (specifically Solka Floc BW-40) with 30 cc. of a 30% solution of monochloroacetic acid. The powdery mass resulting from addition of the acid solution to the cellulose was stirred vigorously for a few minutes to insure intimate mixture and was then allowed to stand for 3 hours at room temperature. Thereupon a 36% sodium hydroxide solution, comprising 86.5 grams of NaOH dissolved in 153.5 cc. of water, was added to the above mixture and the mass was stirred for a few minutes. The temperature rose to 41° C. The jar containing the mixture was closed and allowed to stand at room temperature with occasional shaking. After one hour this reaction mass was neutralized with 450 ml. of 30% acetic acid, being placed in an ice bath during such neutralization, to prevent an undue rise of temperature. After cooling for some time the mass was filtered through a Buchner funnel and was washed with water until free of chloride ion. The product was then spread out on a drying pan and partially dried at room temperature. This composition consisted of partially carboxy methylated cellulose and was thereupon utilized to make a viscose solution, e. g. by treatment with further sodium hydroxide in solution and by addition of carbon disulfide and with appropriate shaking and conditioning as conventional in the xanthation process, it being found, however, that somewhat longer time was required in order to yield a solution having a satisfactorily high percentage of the cellulose converted to cellulose xanthate. After ripening, the viscose solution was then spun through the usual fine orifices into a coagulating bath, from which it was drawn upon a perforated bobbin, regenerated, desulfurized and then acidified, as in Example I.

A batch of fibers thus made was found to contain acid carboxy groups in a quantity or relation essentially equivalent to fiber containing 0.75 to 3% added CMC depending on the length of reaction time.

The fiber thus prepared, while remaining unrelaxed on the bobbin, was flame-proofed by heating it for 30 minutes at 55° C. in 6% PDPA solution, then drying at 90° to 110° C. and finally heating in 1% sulfuric acid solution for 30 minutes at about 55° C. The treated fibers were then washed and dried. These fibers were found effectively flame-resistant even after 100 days leaching in water and a plurality of laundering tests using a hot 0.5% Ivory soap solution and rinsings in hot water followed by acetic acid sour and cold water rinsing.

Tests of other flame-proofing operations, for instance as in Examples I and II, with the fiber made from partially carboxy methylated cellulose, yielded results equivalent to or often better than those obtained with the fiber made from viscose to which CMC had been specifically added.

Example IV

In this example, alkali soluble cellulose glycerol ether was first prepared, for addition to viscose solution. For such purpose, 15 grams of pure cellulose (Solka Floc BW-200) were introduced in a suitable jar and 35 grams of 79.5% glycerol monochlorohydrin were added. The mass was mixed intimately and allowed to remain at room temperature (27° C.) for 17 hours. Then a sodium hy-

droxide solution consisting of 40 grams of NaOH in 50 ml. of water was added and thereafter 20 grams of magnesium oxide (powder) and 60 grams of benzene were also added. During the addition of the alkali and further substances, the jar was kept immersed in an ice water bath. The reactants were mixed intimately and kept at 0° C. for 24 hours. The excess benzene was then decanted and the reaction mass was neutralized with approximately 325 cc. of 30% acetic acid. The mass was next filtered by suction through a Buchner funnel, washed with methyl alcohol until free of benzene, and finally washed with water and dried in an oven at about 85° C. The dried product, which weighed 17.7 grams, was dissolved in a solution containing 17.7 grams of sodium hydroxide in 282 cc. of water. The resulting alkaline solution, which was filtered through a stainless steel plate filter, constituted an approximately 5.9% solution of cellulose glycerol ether, and was then used for addition to viscose solutions, e. g. to prepare such viscoses containing from 3.2 to 9.0% of the alkali soluble cellulose glycerol ether.

Thus, for instance, fiber was spun and wound on a bobbin from a viscose containing 6% of the above glycerol ether. While in unrelaxed condition on the bobbin, the fiber was treated with 6% PDPA solution at about 70° C. for 30 minutes, then dried in an oven at about 85° C. for 20 minutes and thereafter immersed in 10% acetic acid solution (aqueous) for 10 minutes, the principal function of the latter treatment being believed to provide for the formation of free antimononic acid in the fiber. The fiber was leached in water for 20 minutes and then dried in an oven at about 110° C. for 10 minutes, this final step being understood to complete the probable reaction between the antimononic acid and the cis 1,2 diol groups of the cellulose glycerol ether.

The treated fiber was found to be effectively flame-resistant by tests of the sort described above, such flame-resistance being also found to survive leaching in water and likewise in cold 1% NaOH solution, for about 8 days. A short series of laundering cycles, however, removing the flame-proofing properties, indicating that although results of some utility had been obtained, the product was definitely less satisfactory than those of other specific procedures above. However, upon repeating the treatment of the fiber, e. g. again heating it in 6% PDPA solution at 55° C. for 30 minutes, drying it, immersing it in 10% acetic acid and then again oven-drying it, the durability of flame-resistance was greatly improved.

Fiber containing cellulose glycerol ether as above, and subjected to the first set of treatments (with PDPA, acetic acid, and heat), was also treated by immersing it directly in ammonium zirconyl carbonate solution (i. e. a 20% aqueous solution of a commercially obtained saturated solution) at 55° C. for 30 minutes. Again, by this last treatment, the durability of the flame-resistance, against leaching or laundering, was markedly improved.

A partial cellulose glycerol ether was also prepared by appropriate treatment of alkaline cellulose with glycerol monochlorohydrin in a fashion analogous to the preparation of the complete ether, and such partial ether was then converted to viscose by conventional treatment with sodium hydroxide and carbon disulfide. Fibers spun and regenerated from this viscose were subjected to various flame-proofing treatments, e. g. as described above for the viscose made with specifically added cellulose glycerol ether. The results were essentially the same, although not appreciably better. For convenience of expression, general reference herein to viscose containing cellulose glycerol ether (or equivalent material) will therefore be understood to mean either such viscose to which the ether has been specifically added, or viscose made from partially treated cellulose, i. e. cellulose in the form of a partial cellulose glycerol ether.

Example V

In this example a pure viscose fiber, i. e. spun and

regenerated in the conventional manner from viscose solution containing no carboxy methyl cellulose or other ingredient of the character described herein as added to or incorporated with viscose solutions, was wound on a perforated bobbin from the spinning bath, and subjected to the usual desulfurization treatment. While remaining in unrelaxed condition, the fiber was then immersed in warm PDPA solution and then thereafter directly into warm 1% sulfuric acid solution for 30 minutes. Whereas the product of this treatment exhibited flame-resistance, its flame-proofing properties did not appear to be resistant to more than a short leaching time in water, e. g. several hours. However, upon subjecting a fiber which had been treated in this manner to successive courses of treatment, i. e. each involving PDPA solution and acid solution in the same way, the stability to leaching in water was vastly improved, generally in proportion to the number of additional treatments until there had been three of them. Whereas after three such further treatments, the fiber was found to be somewhat weakened (although still useful for many purposes) and whereas such weakening appeared to become more serious in proportion to the number of repeat treatments, much less damage to the fiber, and yet effective flame-resistance, can be had by substituting other acids (e. g. acetic acid, formic acid) for the sulfuric acid steps. While the results of this example in general seem somewhat less satisfactory than with fibers containing CMC, it appeared that a fairly permanent flame resistance could be achieved by this simplified treatment or series of treatments of ordinary, pure viscose fiber (all carried out while the fiber remained in unrelaxed condition), it being thus understood that appropriate, difficultly removable molecular structures of antimononic acid were built up and apparently polymerized deep within the cellulose.

Example VI

In this instance a partially carboxy ethylated viscose fiber was employed in the production of an effectively flame-resistant article. A fiber containing carboxy ethyl groups was prepared by adding to a viscose solution (otherwise conventional in character) from 1 to 15% of acrylonitrile (measured by weight of cellulose content in the viscose), the mass being then mixed thoroughly and allowed to stand for at least a few hours (preferably about 4 to 5 hours) for insuring completion of reaction before spinning. Present indications are that a preferred amount of acrylonitrile is from 2 to 5%. While this compound can be added at once to the viscose solution, it may also conveniently be added in portions, e. g. while stirring. The viscose thus treated for partial carboxy ethylation was spun into filaments, e. g. in a conventional regenerating bath or more advantageously (according to present experience) in a salt coagulating bath as explained above. The filaments were suitably processed (e. g. while under tension), for example, by winding onto a bobbin from the coagulating bath, the bobbin-carried product being then subjected to regeneration (in acid bath), and thereafter to desulfurization and acidification steps as above described. The resulting undried and unrelaxed fibers, containing partially carboxy ethylated cellulose, were treated by heating them (e. g. while on the bobbin) in 6% PDPA for 20 to 40 minutes at 40° C. to 60° C., and were then directly treated in a 20% solution of a saturated solution of ammonium zirconyl carbonate, e. g. for 20 to 40 minutes at 40° C. to 60° C. After a short water rinse, followed by drying of the still unrelaxed fiber at room temperature, the process was completed. Upon removal from the bobbin, the fiber was found to have effective flame-resistance, that endured through repeated launderings and prolonged leaching in water.

While for most purposes some short afterglow of a treated fiber is permissible under requirements of flame-resistance, and while as indicated above, there was usually relatively little afterglow with the treated fibers of the present invention, it was found possible to reduce or eliminate the afterglow by supplemental treatments. It

will be understood that afterglow is a glowing condition of the fiber that persists after a flame has been applied, e. g. in that there is no actual flaming of the fiber but a glow remains and dies out, at the actual locality of contact with flame. One procedure for so treating the fibers involved immersing them in a solution of tetraethyl orthosilicate, the impregnated fiber being then treated in a dilute acid such as dilute sulfuric acid, to hydrolyze the added compound to a hydrated silicic acid. Fibers so treated were found to have no afterglow, although as the fiber was subjected to successive washing cycles, the afterglow gradually became apparent again. Some considerable reduction of afterglow effects were also achieved by using 0.8% tetraethyl orthosilicate in the viscose itself, i. e. before spinning and regeneration. The afterglow effects with fibers so made, which were thereafter flame-proofed by the procedures of the invention, were extremely brief and the avoidance of afterglow appearing to be relatively permanent, against leaching and laundering. It will be understood that in general, the use of silicates for reducing afterglow is a known procedure, the foregoing tests thus indicating that the various known silicate and like processes can be successfully used with fibers treated for flame-resistance in accordance with the present invention.

It is apparent that the flame-proofing procedures herein described may be utilized in the manufacture from viscose of other regenerated cellulose articles, e. g. other elongated articles, especially film, flexible sheet and the like similarly formed by extrusion of viscose solution.

It is to be understood that the invention is not limited to the specific processes and products hereinabove set forth but may be carried out in other ways without departure from its spirit.

What is claimed is:

1. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a regenerated viscose cellulose fiber containing therein reactive cellulose material having a reactive group selected from the class consisting of carboxy methyl, glycerol ether and carboxy ethyl, said reactive group being present in amount providing reactive cellulose as only a minor part of the cellulose content of the fiber, introducing within said fiber, while the fiber is maintained in undried condition, a compound of a metal which has flame-proofing properties and which is adapted to react with said selected reactive group, and reacting said compound with the selected group to produce an insoluble compound of the metal embodied within said cellulose fiber.

2. Procedure as described in claim 1 wherein the reactive group of the reactive cellulose material is carboxy methyl.

3. Procedure as described in claim 1 wherein the reactive group of the reactive cellulose material constitutes a glycerol ether of cellulose.

4. Procedure as described in claim 1 wherein the reactive group of the reactive cellulose material is carboxy methyl and the introduced metal compound is soluble antimonate.

5. Procedure as described in claim 1 which includes treating said fiber, to enhance the retention of the insoluble metal compound within the cellulose structure of the fiber, with a solution of a substance selected from the class consisting of: acids in which the oxide of the said metal is insoluble, dehydrating agents, and soluble zirconium compounds capable of reacting with the aforesaid combined metal in the fiber to provide an insoluble zirconium compound.

6. Procedure as described in claim 1 wherein the introduced metal compound is a compound of a metal selected from the class consisting of antimony, zirconium, tin, tungsten and titanium.

7. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a regenerated viscose cellulose product containing carboxy methyl cellu-

lose therein, and treating said product with a soluble compound of a metal which has flame-proofing properties and which is adapted to react in the presence of said carboxy methyl cellulose, for producing, by said reaction, an insoluble compound of the metal within the cellulose product.

8. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a regenerated viscose cellulose fiber containing therein reactive cellulose material having a reactive group selected from the class consisting of carboxy methyl, glycerol ether and carboxy ethyl, said reactive group being present in amount providing reactive cellulose as only a minor part of the cellulose content of the fiber, introducing within said fiber a compound of a flame-proofing metal which is selected from the class consisting of antimony, zirconium, tin, tungsten and titanium and which is adapted to react with said selected reactive group, and reacting said compound with the selected group to produce an insoluble compound of the metal embodied within said cellulose fiber.

9. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a regenerated viscose cellulose fiber containing carboxy methyl cellulose therein, and while maintaining said fiber in undried and unrelaxed condition, treating said fiber with a solution of a soluble compound of a flame-proofing metal which is adapted to react in the presence of said carboxy methyl cellulose, for producing, by such reaction, an insoluble compound of the metal in molecular form retained within the cellulose structure of said fiber.

10. Procedure as described in claim 9 wherein the soluble compound is potassium dihydro pyroantimonate.

11. Procedure as described in claim 9 wherein the content of carboxy methyl groups in said cellulose fiber is equivalent to that of cellulose fiber spun and regenerated from viscose solution to which from 0.5% to 25% carboxy methyl cellulose has been added.

12. Procedure as described in claim 9 in which the content of carboxy methyl groups in said cellulose fiber is equivalent to that of cellulose fiber spun and regenerated from viscose solution to which from 0.3% to 10% carboxy methyl cellulose has been added; in which the soluble compound comprises antimonate which reacts with the carboxy methyl cellulose to produce a hydrated oxide compound of antimony within the cellulose structure; and which includes treating said fiber, to enlarge the molecular structure of said oxide compound therein, with a solution of a substance selected from the class consisting of: acids in which said oxide compound is insoluble, dehydrating agents, and soluble zirconium compounds capable of reacting with said oxide compound to provide an insoluble zirconium compound.

13. Procedure as described in claim 9 in which the soluble compound comprises antimonate which reacts to produce an insoluble antimony compound in the fiber, and which includes thereafter treating the fiber with an acid in which said compound is insoluble, to enhance the retention of the antimony compound within the cellulose structure of the fiber.

14. Procedure as described in claim 9 in which the soluble compound comprises antimonate which reacts to produce an insoluble antimony compound in the fiber, and which includes treating the fiber with a zirconium compound selected from the class consisting of zirconium sulfate, zirconyl acetate and ammonium zirconyl carbonate, to provide enlarged molecular structure of flame-proofing metal compound material within the fiber.

15. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a viscose solution containing carboxy methyl cellulose, converting said viscose solution into a regenerated cellulose product, thereafter while said product remains in undried condition, treating said product with potassium dihydro pyroantimonate, for reaction in the presence of said carboxy

methyl cellulose to precipitate an insoluble antimony compound in said regenerated cellulose, for imparting flame-proofing properties thereto, and treating the fiber with ammonium zirconyl carbonate for reaction with said insoluble antimony compound to enhance the permanent flame-proofing properties of the fiber.

16. In the manufacture of flame-resistant viscose cellulose material, the steps of producing, in undried and unrelaxed condition, a viscose cellulose fiber containing carboxy methyl cellulose and treating said fiber, while it remains in said condition, with antimonate to react in the presence of said carboxy methyl cellulose for precipitation of an insoluble antimony compound within said viscose cellulose.

17. In the manufacture of flame-resistant viscose cellulose material, the steps of producing, in undried and unrelaxed condition, a regenerated viscose cellulose fiber containing glycerol ether of cellulose, treating said fiber while it remains in said condition with a solution of antimonate, and converting the deposited antimonate to antimonic acid in said fiber and reacting said antimonic acid with said glycerol ether of cellulose to produce, within the fiber, an insoluble antimony compound having molecular characteristics impeding its subsequent removal from the regenerated cellulose structure of said fiber.

18. In the manufacture of flame-resistant viscose cellulose material, the steps of establishing a regenerated viscose cellulose fiber containing carboxy methyl cellulose therein, and subjecting said fiber to a plurality of treatments in succession, each of said treatments comprising treating the fiber with antimonate and then immediately with an acid in which antimonic acid is insoluble and which is adapted to enlarge the molecular structure of antimony oxide compound material in the fiber.

19. Procedure as described in claim 18 in which the acid is dilute sulfuric acid.

20. Procedure as described in claim 18 in which the acid is acetic acid.

21. Procedure as described in claim 18 in which the acid is formic acid.

22. Flame-resistant regenerated viscose fiber containing within the cellulose structure thereof a hydrated oxide compound of antimony polymerized in place and having molecular properties which impede removal of said compound from said structure, said antimony compound being incorporated in said fiber by procedure as defined in claim 1 wherein the soluble compound used for treatment of the fiber is a soluble compound of antimony.

23. Procedure as described in claim 1, wherein the regenerated cellulose fiber consists of partially carboxy ethylated cellulose, the reactive cellulose content of the fiber having been provided by partial carboxy ethylation of the viscose.

24. In the manufacture of flame-resistant viscose cellulose material, the procedure of establishing within a regenerated viscose cellulose product an insoluble compound of a metal which is pentavalent antimony and which has flame-proofing properties, by treating the product, while said product remains in undried condition, with a solution of antimonate to introduce said metal in combined form into the product and converting said combined pentavalent antimony into said insoluble compound within the unrelaxed product, said last-mentioned step including treating the product with a solution of a substance selected from the class consisting of: acids in which the oxide of said metal is insoluble, dehydrating agents, and soluble zirconium compounds capable of reacting with the aforesaid combined metal in the product to provide an insoluble zirconium compound.

25. In the manufacture of flame-resistant viscose cellulose material, the procedure of establishing within a regenerated viscose cellulose product an insoluble compound of pentavalent antimony by treating said product,

while said product remains in undried condition after the regeneration of said product from viscose, with a solution of antimonate, and converting said antimonate within the product, into a hydrated antimony oxide compound in retained state in said product.

26. In the manufacture of flame-resistant viscose cellulose material, the steps of producing a regenerated viscose cellulose product in undried condition after regeneration of said product from viscose, treating said product, while it remains in said condition, with a solution of antimonate, to establish a compound of antimony therein, and thereafter treating the product with a solution of a soluble zirconium compound, for reaction with the antimony compound in the product to produce, in retained state within the said regenerated cellulose, an insoluble complex compound of antimony and zirconium.

27. In the manufacture of flame-resistant viscose cellulose material, the steps of producing a regenerated viscose cellulose product in undried condition after regeneration of said product from viscose, and establishing within said product an insoluble compound of a metal which is antimony and which has flame-proofing properties, by subjecting the product to a plurality of cycles of treatment in succession, each of said cycles of treatment comprising treating the product with a solution of antimonate to introduce said metal in combined form into the product and converting said antimonate into said insoluble compound in retained state in the product, said converting step of each cycle comprising treating the product with a solution of a substance selected from the class consisting of: acids in which the oxide of the said metal is insoluble, dehydrating agents, and soluble zirconium compounds capable of reacting with the aforesaid combined metal in the product to provide an insoluble zirconium compound; at least the first of said cycles of treatment being effected while the product remains in its aforesaid undried condition.

28. In the manufacture of flame-resistant viscose cellulose material, the steps of producing a regenerated viscose cellulose product in undried condition after regeneration of said product from viscose, and establishing within said product an insoluble compound of a metal which is pentavalent antimony and which has flame-proofing properties, by subjecting the product to at least three cycles of treatment in succession, each of said cycles of treatment comprising treating the product with a solution of antimonate to introduce said metal in combined form into the product and converting said antimonate within the product into said insoluble compound of pentavalent antimony in retained state in said product, and each of said cycles of treatment being effected while the product remains in its aforesaid undried condition.

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