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NONFIBROUS CELLULOSIC STRUCTURE AND
METHOD OF PRODUCING SAME

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This invention relates to the production of non-fibrous, cellulosic structures. More particularly, it relates to the production of non-fibrous cellulosic structures containing certain specific flame-proofing and softening agents.

The present application is a continuation in part of my copending application, Serial No. 132,617, filed March 23, 1937.

It is an object of this invention to provide non-fibrous, cellulosic structures, such as thread, filaments, films, fabrics, caps and bands, and sponges containing highly desirable flame-proofing and softening agents.

It is another object of this invention to provide a method for the production of highly desirable flame-proof and softened non-fibrous, cellulosic structures.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by incorporating on or in non-fibrous, cellulosic structures, or adding to the materials from which said structures are made, sulfamic acid or certain of its salts, as will be described in greater detail hereinbelow.

A generally satisfactory method of carrying out the invention comprises the wetting or impregnating of the non-fibrous, cellulosic structure to be treated with an aqueous solution or dispersion of the sulfamic acid or salt thereof, of suitable strength, and drying the same. Non-fibrous, cellulosic structures thus impregnated or covered show a decreased tendency to ignite and burn, and/or a decreased rate of burning. Many of such structures will not propagate a flame under conditions whereby untreated structures are readily destroyed by fire. The flame-proofing agents of the present invention have furthermore been found to be valuable softening agents for non-fibrous, cellulosic structures and may be used in part or in whole as a substitute for previously known softening agents such as, for example, glycerol, ethylene glycol, foramide, carbamide and the like.

The following examples illustrate methods for practicing the invention, it being understood that the invention is not to be limited by the details set forth therein.

Example I

A medium weight crepe fabric made from viscose rayon yarn was immersed in an aqueous solution containing 10% by weight of the ammonium salt of sulfamic acid. The cloth was next passed through tightly fitted rubber rollers

to remove excess solution and was then dried. The dry, treated fabric retained about 12% by weight of ammonium sulfamate based on the original weight of the fabric. When the treated crepe fabric was brought into contact with a flame, it did not ignite and it showed no tendency to propagate a flame. An untreated sample readily burned when ignited.

When samples of the same cloth were similarly impregnated with salts of sulfamic acid other than the ammonium salt, for example, the trimethylamine, pyridine, zinc, aluminum and ethylenediamine (disulfamate) salts, the treated samples likewise showed a lower rate of combustion. Such treated samples contained from 11 to 13% of the sulfamate. The ammonium sulfamate and ethylenediamine disulfamate were more effective as fire-retardants than the trimethylamine salt and the pyridine salt, and, of the metal salts, the aluminum, sodium and calcium salts were more effective than the zinc salt.

Example II

A sheet of gel regenerated cellulose was passed through a 6% aqueous solution of ammonium sulfamate, the excess solution removed by rolls, and the sheet then dried on a series of drying rolls. (The expression "sheet of gel regenerated cellulose", or "regenerated cellulose sheeting in gel form", here has reference to a sheet of cellulose which has been regenerated in the manner well known in the art from a solution of cellulose xanthate (viscose), washed and purified, but not dried. Regenerated cellulose sheeting in gel form may likewise be obtained from solutions of other suitable cellulose derivatives, e. g., cuprammonium solutions.) The dried cellulose sheet thus prepared contained about 15% by weight of ammonium sulfamate. The sheet was soft, flexible, clear and transparent and showed no crystallization of ammonium sulfamate even under conditions of low temperature and/or low humidity. When brought into contact with a flame, the sheet showed excellent flame-proof properties. Under no conditions could the sheet, or a bundle of thin strips cut from such sheets, be made to propagate a flame. The sheet was charred only at the point of contact with the flame showing little or no afterflow when the flame was removed.

Similar sheets prepared as described above but with addition of glycerol to the ammonium sulfamate bath, so that the final product contained about 5% glycerol and 18% by weight ammonium sulfamate, were equally flame-resistant.

Sheets of gel regenerated cellulose which had

been treated with 5% aqueous solutions of ordinary fire-retardants such as ammonium phosphate and ammonium sulfate and dried showed undesirable crystallization of such salts in the film so that the sheet became opaque and had a very rough crystalline surface. Also, these sheets were considerably more brittle than untreated sheets or sheets containing ammonium sulfamate.

Example III

Regenerated cellulose sheeting in the gel form was immersed in a 10% solution of ethylenediamine disulfamate for one minute, removed, and dried on a frame for 10 minutes at 100° C. After cooling, the cellulose sheet was soft, flexible, clear and transparent and showed excellent fire-retardant properties.

Regenerated cellulose similarly impregnated with other salts of sulfamic acid such as the pyridine, trimethylamine, zinc, aluminum, sodium and calcium salts, showed either a low tendency to burn or a retarded rate of burning, compared with plain untreated regenerated cellulose sheet. Such products showed either no crystallization or only slight crystallization of sulfamate within the transparent film under ordinary atmospheric conditions. Regenerated cellulose was similarly impregnated with unneutralized sulfamic acid and the product likewise showed definite fire-retardant properties compared to the untreated product.

As has been stated above, sulfamates have a softening as well as a fire-retarding action on regenerated cellulose, as is illustrated by the results given in the following table:

Agent	Elongation at break	Tensile strength at break
	Percent	Lbs./sq. in.
None	11-13	17,400
Calcium sulfamate	15	14,000
Sodium sulfamate	17	13,000
Ammonium sulfamate	16	10,000

The samples used in the above tests (except the control) were prepared by immersing the regenerated cellulose sheeting in 4% aqueous solutions of the sulfamates for one minute, removing and drying them at 100° C. for 13 minutes and conditioning them at 25° C. and 50% relative humidity for 24 hours. The measurements were made on the standard Scott machine. The control was identical in source and preparation with the other samples except that it contained no sulfamate. The higher elongation and lower tensile strength at break in the case of the samples containing sulfamates indicates the latter exert a plasticizing action. Similar effects in the case of paper and textiles can be recognized by one skilled in the art.

Example IV

A velvet fabric of woven silk with a rayon (regenerated cellulose) pile was brought into contact with an 8% aqueous solution of ammonium sulfamate in such manner that only the back-side of the fabric was moistened while the rayon pile surface was not wetted. After drying, the weight of the treated fabric had increased about 15% of its original weight owing to the ammonium sulfamate which had been absorbed. The dry fabric showed no visible crystallization of ammonium sulfamate and showed no tendency to dust or creak (a common result

with ordinary fire-retardants on pile fabrics). Moreover, the fabric showed no increased harshness in handle or feel while the luster, gloss, and general appearance was improved by the above treatment. When brought into contact with a flame, the treated velvet fabric was difficult to ignite and would not propagate a flame, while the untreated fabric was easily ignited and burned rapidly.

Example V

Regenerated cellulose sheeting in the gel form was immersed in a 15% solution of monoethanolamine sulfamate for one minute, removed, and dried on a frame for 10 minutes at 100° C. After cooling, the cellulose sheet was very soft, flexible, clear and transparent, and showed very good fire-retardant properties.

Of the various salts of sulfamic acid, I have found the ammonium salt to be most effective as a fire-retardant. Of the salts of organic bases, such as amines, only those in which the ratio of carbon atoms to nitrogen atoms is less than about 3:1 are effective, this probably being due to excessive heat of combustion derived from the burning of large organic carbon residues, which tends to nullify the effect of the protective incombustible gases (ammonia and/or nitrogen) which are apparently formed. However, regardless of the accuracy of this theory, the above generalization is indicated as approximately correct from tests with a variety of sulfamates. Thus, ammonium sulfamate, which has no carbon and two nitrogens, is most effective. Mono-methylamine sulfamate and ethylenediamine disulfamate, which have a carbon-nitrogen ratio of 1:2, are excellent fire-retardants though not quite so effective as ammonium sulfamate. Trimethylamine sulfamate having a carbon-nitrogen ratio of 3:2 is only moderately effective as are the dimethylamine, the monoethanolamine, and ethylamine sulfamates, whose ratio is 1:1. Pyridine sulfamate, wherein the carbon-nitrogen ratio is 5:2, is a relatively poor fire-retardant and aniline sulfamate, of ratio 3:1 while effective to some extent, especially in higher concentration, is less effective than would ordinarily be desired for commercial use. The above statements are made of course on the basis of comparable quantities of sulfamate and it should be made clear that in the majority of cases excellent results may be obtained with the lesser effective sulfamates if they are employed in sufficiently large amounts.

In the case of salts from sulfamic acid and inorganic bases (i. e., metallic salts), only those having a metallic content of less than about 52% by weight of the anhydrous salt have any detectable effect. This may be due to the relatively lower amount of non-combustible gases capable of liberation by the very heavy metal sulfamate molecule, but, regardless of the explanation, the generalization appears, on the basis of tests I have carried out with several metallic sulfamates, to be a correct approximation. Thus aluminum sulfamate of 8.6% metallic content, is a very good fire-retardant whereas anhydrous zinc sulfamate of metallic content 25.4% is only moderately effective on an equal weight basis though in large amounts it approaches the aluminum salt in effectiveness. At the lower end of the scale, lead sulfamate of metallic content 51.9% has only a slight fire-retarding action. The sodium, potassium, calcium, magnesium, cobalt, nickel, manganese, and calcium salts all impart flame-resis-

tance to a degree proportionate to the non-metallic content of the sulfamate. All these tests bear out the conclusion that the metallic content of the sulfamate should be less than 52% if the sulfamate is to have any detectable effect and less than about 26% if it is to have any very important effect. Conversely, the nonmetallic content (including sulfur) should be at least 48% and preferably at least 74%.

Many of the sulfamic acid salts, such as zinc sulfamate, readily absorb water of crystallization. The hydrated salts may be used if desired in the present invention.

Sulfamic acid itself may also be used as a fire-retardant and its effectiveness is only slightly less than the ammonium salt. However, the use of sulfamic acid in many instances is not desirable because of its acidity and the corresponding deterioration effects which may result from such acidity. The salts of sulfamic acid are practically neutral and therefore more practical when an acid reaction is not desirable.

Salts of sulfamic acids in which a hydrogen atom of the NH_2 group is replaced by a hydrocarbon radical, such as ammonium salts of N-methyl and N-isobutyl sulfamic acids, are effective as fire-retardants, as are salts of iminodisulfamic acid such as diammoniumiminodisulfonate ($\text{NH}_4\text{SO}_3\text{NHSO}_3\text{NH}_4$).

The compounds with which the present invention is concerned are all included by the comprehensive formula $(\text{R}'-\text{NH}-\text{SO}_3)_x\text{R}$ in which R' is preferably hydrogen but may be a hydrocarbon radical or the radical NH_4SO_3- , and R is a cation of valence x , which compound has less than three carbon atoms for each nitrogen atom and a non-metallic content of at least 48%.

In the practice of the present invention, the sulfamic acid or salt thereof may be employed in conjunction with ordinary fire-retardants such as ammonium phosphates, ammonium sulfate, boric acid, borax, ammonium carbonate, and ammonium halides with results and advantages proportionate to the relative amount of sulfamic acid or sulfamate employed.

The concentration of impregnated fire-retardant which is necessary will vary with the effectiveness of the retardant, the degree of fire-retardance desired, and the relative combustibility of the non-fibrous cellulosic material to which applied. In general, materials such as regenerated cellulose or lowly etherified or lowly esterified cellulose derivatives, require from 15 to 20% of their weight of ammonium sulfamate, or its equivalent, to give products which will not propagate a flame and which ignite with difficulty at the point of contact with the igniting flame. Lower amounts of ammonium sulfamate give less effective protection but in every case show a decreased rate of burning compared to untreated materials. Lead sulfamate is only slightly effective as a fire-retardant for regenerated cellulose film. On the other hand, the zinc salt is definitely effective with all these types of materials, and the aluminum salt is highly effective with all of them.

In the examples, the sulfamate is applied from aqueous solution. Fire-retarding effects may also be obtained when the sulfamate is applied by any method. For example, powdered crystals may be dusted upon a damp surface or surface treated with adhesive; the sulfamate may be applied from solution or suspension in an organic liquid; or in the case of a liquid the sulfamate may be incorporated by mixing or milling.

The sulfamates of the amines may be prepared by the reaction of sulfamic acid with the amine preferably in aqueous solution. Metallic salts may be prepared by the methods known in the art, e. g., reaction of a freshly precipitated, washed, hydroxide or carbonate of the metal with an aqueous solution of sulfamic acid.

An outstanding advantage of ammonium sulfamate and related salts over the more commonly used prior art flame-proofing agents for textile fabrics is the fact that they do not cause the harshness which normally characterizes fabrics treated with the prior art fire-retardant or flame-proofing materials and in many instances they have a softening effect of their own. As flame-proofing agents for regenerated cellulose film, ammonium sulfamate, monoethanolamine sulfamate and related salts have an advantage over prior art materials in that, even when present in the film in amounts up to about 23%, they do not crystallize out on the surface of the film under ordinary atmospheric conditions (24°C . and 35% relative humidity) as is characteristic of prior art flame-proofing materials. Under favorable conditions, the amount may be as high as 30% without crystallizing out. Furthermore, ammonium sulfamates not only render cellulose and its manufactures (film, thread, fabrics, caps, bands, sponges, etc.) flame-proof, but also impart to these materials a certain degree of softness. Hence the sulfamates may also be used, either alone or in conjunction with glycerol or other common softeners, as combined softening and flame-proofing agents. In the case of rayon, the sulfamate may be included in the viscose spinning bath, or it may be applied to the rayon thread or fabric. In the case of cellulose film, the sulfamate may be added with good results to the viscose, to the undried sheet, or to the dried sheet before or after application of moisture-proofing lacquers, such as those of Charch and Prindle (U. S. Patents Nos. 1,737,187 and 1,826,696). The fact that the moistureproofing lacquer may contain highly inflammable substances does not seem to make any appreciable difference. The cellulose thread, fabric, or film which has been impregnated with the sulfamate may be stored for prolonged periods without deterioration by the sulfamates inasmuch as the latter are substantially neutral.

Sulfamic acid and its salts may also be employed as fire-retardants for other non-fibrous cellulosic materials, than regenerated cellulose, for example, cellulose esters such as the nitrate, acetate, propionate, butyrate, and phthalate and cellulose ethers such as methyl-, ethyl-, benzyl-, crotyl-, hydroxyethyl- and carboxymethylcelluloses. These cellulose derivatives may be undegraded or highly degraded, of any degree of substitution, and of any degree of water-sensitivity. A particular illustration of the flame-proofing of a cellulose derivative is the inclusion of ammonium sulfamate in cellulose nitrate compositions containing pigments and softeners which are to be applied to fabrics; alternatively the sulfamate may be applied to the already coated fabric.

Fabrics that have been treated with sulfamic acid and those of its salts with which this invention is concerned, and thus rendered fire resistant, may be subsequently rubberized and the rubber coating vulcanized under the usual conditions (about 2 to 3 hours at about 120°C .) without appreciable tendering of the fabric.

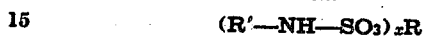
Sulfamic acid and those of its salts specified

herein are effective as fire-retardants, so far as is known, for any non-fibrous cellulosic structure. Cellulosic materials, with which the advantages of this invention are most apparent, have been discussed in detail.

The above description and examples are intended to be illustrative only, any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. A non-fibrous, cellulosic structure containing, as a flame-proofing and softening agent, a compound of the formula



wherein R' is hydrogen, a hydrocarbon radical or NH_4SO_3 , R is a cation of valence x, said compound having less than three carbon atoms for each nitrogen atom and having a non-metallic content of at least 48%.

2. A non-fibrous, cellulosic structure containing, as a flame-proofing and softening agent, a compound of the formula

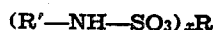


R being a cation of valence x, which compound has a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

3. A non-fibrous, cellulosic structure containing, as a flame-proofing and softening agent, a salt of sulfamic acid having a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

4. A non-fibrous, cellulosic structure containing, as a flame-proofing and softening agent, a salt of sulfamic acid having a non-metallic content of at least 74% and less than three carbon atoms for each nitrogen atom.

5. A regenerated cellulose structure containing, as a flame-proofing and softening agent, a compound of the formula



wherein R' is hydrogen, a hydrocarbon radical or NH_4SO_3 , R is a cation of valence x, said compound having less than three carbon atoms for each nitrogen atom and having a non-metallic content of at least 48%.

6. A regenerated cellulose structure containing, as a flame-proofing and softening agent, a compound of the formula



R being a cation of valence x, which compound has a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

7. A regenerated cellulose structure containing,

as a flame-proofing and softening agent, a salt of sulfamic acid having a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

8. A regenerated cellulose structure containing, as a flame-proofing and softening agent, a salt of sulfamic acid having a non-metallic content of at least 75% and less than three carbon atoms for each nitrogen atom.

9. In the production of non-fibrous cellulosic structures, the step which comprises adding thereto, as a flame-proofing and softening agent, a compound of the formula



wherein R' is hydrogen, a hydrocarbon radical or NH_4SO_3 , R is a cation of valence x, said compound having less than three carbon atoms for each nitrogen atom and having a nonmetallic content of at least 48%.

10. In the production of regenerated cellulosic structures, the step which comprises treating the structures with a flame-proofing and softening agent comprising a compound of the formula



where R' is hydrogen, a hydrocarbon radical or NH_4SO_3 , R is a cation of valence x, said compound having less than three carbon atoms for each nitrogen atom and having a non-metallic content of at least 48%.

11. In the production of regenerated cellulosic structures, the step which comprises treating the structures with a flame-proofing and softening agent comprising a compound of the formula



R being a cation of valence x, which compound has a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

12. In the production of regenerated cellulosic structures, the step which comprises treating the structures with a flame-proofing and softening agent comprising a salt of sulfamic acid having a non-metallic content of at least 48% and less than three carbon atoms for each nitrogen atom.

13. In the production of regenerated cellulosic structures, the step which comprises impregnating the structures while in the gel state with a flame-proofing and softening agent comprising a compound of the formula



wherein R' is hydrogen, a hydrocarbon radical or NH_4SO_3 , R is a cation of valence x, said compound having less than three carbon atoms for each nitrogen atom and having a non-metallic content of at least 48%.

MARTIN ELI CUPERY.