

Nov. 20, 1956

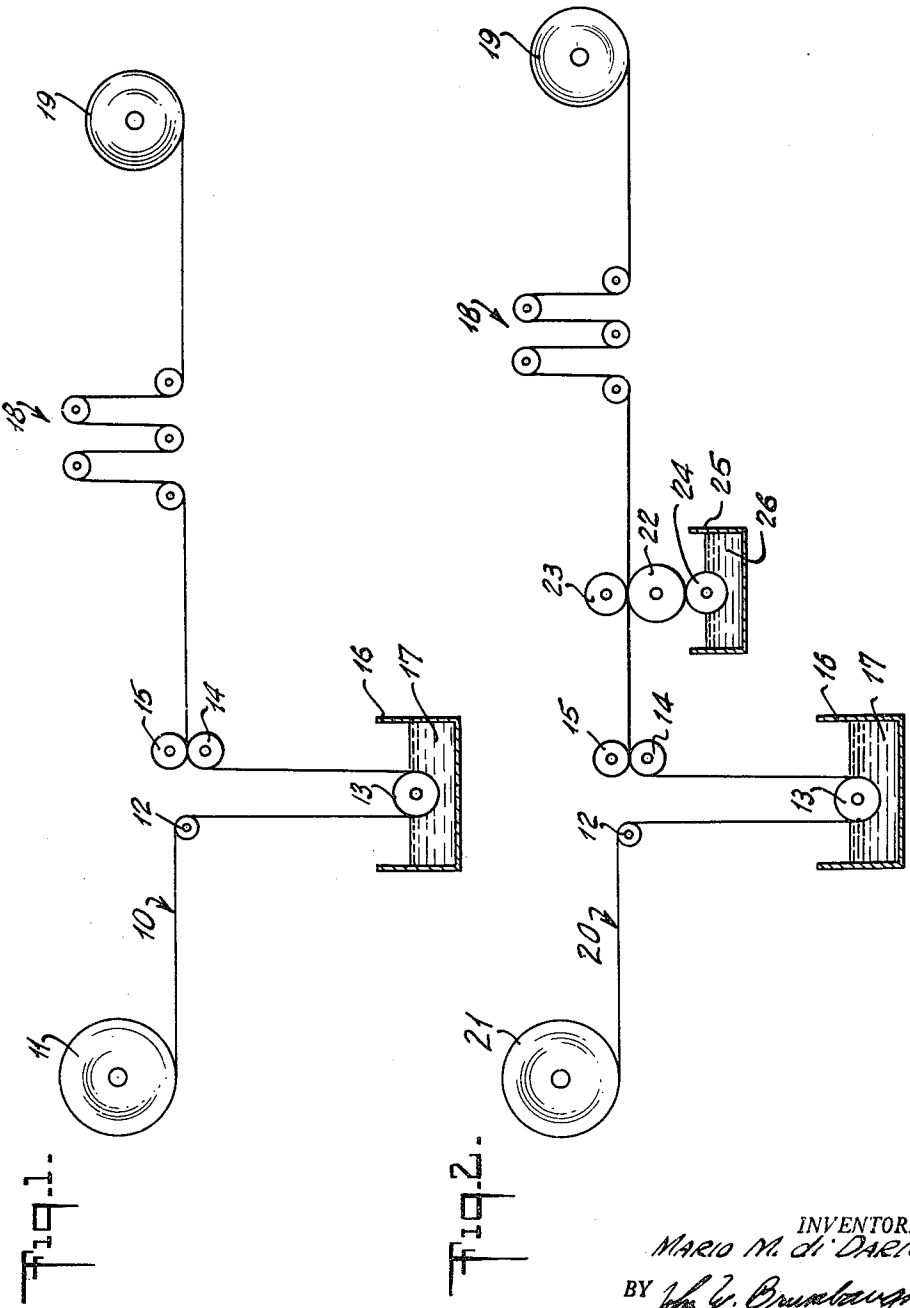
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2,771,379

STABILIZED-FLAMEPROOFED FABRIC AND METHOD

Filed Dec. 30, 1952

3 Sheets-Sheet 1



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STABILIZED-FLAMEPROOFED FABRIC AND METHOD

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Fig. 3.

CONTROL

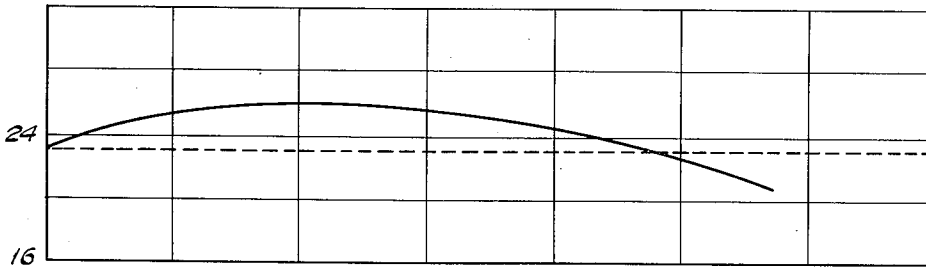


Fig. 4.

TEST I

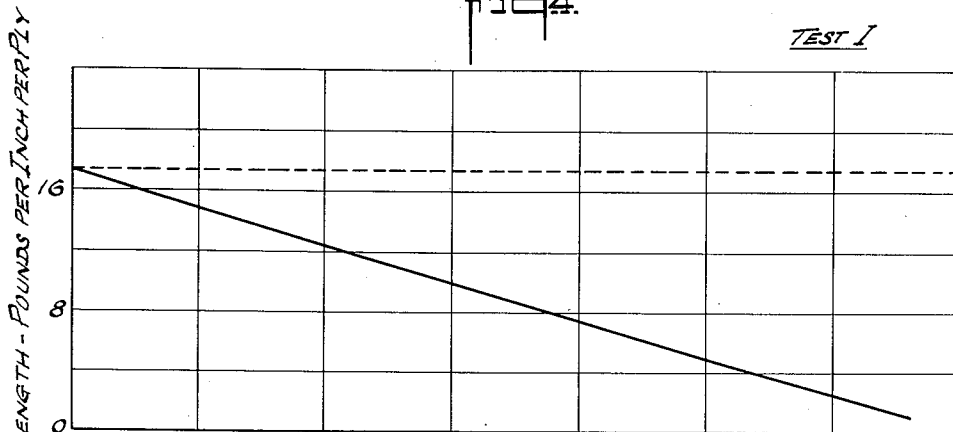
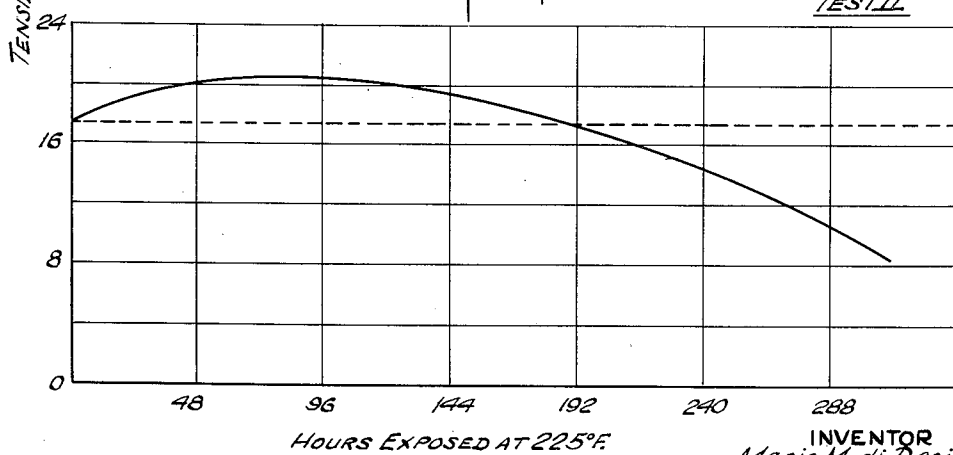


Fig. 5.

TEST II



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Fig. 6.

TEST III

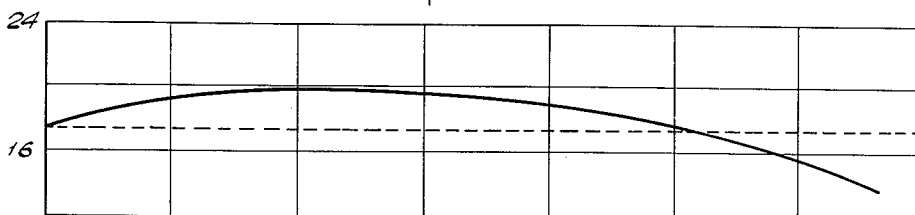


Fig. 7.

TEST IV

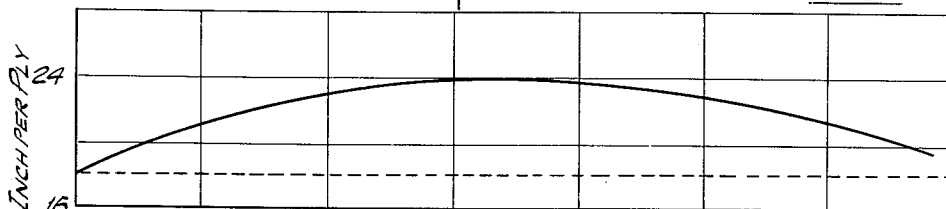
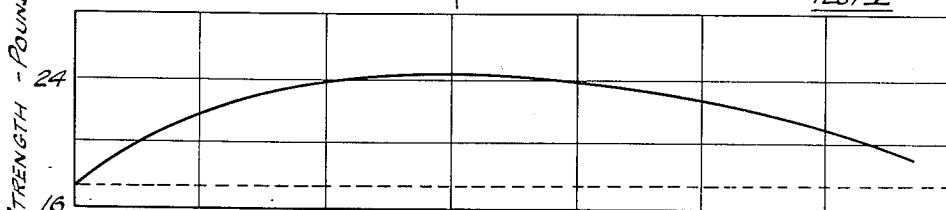


Fig. 8.

TEST V



TEST VI

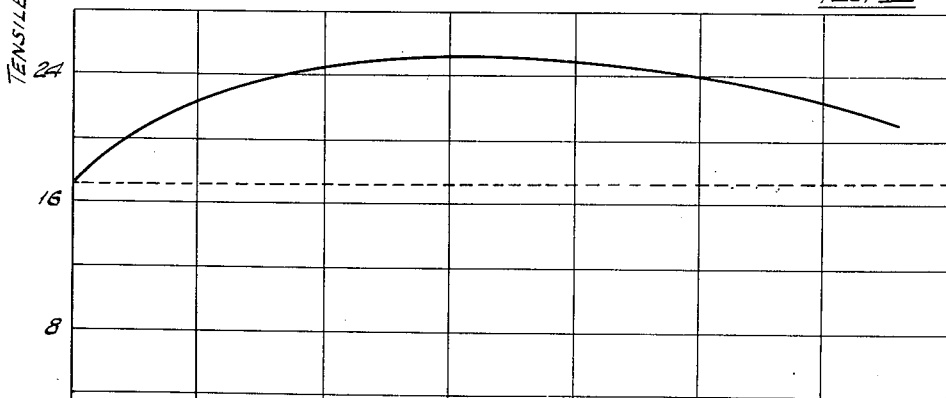


Fig. 9.

HOURS EXPOSED AT 225°F

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## STABILIZED-FLAMEPROOFED FABRIC AND METHOD

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Application December 30, 1952, Serial No. 328,554

10 Claims. (Cl. 117—76)

This invention relates to the flameproofing of fabrics, and more particularly to the agents incorporated in the fabrics to modify and remove deleterious side effects produced by flameproofing agents which are nonpermanent, i. e., water soluble.

The flameproofing of combustible fabrics, such as cotton or rayon draperies, has become necessary to avoid what otherwise would be a dangerous fire hazard. In fact, many states now require the flameproofing of all draperies that are hung in public places. Nonwoven fabrics produced, for example, by intermittent adhesive bonding of a number of superimposed card webs, in accordance with Goldman Patent 2,039,312, have recently assumed a prominent place as drapery materials. These nonwoven draperies are finding widespread use in public places such as hotels and restaurants, for their initial cost is low and they can be replaced when needed rather than being dry cleaned.

Among the many chemical compounds that have been proposed as flameproofing agents, ammonium sulfamate is well-known and extensively used, but it possesses several quite serious disadvantages. In the first place, it decomposes during aging and exposure to heat and light to release ammonia and sulfamic acid. The sulfamic acid formed as a result of this decomposition produces a serious reduction in the tensile strength of the fabric due to its tendering action on cellulosic fibers, and for dyed fabrics a very noticeable bleaching, yellowing or change in color also results. Further, when iron or metal drapery supports are employed, this decomposition causes undesirable corrosion of the metal support.

One advantage obtained by the present invention is the elimination or minimizing of these disadvantages which are inherent in the use of ammonium sulfamate as a fabric flameproof.

According to the present invention, dicyandiamide is incorporated in fabrics containing ammonium sulfamate to modify and minimize the undesirable side effects produced by the decomposition of the ammonium sulfamate. The dicyandiamide stabilizes the ammonium sulfamate against this decomposition and enables the fabric thus treated to possess flameproof properties without a concomitant sacrifice in the other fabric properties of tensile strength and appearance.

The amount of dicyandiamide is controlled in proportion to the amount of ammonium sulfamate flameproofing present to give the stabilizing effect desired or required. Substantial stabilizing effect may be noted when the stabilizer is present in ratios as low as about 5 parts by weight dicyandiamide to 100 parts ammonium sulfamate. Amounts larger than this produce increased stability up to about 20 parts dicyandiamide per 100 parts ammonium sulfamate. Above the ratio of about 20, the rate of improvement with increase in stabilizer decreases somewhat. It is noted further than since dicyandiamide per se is not a potent flameproof, replacement of the ammonium sulfamate by the dicyandiamide will eventually

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decrease flameproofing properties. As the dicyandiamide ratio is increased to about 30 to 35% based on ammonium sulfamate, however, light stability and anti-rusting properties increase. Accordingly, the optimum range of ratio of stabilizer to flameproofing is approximately 20 to 35 parts stabilizer per 100 parts flameproofing. Above a ratio of about 50, no substantial increase in stability is noted, and in view of desired flame resistance, compositions having an ingredient ratio above this level are generally not used.

The amount of ammonium sulfamate necessary to produce flame-resistant properties in a fabric may be as low as about 7% based on the weight of the bonded dry fabric, that is, 50 grains per square yard for a 750 grain (including bonding agent) fabric, preferably at least 10%, or 75 grains per square yard. Excessive amounts of solid impregnants tend to produce stiffness in the fabric. The maximum amount of ammonium sulfamate will be determined by the desired flexibility and hand of the fabric as well as by economy. Preferably, the ammonium sulfamate content will be not more than about 15%, and the total amount of both stabilizer and flameproofing will be not greater than about 20%, that is, 150 grains per square yard for a 750 grain fabric. Generally, to avoid undue fabric stiffness, total content of flameproofing and stabilizer is not greater than about 30% based on the weight of dry fabric.

Treated fabric is prepared by forming an aqueous solution of the stabilizer and flameproofing in the desired ratio and suitable concentration, impregnating the fabric with this solution, and then drying the fabric. The drying temperature selected will be a balance between the drying time available (limiting the minimum temperature) and the temperature at which degradation of the fabric occurs (limiting the maximum temperature); that is, drying may be carried out at room temperature if sufficient time is available. However, temperatures just above the boiling point of water afford a reasonably rapid rate of drying and relatively convenient operation. Higher temperatures may be used in special circumstances. However, at about 300° F. and above, fiber degradation, evidenced by loss in tensile strength, may be found to occur. Further, the stabilizing effect of dicyandiamide on ammonium sulfamate is considered to be a function of the individual compounds in the unreacted state, and hence temperature is maintained below levels at which any chemical reaction between the stabilizer, flameproofing, or cellulose of the fibers is likely to occur. Accordingly, drying temperatures are preferably maintained below 300° F. Details of the operation may be conveniently understood by reference to the attached drawings.

Fig. 1 is a diagrammatic flow sheet of one embodiment of the process provided by the present invention.

Fig. 2 is another diagrammatic flow sheet of a different embodiment of the present invention.

Fig. 3 through Fig. 9 are graphs showing the effect of aging time upon the tensile strength of fabrics treated with various amounts of dicyandiamide and ammonium sulfamate and then subjected to elevated temperatures.

Referring now to Fig. 1, a non woven fabric 10, which may be prepared in any of the known manners, as for example in accordance with Goldman Patent 2,039,312, is drawn from supply roll 11 and passed through a path defined by guide roll 12, dip roll 13, and squeeze rolls 14 and 15. Dip roll 13 is immersed in tank 16 in which an aqueous flameproofing solution 17 is provided. Solution 17 is picked up by fabric 10 as it passes around dip roll 13, and then excess solution is removed by squeeze rolls 14 and 15 to give the desired amount of liquid on the fabric as will be more fully described hereinafter.

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The wet impregnated nonwoven fabric is passed over a plurality of drying cans generally designated as 18 and then collected on a takeup roll 19.

Fig. 2 depicts an embodiment wherein a layer of card webs 20 is drawn from supply roll 21 and then passed through a path, identical to that of the embodiment described above, which comprises guide roll 12, dip roll 13 and squeeze rolls 14 and 15. Dip roll 13 is immersed in tank 16, in which flameproofing solution 17 is provided.

The wet impregnated layer of card webs is then passed between applicator roll 22 and back-up roll 23. Applicator roll 22 is contacted by kiss roll 24, partially submerged in tank 25 which contains bonding liquid 26. As the fabric passes between rolls 22 and 23 binder is applied to the webs as described in the aforesaid Goldman patent.

The web is then passed over dry can 18, whereupon excess moisture is expelled and the nonwoven fabric is formed, and then collected on windup roll 19.

It will be noted that in the first of the above embodiments the nonwoven fabric is first formed and then flameproofing solution is applied. In the second embodiment, the flameproofing solution is applied first and then the binder is added to give the nonwoven fabric.

Other variations in procedure in carrying out the invention, particularly in the sequence of the operating steps described, may now suggest themselves. In each case, however, any dye applied is introduced prior to the ammonium sulfamate and dicyandiamide (due to their water solubility).

Dicyandiamide exerts stabilizing properties toward ammonium sulfamate regardless of the nature of the fabric, be it woven or nonwoven. However, from the standpoint of maintaining the softness and hand in nonwoven fabrics and compatibility with the binders necessarily used in nonwoven fabrics as compared with woven fabrics, the invention finds particularly advantageous use in connection with nonwoven fabrics, and hence the latter is a preferred embodiment.

Following are examples illustrating the invention in nonwoven fabric preparation. These examples are to be considered as illustrative of the invention and not to be construed in a limiting sense.

## EXAMPLE 1

Samples of a nonwoven fabric carded web of 100% bright viscose fibers intermittently bonded with polyvinyl acetate binder and having a weight of 750 grains per square yard (including 75 grains per square yard of

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Table 1

| Test No.     | Percent Ammonium Sulfamate | Percent Dicyandiamide | Parts Dicyandiamide Per 100 Parts Ammonium Sulfamate |
|--------------|----------------------------|-----------------------|------------------------------------------------------|
| I.....       | 14.                        | 0                     | 0:100                                                |
| II.....      | 13.8                       | 1.4                   | 10:100                                               |
| III.....     | 13.7                       | 2.7                   | 20:100                                               |
| IV.....      | 13.5                       | 4.1                   | 30:100                                               |
| V.....       | 13.3                       | 5.4                   | 40:100                                               |
| VI.....      | 13.1                       | 6.5                   | 50:100                                               |
| Control..... | 0                          | 0                     |                                                      |

Each of the solutions also contained a small amount of a nonionic wetting agent. Test samples of drapery fabric stock in white, green and rose colors were treated with each of the above solutions by immersing the respective fabric samples in the solutions, wringing out between pressure rollers, air drying, and ironing for a few seconds at about 225° F. The pressure on the rolls was controlled so that the total pickup of ammonium sulfamate and dicyandiamide by each test sample from the solution approximated 100 grains per square yard, or approximately 13% based on dry fabric weight. The percentages of ammonium sulfamate and dicyandiamide, based on the weight of the dry fabric, were as follows:

Table 2

| Test     | Weight, Grains Per Square Yard |               | Percentage on Dry Fabric |               |
|----------|--------------------------------|---------------|--------------------------|---------------|
|          | Ammonium Sulfamate             | Dicyandiamide | Ammonium Sulfamate       | Dicyandiamide |
| I.....   | 100                            | 0             | 13.3                     | 0             |
| II.....  | 91                             | 9             | 12.1                     | 1.2           |
| III..... | 83.5                           | 16.5          | 11.1                     | 2.2           |
| IV.....  | 77                             | 23            | 10.3                     | 3.1           |
| V.....   | 71                             | 29            | 9.5                      | 3.9           |
| VI.....  | 67                             | 33            | 8.9                      | 4.4           |

One-inch width samples were cut in the longitudinal fiber direction and placed in a circulating hot air oven held at 225° F. Samples were withdrawn periodically for tensile strength and color fastness measurements. Tensile strengths, representing the average strength of 9 samples, were determined and are listed in Table 3. Control samples are those of same base composition which was not flameproofed.

Table 3

| Group        | Color      | Average Char Length, Inches | Tensile Strength—Pounds per Inch (1 ply)—Hours at 225° F. |      |      |       |      |      |      |      | Long Tensile Deviation |
|--------------|------------|-----------------------------|-----------------------------------------------------------|------|------|-------|------|------|------|------|------------------------|
|              |            |                             | 0                                                         | 24   | 48   | 96    | 144  | 192  | 264  | 312  |                        |
| I.....       | White..... | 2.83                        | 16.9                                                      | 13.8 | 13.1 | 12.1  | 10.9 | 8.03 | 5.7  | 2.1  | 87.5% loss.            |
|              | Green..... | 3.2                         | 16.6                                                      | 11.3 | 11.5 | 10.45 | 7.67 | 4.52 | 1.75 | 2.58 | 84.5% loss.            |
|              | Rose.....  | 3.3                         | 16.8                                                      | 13.8 | 13.1 | 12.1  | 10.9 | 8.03 | 5.7  | 2.12 | 84.0% loss.            |
| II.....      | White..... | 3.58                        | 16.4                                                      | 12.0 | 19.8 | 17.8  | 18.4 | 17.7 | 15.3 | 8.45 | 47.5% loss.            |
|              | Green..... | 3.58                        | 18.0                                                      | 16.6 | 17.9 | 13.7  | 19.9 | 17.4 | 15.5 | 8.5  | 51.2% loss.            |
|              | Rose.....  | 3.75                        | 15.3                                                      | 17.8 | 16.4 | 17.8  | 17.3 | 15.9 | 13.9 | 9.2  | 39.8% loss.            |
| III.....     | White..... | 3.58                        | 16.8                                                      | 20.8 | 20.4 | 19.6  | 22.3 | 20.6 | 19.2 | 11.8 | 29.8% loss.            |
|              | Green..... | 3.75                        | 18.0                                                      | 18.9 | 18.2 | 18.8  | 18.7 | 17.8 | 19.4 | 13.8 | 23.4% loss.            |
|              | Rose.....  | 3.5                         | 16.6                                                      | 16.7 | 19.2 | 18.7  | 19.1 | 19.3 | 15.6 | 12.9 | 22.3% loss.            |
| IV.....      | White..... | 3.58                        | 18.0                                                      | 24.2 | 22.4 | 23.4  | 24.0 | 23.2 | 21.5 | 21.6 | 20.0% gain.            |
|              | Green..... | 4.33                        | 17.4                                                      | 19.6 | 20.4 | 23.9  | 21.7 | 22.7 | 21.3 | 19.4 | 11.5% gain.            |
|              | Rose.....  | 3.75                        | 16.7                                                      | 21.8 | 19.7 | 23.7  | 22.0 | 22.2 | 19.7 | 19.0 | 13.8% gain.            |
| V.....       | White..... | 4.25                        | 17.8                                                      | 23.9 | 25.9 | 23.8  | 22.6 | 24.1 | 21.2 | 18.9 | 6.2% gain.             |
|              | Green..... | 3.75                        | 19.4                                                      | 20.7 | 21.8 | 25.2  | 27.0 | 25.5 | 23.6 | 22.6 | 17.7% gain.            |
|              | Rose.....  | 5.50                        | 17.4                                                      | 19.0 | 21.5 | 22.8  | 20.4 | 23.4 | 21.2 | 21.1 | 21.3% gain.            |
| VI.....      | White..... | 5.2                         | 17.3                                                      | 23.4 | 22.1 | 23.7  | 25.2 | 25.2 | 22.5 | 20.7 | 19.6% gain.            |
|              | Green..... | 5.25                        | 17.8                                                      | 20.7 | 20.0 | 24.8  | 23.3 | 25.2 | 22.2 | 21.9 | 23.0% gain.            |
|              | Rose.....  | 5.08                        | 17.2                                                      | 19.0 | 21.5 | 22.8  | 20.4 | 23.4 | 21.2 | 20.9 | 21.5% gain.            |
| Control..... | White..... |                             | 23.0                                                      | 23.6 | 24.1 | 23.8  | 24.1 | 24.8 | 23.9 | 21.4 | 6.95% loss.            |
|              | Green..... |                             | 23.4                                                      | 22.6 | 24.2 | 26.5  | 26.5 | 25.0 | 21.9 | 21.1 | 9.35% loss.            |
|              | Rose.....  |                             | 23.6                                                      | 19.7 | 24.6 | 25.2  | 26.9 | 27.5 | 25.0 | 23.3 | 1.27% loss.            |

binder) were treated with aqueous solutions of ammonium sulfamate-dicyandiamide as follows:

The Table 3 tensile strength data are plotted graphically in the attached drawings, each of the graphs being

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designated by a corresponding test number which it represents. The dashed lines show the initial fabric strength. The fire retardant properties of the samples were also measured in accordance with standard procedure outlined by A. S. T. M. The average char lengths are listed in the third column of Table 3. The color fastness properties of the several samples of white (undyed) fabric treated and tested as above are indicated by the data in Table 4.

Table 4

| Test No.     | 5 Hours   | 20 Hours                | 48 Hours     | 192 Hours   |
|--------------|-----------|-------------------------|--------------|-------------|
| I.....       | Brownish  | Brown                   | Brown        | Dark brown. |
| II.....      | Unchanged | Binderyellow            | Brownish     | Brownish.   |
| III.....     | do        | do                      | do           | Do.         |
| IV.....      | do        | do                      | Binderyellow | Do.         |
| V.....       | do        | do                      | do           | Do.         |
| VI.....      | do        | Binder slightly yellow. | do           | Do.         |
| Control..... | do        | Unchanged               | Unchanged    | Unchanged.  |

Portions of test samples described in Table 1 were wrapped around individual iron rods and enclosed with polyethylene film. The polyethylene wrap was used in order to exclude atmospheric moisture. The iron rods were inspected after aging at room temperature for 7, 15, 22, and 29 days with the following observations:

Table 5

| Sample       | 7 Days             | 15 Days            | 22 Days         | 29 Days         |
|--------------|--------------------|--------------------|-----------------|-----------------|
| I.....       | Badly corroded.    | Badly corroded.    | Badly corroded. | Badly corroded. |
| III.....     | Slightly corroded. | Slightly corroded. | Corroded        | Corroded.       |
| IV.....      | No corrosion       | No corrosion       | No corrosion    | No corrosion.   |
| V.....       | do                 | do                 | do              | Do.             |
| Control..... | do                 | do                 | do              | Do.             |

## EXAMPLE 2

A nonwoven carded fabric web of 100% bright viscose fibers intermittently bonded with plasticized polyvinyl acetate binder, composed of 675 grains per square yard of fibers and 75 grains per square yard of binder, and dyed chartreuse, was impregnated with the following aqueous solutions:

Ammonium sulfamate—13.5%

Dicyandiamide—3.5%

Wetting agent—0.4%

Ammonia (NH<sub>3</sub>)—trace

Ratio of dicyandiamide-ammonium sulfamate—0.26

The fabric after impregnation was wrung out between pressure rollers and dried by passing it over drying cans heated with steam at 15 p. s. i. gauge pressure for one-quarter to one-half minute. All the ammonia picked up from the solution was evaporated. The dried fabric contained about 100 grains per square yard of ammonium sulfamate and dicyandiamide picked up from the solution. The fabric passed the 40-hour "Fadometer" light-fastness test. The heat-resistant properties were considerably superior to those obtained when the same fabric was treated with ammonium sulfamate without dicyandiamide.

Comparison of Figs. 3 and 4 shows that there is considerably more "tendering" upon aging of fabric treated with ammonium sulfamate than untreated fabric. Figs. 5 and 6 indicate that even small amounts of dicyandiamide reduce tendering to a point comparable to that of fabric containing no flameproofers. The increase in tensile strength shown in Figs. 7, 8 and 9 is quite remarkable.

The scope of the invention is not limited to the foregoing specific description, since many modifications will now be apparent. The scope of protection is to be limited

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only by the appended claims as interpreted in view of the prior art.

The claims are:

1. A fabric containing ammonium sulfamate as flame retarder and mixed therewith dicyandiamide in an amount in the range of 5 to 50 parts by weight per 100 parts of ammonium sulfamate sufficient to stabilize substantially said ammonium sulfamate.

2. A fabric of claim 1 wherein the amount of dicyandiamide is in the range of 20 to 35 parts.

3. A nonwoven fabric of claim 1 containing at least about 7% of ammonium sulfamate and not over about 30% of the mixture of ammonium sulfamate and dicyandiamide based on the weight of the fabric.

4. A nonwoven fabric of claim 3 wherein the amount of dicyandiamide is in the range of 20 to 35 parts and the weight of the mixture is not over about 20%.

5. A flameproofed nonwoven drapery fabric of claim 4 wherein the amount of the ammonium sulfamate is in the range of 10 to 15% and the amount of dicyandiamide is in the range of 2 to 5%, said fabric being resistant to tendering and discoloration on prolonged exposure to heat and light.

6. The method of preparing a fabric of claim 1 which method comprises applying to the fabric the mixture of ammonium sulfamate and dicyandiamide in aqueous solution, and drying at a temperature below 300° F. such that the ammonium sulfamate retains its flameproofing properties and the dicyandiamide retains its stabilizing properties, the total amount of the mixture of ammonium sulfamate and dicyandiamide being sufficiently low to avoid undesirable stiffness in the final fabric.

7. The method of claim 6 wherein the amount of dicyandiamide is in the range of 20 to 35 parts, and the dried fabric contains at least about 7% ammonium sulfamate and not over about 20% of the mixture of ammonium sulfamate and dicyandiamide.

8. The method of claim 6 wherein the fabric is nonwoven and an adhesive binder is applied to the web just before the drying step.

9. The method of claim 8 wherein the amount of dicyandiamide is in the range of 20 to 35 parts.

10. The method of claim 9 wherein the aqueous solution contains a nonionic wetting agent and the binder is a plasticized polyvinyl acetate.

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