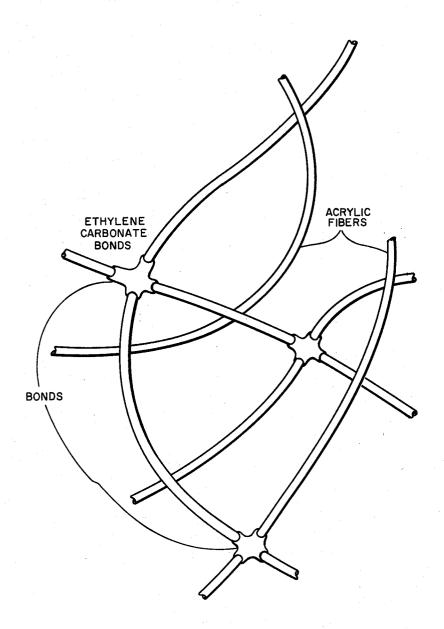
J. R. BILES ETAL STABILIZED ACRYLIC FABRICS AND METHOD FOR TREATMENT OF ACRYLIC FABRICS Filed Oct. 9, 1961



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3,152,919 STABILIZED ACRYLIC FABRICS AND METHOD FOR TREATMENT OF ACRYLIC FABRICS James R. Biles, Doyle C. Nicely, and G. W. Franklin Sellers, Decatur, Ala., assignors, by mesne assignments, to Monsanto Company, a corporation of Delaware Filed Oct. 9, 1961, Ser. No. 143,536

16 Claims. (Cl. 117—138.8)

This invention is concerned with the treatment of the 10 raised surface of woven, non-woven and knitted synthetic fabrics to prevent distortion of the raised surface due to normal wearing and laundering conditions. More specifically, this invention is concerned with preventing the matting, shedding and pilling of the nap of acrylic fabrics, as 15 well as preserving a soft hand, after subjecting these fabrics to normal laundering and wearing conditions.

In the past the raised surfaces of fabrics composed of synthetic fibers have been stabilized by the use of salts which were toxic and corrosive; therefore, special and expensive production equipment was necessary to apply these salts, usually as a solution, to the raised surface of the fabrics. Some of the salts were the pure metal halides such as zinc chloride, lithium bromide and water soluble thiocyanates. These salts were very corrosive to the 25standard finishing mill equipment. In addition, these salts gave the fabrics a harsh; brittle or gritty hand which was very undesirable and affected the color to such an extent that the fabrics were unacceptable. The use of ethylene carbonate has been disclosed in a pending application, 30 S.N. 133,299, dated August 23, 1961.

An object of this invention is to provide a method by which the nap of synthetic fabrics are stabilized against normal wearing and laundering conditions.

Another object of this invention is to provide a stabiliz- 35 ing composition to prevent excessive matting, pilling and shedding of the nap of synthetic fabrics.

Another object of this invention is to provide a stabilizing composition for the nap of synthetic fabrics which gives a soft hand.

Another object of this invention is to provide a stabilizing composition for the nap of synthetic fabrics which does not deleteriously affect the color.

Another object of this invention is to provide a stabilizing composition for the nap of acrylonitrile fabrics which renders the fabrics free of excessive matting, pilling and shedding under normal laundering conditions and normal wearing conditions as well as preserving a soft hand.

Another object of this invention is to provide permanent stability of high pile fabrics against matting, pilling, shed-

Other objects and advantages of this invention will become apparent from the hereinafter detailed description.

The objects of this invention are generally accomplished by applying an aqueous solution of ethylene carbonate and a coplymer of ethyl acrylate and methyl methacrylate to the nap or raised surface of synthetic fabrics, either woven, non-woven or knitted. This composition may be applied by spraying, fogging or padding. Other agents may be added on the fabrics during this operation such as an anti-static agent of Aston 108 which is a polyamine resin such as diethylene-triamine crossed linked with polyethylene glycol diiodide or an epoxy resin and a water repellent agent such as Phobotex F.T.C., a melamine 65 derivative. These agents will not affect the hand or color of the fabrics but do give additional useful properties.

More specifically, the synthetic fabrics, either woven, non woven or knitted, were napped and then treated with an aqueous solution of ethylene carbonate and a copolymer of ethyl acrylate and methyl methacrylate. In this stabilizing composition the ethylene carbonate and the

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copolymer vary in a ratio of 1 to 1, 2 to 1 and 1 to 2 based on the weight of the aqueous solution with the preferred ratio being 1 part of ethylene carbonate to 1 part of the copolymer. The napped and treated fabrics were then heated in a conventional drying apparatus, such as a chain dryer or an oven, to evaporate any water and to cure the copolymer; in addition, during this heating step, ethylene carbonate is concentrated at the points of intersection of the fibers in the nap to form a durable bond between and among themselves as depicted in the drawing. The period of time the fabrics were heated ranged from 2 minutes to 15 minutes, with the preferred being 4 to 5 minutes, at a temperature of from 250° F. to 350° F. with the preferred temperature being 280° F. The napped fabrics were then withdrawn from the drying apparatus, and it was found that the hand was of acceptable softness and the color was unaffected. The stabilizing composition was added onto the nap by conventional spraying or fogging methods well known in the textile field. Other agents such as water repellents and anti-static agents may be added to the original stabilizing composition solution which would have resulted in giving the napped fabrics not only stability to laundering, wearing, and a soft hand, but a permanent anti-static and water repellent property. The dyed fabrics were then washed and their shedding, pilling and matting properties were observed along with the hand. There was no excessive shedding, pilling and matting and the hand remained soft.

While this application has been generally directed to synthetic fabrics, it is especially useful in stabilizing the nap of fabrics made from fibers of acrylic polymers. The polymeric materials, which may be employed in the practice of the present invention, are polyacrylonitrile, copolymers, including binary and ternary polymers containing at least 80 percent by weight of acrylonitrile in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising acrylonitrile with from 2 to 50 percent of another polymeric material, the blend having an overall polymerized acrylonitrile content of at least 80 percent by weight. While the preferred polymers employed in the instant invention are those containing at least 80 percent of acrylonitrile, generally recognized as the fiber-forming acrylonitrile polymers, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent acrylonitrile. The acrylonitrile polymers containing less than 80 percent acrylonitrile are useful in forming films, coating compositions,

molding operations, lacquers, etc.

For example, the polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing the >C=C< linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esers of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromo-ethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloroacrylamide; or monoalkyl substitution products thereof; methylvinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic esters; N-vinylcarbazole; vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, betadicarboxylic acids or their anhydrides or derivatives, such as diethylcitraconate, diethylmesaconate, styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, etc.; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, and other >C=C< containing polymerizable materials.

The polymer may be a ternary or higher interpolymer, 5 for example, products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, and preferably, the ternary polymer comprises acrylonitrile, methacrylonitrile, and 2-vinylpyridine. The ternary polymers preferably contain from 80 to 98 percent by acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another substance such as methacrylonitrile or vinyl chloride.

The polymer may also be a blend of a polyacrylonitrile or of a binary interpolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other >C=C< containing substance with from 2 to 50 percent of the weight of the blend of a copolymer of from 20 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other >C=C< containing polymerizable monomer. Preferably, when the polymeric material comprises a blend, it will be a blend of a copolymer of 90 to 98 percent acrylonitrile and from 2 to 10 percent of 25 another monomer-olefinic monomer, such as vinyl acetate, which is not receptive to dyestuff, with a sufficient amount of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine, such as vinylpyridine or 1-vinylimid- 30 azole, to give a dyeable blend having an overall vinylsubstituted tertiary heterocyclic amine content of from 2 to 10 percent, based on the weight of the blend.

The following examples are cited to illustrate the invention. They are not intended to limit it in any way. 35 Unless otherwise noted, percentages as expressed in the examples indicate percent by weight.

### Example 1

In the following chart the fabric samples were composed of fibers of 94 percent acrylonitrile and 6 percent vinyl acetate. Also, the samples were all treated by spraying with an aqueous solution of 1 to 1 ratio by weight of ethylene carbonate and the copolymer of ethyl acrylate and methyl methacrylate; all samples were dryed for 4 minutes at 290° F.; in addition the solution contained 10 percent solids of the copolymer.

Sample No.	Dry wt., grams	Wet wt. in grams	Diff.	Percent addon	Solution conc. of ethylene carbonate		after wash- ing 5
-	1.5				e e ja eras i	washing	times
1	32.0 31.7	33.1 32.8	1.1	3.5 3.5	10.0 5.0	3 3, 5	3.5
3 4	28. 5 31. 3	29. 7 33. 5	1. 1 2. 2	3. 9 7. 0	2. 5 2. 5	3. 5 3. 5	- 3 3
6	30.8	32.7	$\frac{1.6}{2.1}$	5. 1 6. 8	2. 5 1. 25	3.5 4	3.5
7	30.5	32.2	1.7	5.6	1.25	4	3

Thus with a stabilizing composition solution of 1.25 percent concentration, and addons in the range of 5 percent to 7 percent, after five consecutive launderings of the treated fabric there is good resistance to pilling, matting, shedding and a soft hand is still present, in fact generally improved. The color of the sample was not affected after the treating and washing process of this invention. This is also the result with a 2.5 percent concentration of the stabilizing composition with addons in the range of 3 percent to 7 percent as well as 3.5 percent addons and a 10 percent concentration and a 3.5 percent addons and a 5 percent concentration. The rating was done according to a 1 to 5 rating with 3 being commercially acceptable, with all ratings above 3 being of superior quality as to shedding, pilling, matting and soft hand.

### Example 2

In the following chart the fabric samples were composed of fibers of 94 percent acrylonitrile and 6 percent vinyl acetate. Also, the samples were all treated by spraying with an aqueous solution of a 2 to 1 ratio by weight of ethylene carbonate to the copolymer of ethyl acrylate and methyl methacrylate, with 5 percent solids of the copolymer. All samples were dried for 4 minutes at a temperature of 300° F, and then subjected to 5 consecutive washings under normal laundering conditions.

5	Sample No.	Dry Wt.	Wet Wt.	Diff.	Percent addon	Conc. of ethylene earbonate	Hand and appear- ance before washing	Rating after 5 wash- ings
0	1	32. 1	32. 9	.8	2. 5	10	3.5	4. 0
	2	32. 7	34. 3	1.6	4. 9	5	4.0	3. 5
	3	34. 3	35. 1	.8	2. 3	5	4.0	3. 5-4. 0
	4	33. 4	34. 5	1.1	3. 3	2.5	3.5	3. 5-4. 0
	5	33. 0	33. 5	1.5	4. 6	2.5	4.0	3. 5
	6	32. 7	34. 6	1.9	5. 8	1.25	3.5	3. 0-3. 5

Thus with a stabilizing composition solution of 10 percent and 2.5 percent addon, after the 5 consecutive launderings of the treated fabric, there was good resistance to pilling, matting, shedding and a soft hand was still present, in fact generally improved. The color of the sample was not affected. This was also the result with a 5 percent concentration of the stabilizing composition and a range of 2 percent to 5 percent addon, a 2.5 percent concentration of the stabilizing composition and a range of 3 percent to 5 percent addons and with a 1.25 percent concentration and 5.8 percent addon.

#### Example 3

In the following chart, the fabric samples were composed of fibers of 94 percent acrylonitrile and 6 percent vinyl acetate. Also, the samples were all treated by spraying with an aqueous solution of a 2 to 1 ratio by weight of ethylene carbonate and the copolymer of ethyl acrylate and methyl methacrylate, the copolymer being 2.5 percent solids; all samples were dried for 4 minutes at 300° F., and then subjected to a shedding test.

45	10.00	1 :	1 1		1 3	900	T	1	. 1	
	Sample No.	Dry Wt.	Wet.	Diff.	Per- cent addon	ene .	Hand before	before	Wt. after shed- ding	Per- cent lost due to shed-
50		grand d								ding
55	1234	66. 9 66. 3 65. 8 64. 6 67. 5 65. 7	69. 9 69. 3 :68. 6 67. 5 70. 4 68. 7	3.0 3.0 2.8 2.9 2.9 3.0	4.5 4.5 4.3 4.5 4.3 4.6	5. 0 5. 0 5. 0 2. 5 2. 5 2. 5	3 3 3 3 3	66. 9 66. 3 65. 8 64. 5 67. 4 65. 7	66. 3 65. 7 65. 2 64. 0 66. 7 65. 1	.6 .6 .6 .5

Thus with a stabilizing composition solution of 5 percent and addons from 4 percent to 5 percent, there was only 0.6 percent shedding which is excellent as a percent loss of up to 1 percent is commercially acceptable. This was also the result with a 2.5 percent concentration of the stabilizing composition solution and addons from 4 percent to 5 percent.

Thus with a concentration of the stabilizing composition, composed of ethylene carbonate and the copolymer
of ethyl acrylate and methyl methacrylate in a ratio of 1
to 1, 1 to 2 and 2 to 1 based on the weight, varying from
1.25 percent to 10 percent and addons varying from 1 percent to 7 percent, depending upon the concentration of
70 the solution, the inventors have been very successful in
stabilizing the napped surfaces of synthetic linear acrylic
fabrics to pilling, matting, shedding as well as maintaining a soft and acceptable hand after numerous launderings under normal laundering conditions.
75 It is understood that changes and variations may be

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made in the present invention by one skilled in the art without departing from the spirit and scope thereof as defined in the appended claims.

We claim:

1. An article composed of the napped fabric of fibers of linear polymers of acrylonitrile stabilized with a composition comprising ethylene carbonate and a copolymer of ethyl acrylate and methyl methacrylate, wherein the amount of ethylene carbonate varies from 0.1 to 10 percent based on the weight of the fibers.

2. The article of claim 1 wherein the napped fabric is composed of fibers of a copolymer of acrylonitrile and up to 20% of a copolymerizable olefinic monomer.

3. The article of claim 2 in which the napped fabric is composed of fibers of a copolymer of 94 percent acrylo-

nitrile and 6 percent vinyl acetate.

4. The article of claim 2 wherein the napped fabric is composed of a blend of fibers composed of 88 percent of one copolymer of 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of another copolymer 20 of 50 percent acrylonitrile and 50 percent methyl vinyl pyridine.

5. A method of stabilizing the napped fabric of fibers of linear polymers of acrylonitrile which comprises impregnating the napped fabric with an aqueous solution comprising ethylene carbonate and a copolymer of ethyl acrylate and methyl methacrylate, wherein the amount of ethylene carbonate varies from 0.1 to 10 percent based on the weight of the fibers, and heating the impregnated napped fabric.

6. The method of claim 5 wherein the napped fabric is composed of fibers of a copolymer of acrylonitrile and up to 20 percent of a copolymerizable olefinic monomer.

7. The method of claim 6 in which the fibers are composed of a copolymer of 94 percent acrylonitrile and 6 35 percent vinyl acetate.

8. The method of claim 6 in which the fibers are composed of a blend of 88 percent of one copolymer of 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of another copolymer composed of 50 percent 40 acrylonitrile and 50 percent methyl vinyl pyridine.

9. A method of stabilizing the napped fabrics of fibers of a copolymer of acrylonitrile and up to 20 percent of a copolymerizable olefinic monomer which comprises impregnating the napped fabric with an aqueous solution 45

comprising ethylene carbonate and a copolymer of ethyl acrylate and methyl methacrylate, wherein the ratio of ethylene carbonate to copolymer in said aqueous solution is from 2 to 1, or 1 to 2, and the weight of the ethylene carbonate is from 0.1 to 10 percent based on the weight of the fibers, heating the impregnated napped fabric at a temperature of from 250° F. to 350° F. for a period of time from 12 to 15 minutes.

10. The method of claim 9 in which the ratio is 1 to 1 and the impregnated napped fabric is heated to 280° F.

for 4 minutes.

11. The method of claim 9 in which the ratio is 2 to 1 and the impregnated napped fabric is heated to 300° F. for 2 minutes.

12. The method of claim 9 in which the ratio is 1 to 2 and the impregnated napped fabric is heated to 300° F, for 2 minutes.

13. A method of stabilizing the napped fabric of fibers of a copolymer of 94 percent acrylonitrile and 6 percent 20 vinyl acetate which comprises spraying onto the nap of the fabric an aqueous solution comprising ethylene carbonate and a copolymer of ethyl acrylate and methyl methacrylate, wherein the ratio of ethylene carbonate to copolymer in said solution is from 2 to 1 to 1 to 2 with 25 the amount of ethylene carbonate varying from 0.1 to 10 percent based on the weight of the fibers, heating the sprayed napped fabric in a drying oven to a temperature of 280° F. for 4 minutes, removing said sprayed napped fabric from the drying oven and allowing the same to 30 cool to room temperature.

14. The method of claim 13, in which the fibers are composed of a blend of 88 percent of one copolymer a 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of another copolymer composed of 50 percent acrylonitrile and 50 percent methyl vinyl pyridine.

15. The method of claim 13 in which the ratio is 2 to 1.

16. The method of claim 14 in which the ratio is 2 to 1.

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