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TREATMENT OF CELLULOSIC YARNS BY RUBBERY MATERIALS, AND TEXTILES THEREOF

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The present invention relates to the treatment of textiles with polymeric materials. More particularly, it relates to a method for treating cellulose-containing materials, especially cotton, in the form of yarn with a copolymer containing a butadiene hydrocarbon and an acrylic nitrile and to the product of such method.

It is conventional practice to apply starch as a size material to cellulose-containing textile yarns prior to weaving them into cloth. The starch reduces the shedding of the yarn as it is woven, that is, it reduces the loss of fine fibers or filaments of the yarn as it travels through the weaving machinery as well as increasing the abrasion resistance of the yarn. The starch also gives some stiffness to the woven fabric so that it can readily be cut into the desired pieces and shapes when being manufactured into garments. However, starch is not a permanent size, and on washing it is very rapidly lost from the cloth to materially reduce its abrasion resistance and consequently its life and usefulness. Moreover, during washing the dyes used are removed so that the color fades or bleeds or crocking occurs. Furthermore, in new, unlaundered fabrics a drop of water or other starch solubilizing liquid will cause spotting of the cloth due to loss of starch or its redistribution at that point, necessitating extreme care in manufacturing and handling operations to avoid the production of unsightly, second grade material. To remove the starch from the finished fabric and to treat the fabric with fabric-strengthening materials requires several subsequent treating steps which add materially to the cost of finished goods so that such methods are uneconomical and impracticable. On the other hand, leaving the starch in the fabric and applying a fabric-strengthening coating is also undesirable since permanent abrasion resistance is not materially improved.

The difficulties alluded to above are particularly troublesome when using blue denim yarn to make fabric. Blue denim is normally made from relatively short staple cotton averaging $1\frac{5}{16}$ inch in length and is dyed with indigo which is actually a pigment rather than a dye. The blue pigment is on the surface of the yarn and is rather easily removed by abrasion. Moreover, the abrasion resistance of blue denim fabric is rather poor. However, there are no known methods of improving the yarn and fabric without very substantially increasing the costs of the fabric so that it is noncompetitive.

Accordingly, it is a primary object of the present invention to provide cellulose-containing textiles with a permanent size.

It is another object of the present invention to provide dyed or undyed cellulose-containing yarns with a permanent size material which produces a yarn having low shed value and high abrasion resistance.

It is still another object of the present invention to provide dyed or undyed cellulose-containing fabrics from yarns having a permanent size thereon, said fabrics characterized by exhibiting an abrasion resistance after repeated laundering substantially superior to the abrasion resistance of a similarly laundered fabric made from starch-sized warp yarns.

A further object of this invention is to provide a method for treating cellulose-containing yarns with a permanent size.

Yet another object of this invention is to provide a method for applying a permanent size material to cellulose-containing yarn which may then be woven into cloth, said yarn and said cloth being dyed or undyed.

Still another object is to provide a method for simultaneously dyeing and permanently sizing cellulose-containing yarn and weaving said yarn into cloth which exhibits high abrasion resistance after repeated laundering with little or no loss of color.

These and other objects and advantages of the present invention will become more apparent to those skilled in the art from the following detailed description, examples and tables.

It now has been found according to the present invention that cellulose-containing textile yarns can readily be provided with a permanent size by treatment with an aqueous dispersion or latex of a copolymer of a butadiene hydrocarbon and an acrylic nitrile to provide a minor amount of a discontinuous coating of the copolymer on the yarn. The copolymer affords low shed value and high abrasion resistance. Yarns treated according to the present invention can be readily woven into cloth which exhibits excellent hand. After repeated launderings, the yarn as well as the cloth retain a substantial degree of their original abrasion resistance and show little if any bleeding of dyes or pigments contained therein.

The copolymer employed in the sizing bath is a copolymer containing a butadiene hydrocarbon and an acrylic nitrile. Examples of butadiene hydrocarbon monomers copolymerizable with the acrylic nitrile monomer are those open-chain conjugated dienes having from 4 to 8 carbon atoms such as butadiene-1,3, isoprene, 1,3-pentadiene, methyl pentadiene and the like and mixtures thereof, butadiene-1,3 being preferred. One or more acrylic nitrile monomers copolymerizable with the butadiene hydrocarbon monomers are acrylonitrile itself, methyl acrylonitrile, ethyl acrylonitrile, and chloroacrylonitrile. Of this group, acrylonitrile is the preferred monomer. The copolymer of butadiene hydrocarbon monomer and acrylic nitrile monomer will contain from 35 to 90% butadiene hydrocarbon monomer. Preferred copolymers contain from about 55 to 70% by weight of the butadiene hydrocarbon monomer with the balance being essentially the acrylic nitrile monomer. Moreover, the butadiene hydrocarbon-acrylic nitrile copolymer can contain at least one other monomer copolymerizable therewith such as styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl, vinyl ketone, and vinylidene chloride in amounts up to 35% by weight.

The copolymer is employed generally in neutral or alkaline latex form although acid latex may be used. It can be used as a dispersion of from 3 to 55% total copolymer solids having an average particle size of from about .02 to .20 micron, preferably about .06 micron. However, for ease of application and mixing with other components, the latex is employed preferably in dispersions containing from about 6 to 20% by weight of copolymer solids. It will be understood that a high solids latex may be diluted with the water present in conjunction with the other elements of the textile size treating bath to provide the desired solids content in the dispersion and conversely a dilute latex may be brought to the desired solids content when less water is employed with the other constituents. Moreover, considerable variation can be made in copolymer solids content depending on types of yarn, running speeds, temperatures, particle size of the copolymer, slashing equipment and the like. For example, sizing baths of dispersions of about 1% solids will deposit about 2% solids. Still other dispersions containing 30% solids can be used to deposit 36% solids on the yarn. Further, a dispersion of 20% solids can deposit 8% solids on the yarn where another dispersion of about 10% solids will deposit 4% or 7%. On a dry weight basis the amount of copolymer employed in the treating bath varies as is necessary to achieve a yarn pickup of about 2 to 20% and preferably from about 4 to 14% by weight. The best results are obtained with a pickup of 6–8% on the yarn. Outside of these ranges insufficient copolymer will be present on the yarn to effectively size or too much will be present on the yarn which will coat the rolls and impair the sizing operation or which will cause the yarns to stick together excessively.

While it is unnecessary to add accelerators or vulcanizing agents to the butadiene hydrocarbon-acrylic nitrile copolymer size bath since the copolymer when dried on the yarn is satisfactory, such materials can be added if desired especially if the yarn tends to be somewhat tacky. Moreover, dispersing agents can be used in the bath if found desirable as well as bactericides, flame-proofing agents, fungicides, water repellent materials and the like. Starch may be added to stiffen the fabric and reduce pilling.

The textiles to be treated according to the present invention are predominantly cellulose materials such as cotton, viscose rayon, cellulose acetate, regenerated cellulose and mixtures thereof as well as blends of cellulose materials with other textile materials such as wool, nylon and the like wherein the cellulose material is present in at least a major amount. While the present invention will be described with particular reference to the treatment of warp yarns to be used in weaving fabrics such as square woven fabrics, twills, fancies and the like, it is to be understood that the filling or weft yarns may be similarly treated and likewise, knitted goods and other textile fabrics where a permanent size is desired.

Dyes or pigments can be incorporated into the yarn prior to treatment with the latex dispersion. Alternatively, the latex treated yarns can be dried and then treated with dyes or pigments, or woven into fabric which is then dyed or pigmented. Moreover, dyes or pigments can be incorporated into the bath so that yarn sizing and dyeing are accomplished simultaneously. The dyes or pigments employed may be those which will color the textile or the latex or both with the same or different colors. Cross-dyeing can also be employed. In some instances, the latex deposited on the yarn can be dyed to provide a fabric which has the overall appearance of being completely dyed although microscopic examination will show that only the latex particles on the yarn will actually have been susceptible to the dye.

In sizing yarns according to the method of the present invention, the yarns, preferably warp-yarns, are delivered from beams to the latex size bath and carried over rollers

at a speed sufficient to deposit a minor amount of latex on the outer surface layers of the yarns which are than passed through squeeze rolls to remove the excess latex from the yarns and to cause some impregnation in the outer fiber layers of the yarn. Variations in dipping times will make some change in latex solids on the yarn. However, such do not adversely affect results. For example the bath can be operated at yarn running speeds of from 5 to 10 yards per minute to provide a solids pick-up of from 5.6 to 5.7% with Walker Abrader abrasion cycles of 64–63. If the squeeze rolls become coated with copolymer and tend to cause sticking, they can be coated with silicone grease or similar material which prevents buildup of copolymer or a material such as polyethylene glycol in a minor amount may be added to the size bath, particularly where the yarns themselves tend to exhibit some sticking. The latex treated yarns are next dried in an oven or on dry cans for a sufficient period of time to coagulate and set the latex and reduce the total moisture content to not more than about 5% by weight. Drying of Hycar sized yarns to a moisture content of not more than 5% eliminates essentially all of the tacky and rubbery feeling the sized yarn might exhibit and removes the water of dispersion from the deposited latex. The substantially dried yarns may then be woven into cloth with unsized filling yarns. If desired, the filling yarns can be coated with latex size prior to weaving.

Moreover, the size bath containing the butadiene-nitrile aqueous dispersion of the present invention can be operated at temperatures of from 70 to 180° F. to obtain solids on the yarn averaging from 5.7 to 4.2% by weight of the yarn with Walker Abrader abrasion cycles of 64–70. On the other hand, starch must be made up in special equipment at the boil and must be applied to the yarn hot or at the boil. If it is not used up in a short time, it is subject to mold growth whereas the butadiene-acrylonitrile copolymer latex is essentially unaffected. Moreover, additives are required in many instances to give the starch satisfactory sizing characteristics.

Yarns prepared according to the present invention have a discontinuous thin adherent coating of copolymer thereon rather than a thick impervious continuous coating. Under a microscope the copolymer appears to be distributed as particles over the body of the yarn and may appear to be in the form of a fine network. This arrangement of the copolymer on the yarn and outer fiber layers is advantageous as it permits the yarn to flex without ravelling or shedding during weaving and also permits dyes or pigments to readily penetrate the fibers if it is desired to dye the yarns after latex sizing. The shedding and abrasion resistance of the latex sized yarns is as good as starch sized yarns, and, after repeated launderings, latex sized yarns have up to twice the abrasion resistance of conventional starch sized yarns and do not appreciably bleed as compared to starch sized yarns. The presence of the discontinuous copolymer on the surface of the yarn and in its outer fiber layers as well as in cloth manufactured from such yarn lends itself readily to subsequent compressive shrinkage treatments so that the yarn or fabric may be preshrunk if desired according to known processes without any adverse effects, prior to manufacturing into garments. It, also, is a feature of cloth prepared from the latex sized yarns of the present invention that the latex although in a discontinuous coating on the yarn contacts the filling yarns so that in the area of contact between the warp and filling yarns there is an appreciable amount of copolymer present to prevent abrasion as the yarns flex. This is a contrast to conventional coating processes where only the exposed areas of the yarns not in contact with each other are coated with a thick layer. The importance of using the copolymer of a butadiene hydrocarbon and an acrylic nitrile as a permanent size for yarn is that it offers equal or better shed value and abrasion resistance as compared to starch and increased abrasion

resistance to the finished cloth and eliminates the necessity for removing the starch and applying subsequent coatings of copolymer after the fabric is woven. Thus, applying the copolymer to the yarn itself eliminates many subsequent treatment steps. Also, fabrics woven from yarns sized as disclosed herein have a "hand" which is satisfactory for subsequent manufacturing operations.

The following examples will serve to illustrate the invention with more particularity to those skilled in the art.

EXAMPLE I

A size bath containing a latex dispersion of a 55–45 copolymer of butadiene-1,3 and acrylonitrile (total solids about 6.0% and having a particle size of about 0.06 micron) was prepared in a stainless steel size box of a slasher. Unsized blue denim cotton yarns (8.75's—containing about 11% indigo) on 4 beams each containing 42 ends was fed as a sheet of 168 ends lying side-by-side into the bath at room temperature over rollers and between two rubber coated squeeze rolls into a drying oven at 300° F. and at a rate sufficient to afford a moisture content of about 5% by weight after drying. The dried and sized yarns were separated from each other by means of split bars and then collected on a spool. The percent by weight of copolymer on the yarn was 4.08%.

A portion of the latex treated yarn was tested on a Southern Research Institute Shed Tester which is essentially a miniature loom without the filling motion. It is equipped with a double set of harnesses, a reed, and drop-wires for automatic stop motion when yarns break. In operation the reed is caused to strike an impact bar simulating the action of the reed on a standard loom. About 30 yards of sized (one yard of unsized) warp yarns are passed through the shed tester in each test during the space of about four hours. The fibers and size that are abraded from the yarn drop to the bottom and are collected in an enclosed pan. This material, called shed, is weighed and the result is expressed as percent of the weight of the total yarn tested. Results of shed tests are reproducible to less than 0.1%. When using the above butadiene-acrylonitrile latex, a shed value of 1.57% was obtained. With 8.6% by weight starch as a size on the yarn, the shed value was 1.30% and the control (unsized) showed a shed value of 3.27%. The breaking strengths in pounds of the three types of yarns using ten inch lengths were: latex sized—3.36, starch sized—3.34 and unsized—3.13

Another portion of the above latex treated yarn was tested on a Walker Abrader which is manufactured by the U. S. Testing Company, Hoboken, New Jersey. This machine causes yarns to rub against each other until there is a break. The number of abrading cycles which is required to cause a break is recorded. In practice, 24 strands of a given sample of yarn are mounted on the machine. As each yarn breaks, the machine stops and the number of cycles is read from a counter. After 12 consecutive breaks are recorded, the machine is stopped and the remaining 12 strands are discarded. Four sets of abrasion data are obtained for each yarn sample. The average value is the grand average of all 48 determinations for each yarn sample. Average Walker Abrader cycles for the latex treated yarn were 67 while for the starch sized and unsized yarn it was 38 and 18, respectively.

All shed and abrasion resistance tests were made in a conditioned room controlled at 70° F. and 65% R. H.

The above example shows that shed values for latex treated yarns are nearly equal to those for starch sized yarns even when the amount of latex is half that of starch whereas the abrasion resistance of the latex sized yarn was 76% greater than the starch sized yarns.

Blue denim yarns were also sized in a commercial plant slasher but in a manner similar to that in the above example, and then were woven into fabric, washed in a Launderometer and tested on a Taber Abraser. The results of these tests are shown in Table A below:

Table A

ABRASION RESISTANCE OF FABRIC CONTAINING BUTADIENE-1,3/ACRYLONITRILE TREATED WARP YARNS

Run No.	Fabric designation	Percent by weight latex solids on warp yarns	Launderometer cycles					
			0	1	2	3	4	5
			Taber abraser wear cycles [1]					
1	D	[2] 10	1,501	1,372	1,078	944	905	889
2	D	8	1,312	1,404	1,498	1,591	1,654	1,791
3	D	9.8	1,306	1,388	1,453	1,547	1,623	1,809
4	SD	[2] 10	831	722	685	597	554	538
5	SD	7.4	657	783	913	1,019	1,094	1,167
6	SD	7.1	590	630	807	952	1,047	1,129
7	WB	[2] 10	1,775	1,284	1,273	1,345	1,276	1,151
8	WB	9.2	1,855	1,945	2,049	2,123	2,292	2,407

[1]=CS-10 new calibrase wheels.
[2]=Starch.
D=8 oz. blue denim.
SD=Lightweight sport denim.
WB=11 oz. white back denim.

The above results show that while in some cases the unlaundered fabric in which the warp yarns were sized with latex did not show as high values as the starch sized fabric, the abrasion cycles increased for the latex sized fabrics after repeated launderings whereas the abrasion cycles decreased for the starch sized fabrics. Remarkably, at the end of 5 washings the latex sized yarns are twice as abrasion resistant as the starch sized yarns even when using less latex solids on the yarn than starch solids. Moreover, after 5 launderings the fabrics having latex sized yarns increased in abrasion resistance as much as from 30 to 90% of their abrasion resistance before laundering and exhibited greater abrasion resistances than similar unlaundered fabrics of starch sized yarns. Furthermore, when samples of starch sized fabric were laundered and ironed with white cloth after each cycle they colored the wash water and the white cloth blue whereas the latex sized sample did not appreciably color the wash water and showed only a slight color transfer after the first laundering but no appreciable transfer of color to the white cloth thereafter. It, thus, is seen that in addition to improved abrasion resistance, the latex reduces bleeding or leaching during washing and color transfer or crocking during laundering and ironing.

EXAMPLE II

Blue denim yarns were also treated in the manner described in Example I, above, except that a size bath containing 6% solids of various mixtures of starch and 55–45 butadiene-1,3-acrylonitrile copolymer were used. Tests on these yarns gave the following data:

Table B

PROPERTIES OF YARNS HAVING MIXED COATINGS

Run No.	Percent copolymer in size	Percent starch in size	Percent total size on yarn	Percent shed	Abrasion resistance		
					Initial	After 1 laundering	After 5 launderings
1	80	20	3.95	1.26	43	45	39
2	70	30	4.04	1.27	45	51	36
3	60	40	3.30	1.40	41	48	34
4	50	50	2.44	1.48	38	49	36

The above results show that while mixtures provide good shed values, reduced abrasion resistances are obtained. However, after the second laundering, no color was in the wash water which showed that the copolymer prevented bleeding. Further, while heat is required to bring the starch into the colloidal or dispersed state, no additional heat is required after addition of the copolymer dispersion so that the size bath may operate at room temperature. The bath also is not subject to spoilage for extended periods of time. Accordingly, such mixtures will be useful where a very high abrasion resistance is not required.

EXAMPLE III

Further tests were conducted on yarns and fabrics from these yarns prepared as described in Example I supra but in which the pressure on the squeeze rolls and the type of rolls used in the treatment was varied. The results of the tests are indicated in Table C below:

Table C

VARIATIONS IN METHOD OF APPLYING COPOLYMER SIZE

Run No.	Total latex solids in size bath, percent by weight	Yarn		Fabric (8.75's) Taber abraser cycles, avg.[2]		Slasher conditions
		Total latex solids, percent by weight	Walker abrader cycles, avg.[1]	As received	After 5 launderings	
1	0	0	18	Impossible to weave unsized yarn		
2	[3] 12	[3] 10	52	432	245	1 rubber roll, 1 wool roll, medium pressure.
3	6	2.8	40	438	521	2 rubber rolls, medium pressure.
4	10	3.3	30	343	348	Do.
5	16	3.3	35	361	494	Do.
6	20	6.6	46	445	544	1 rubber roll, 1 yarn wound roll, medium pressure.
7	20	7.3	48	332	504	1 rubber roll, 1 yarn wound roll, high pressure.
8	20	11.6	54	321	499	1 rubber roll, 1 yarn wound roll, high pressure, 5% Santomerse in size bath.

[1] = average of 48 determinations.
[2] = CS-10 calibrase wheels—average of 5 determinations.
[3] = Starch.

These tests show that the squeeze rolls and the pressure thereon can be varied with achievement of comparable results. As was shown in Table A, the latex sized material in Table C also increased in abrasion resistance after laundering as compared to the starch sized material. However, in one instance (test 4 Table C) after 5 launderings the latex sized material was not as abrasion resistant as the unwashed starch sized material, but consideration must be given to the fact that the amount of copolymer on the yarn was only a third of that of the starch.

EXAMPLE IV

Yarns were also sized according to the method of Example I supra except that the amount of latex solids in the size bath was varied. The amount of latex solids on the resulting sized yarn and the abrasion resistance and shed values of the various sized yarns are shown in Table D below:

Table D

RESULTS OF VARYING LATEX CONTENT OF SIZE BATH AND OF YARN

Run No.	Percent by weight latex solids in bath	Percent by weight latex solids on yarn	Walker abrader cycles, avg.	Percent by weight shed
1	0	0	18	3.27
2	12	[1] 8.6	38	1.30
3	0.4	1.8	34	3.22
4	1.2	2.0	43	2.75
5	2.0	2.2	48	2.30
6	3.9	2.5	62	1.70
7	5.9	4.2	68	1.39
8	6.0	[2] 6.6	[3] 61	1.30
9	7.9	6.1	61	1.22
10	9.8	7.0	58	1.21
11	14.0	12.5	57	1.40
12	[4] 15	13.9	[5] 108	1.50
13	[6] 20	8	61	1.20

[1] Starch
[2] Plus 16 PHR of curing agent.
[3] After one laundering—97; after five launderings—130.
[4] Plus minor amount polyethylene glycol.
[5] After one laundering—56; after five launderings—57.
[6] Plant data.

The above table indicates that the amount of latex in the size bath and on the yarn can be varied considerably with obtainment of satisfactory results. The best combination of shed value and abrasion resistance lies in the range of from about 4 to 14.0% by weight of copolymer on the yarn. This range of copolymer can be achieved from baths having various concentrations of copolymer which will deposit varying amounts of copolymer on the yarn. Acceptable coatings can still be obtained where the bath will deposit as little as 2% and as much as 20% copolymer on the yarn.

EXAMPLE V

Still other yarns were sized according to the method of the Example I, above, in which the particle size of the butadiene-1,3-acrylonitrile copolymer in the latex was varied as well as the ratio of diene to nitrile. As shown in Table E below, considerable variation can be realized with obtainment of satisfactory results.

Table E

EFFECT OF COPOLYMER PARTICLE SIZE

Run No.	Ratio diene to nitrile [1]	Average particle size, micron	Percent pickup on yarn	Shed, percent	Walker abrader cycles, avg.	Breaking strength, lb.
1	55-45	0.06	4.08	1.57	67	3.36
2	55-45	0.20	5.26	1.84	42	3.15
3	60-40	0.10-0.15	4.21	1.54	60	2.98
4	[2] 55-42	0.12	5.26	1.38	59	3.43
5	67-33	0.06	4.82	1.79	42	2.99

[1] Charging ratio; resulting polymer ratios are similar.
[2] Plus about 2.86 parts methacrylic acid.

EXAMPLE VI

Cotton yarns which had not been dyed or sized were passed through a 67-33 butadiene-1,3-acrylonitrile size bath containing 10% total solids and dried in an air oven. The actual pickup on the yarns was about 10% by weight based on the weight of the yarn. A portion of the yarns was direct dyed using 4% Pontamine Fast Scarlet G (Du Pont) and another portion was vat dyed using 10% Calcosol Jade Green N (CCC). Controls (no copolymer size) were dyed with the same dyes. Both the test samples and the controls exhibited the same color although the vat dyed-copolymer sized yarn had a slightly deeper shade indicating that it is feasible to employ somewhat less dye in the bath. Swatches from each of the dyeings were tested in the Launderometer, color fastness test No. 2. No fading or discoloration occurred with the vat dyed samples. There was slight fading and transfer of color in the direct dyed samples, although the copolymer sized sample exhibited less discoloration than the control. Cotton cloth woven with copolymer sized warp yarn and subsequently dyed exhibited similar results.

EXAMPLE VII

Cotton yarns were treated in the same manner as Example VI, above, except that the size bath contained 30% total solids and the pickup on the yarns was about 36%. Samples of yarns were dyed in the same manner as shown in Example VI and compared with controls. The results obtained were the same as disclosed above with respect to Example VI. Cotton cloth woven with copolymer sized warp yarn and subsequently dyed exhibited similar results.

Examples VI and VII demonstrate that copolymer sized yarns can be readily dyed with either vat dyes or direct dyes. Further, high solids content of copolymer on the yarn does not adversely affect the action of the dyes. While a large amount of copolymer on the yarn is not generally necessary to afford a yarn having the desired abrasion resistance and shed value, such can be used if desired and will not prevent pickup of dye by the yarn. These results would also indicate that the copolymer is

not deposited as a continuous impervious coating on the yarns but rather as a discontinuous, pervious coating.

EXAMPLE VIII

Unsized and undyed cotton yarns were dipped into a bath containing a dispersion of a 55–45 copolymer of butadiene-1,3 and acrylonitrile (15% total solids). The bath was alkaline and contained additionally 3% by weight of the bath of oxidized indigo. After heating for a few minutes the yarns were withdrawn, dried, and placed in an alkaline bath containing sodium hydrosulfite to reduce the indigo. The yarns were then removed and permitted to air oxidize. They exhibited the conventional blue color of indigo and contained about 6% copolymer solids.

In addition to showing the utility of butadiene-acrylonitrile copolymer sized yarn during dyeing, Example VIII is of special significance when consideration is given to conventional indigo dyeing and starch sizing of denim. In practice the yarn is dipped in reduced indigo dye vats of increasing concentration in a series of six steps followed by oxidation after each step, drying and then finally sizing with starch. On the other hand, Example VIII shows that the entire sequence can be accomplished in only 4 steps including the drying step.

EXAMPLE IX

Unsized and undyed cotton yarns were dipped into a bath containing a dispersion of a 55–45 copolymer of butadiene-1,3 and acrylonitrile (15% total solids). The bath was slightly acid and contained additionally about 3% by weight of an acetate dye (Eastman Eastone Fast Red GLF). After 45 minutes at 180° F., the yarns were removed from the bath and washed. They were colored red and contained about 6% copolymer solids. Microscopic examination of the yarn revealed that the copolymer was distributed over the yarn as fine globules and each particle of the copolymer was dyed rather than the fibers of the yarn.

In summary, the present invention teaches that cellulose-containing yarn can readily be treated with a dispersion or latex copolymer of a butadiene hydrocarbon and an acrylic nitrile and woven into cloth to provide a permanent size. The yarn has a low shed value and high abrasion resistance. Even on repeated launderings the fabric containing the polymer size does not appreciably decrease in abrasion resistance. Moreover, little if any bleeding or crocking the the dyes or pigments occurs when yarn is treated as disclosed herein. The yarns so treated can be dyed and then readily woven into cloth which is unexpected in view of the nature of the copolymer. Alternatively, the dyeing step can follow weaving of the yarn into cloth or dyeing can occur simultaneously with sizing. Furthermore, permanent high abrasion resistance is imparted to the cloth. This process obviates the conventional starch sizing and subsequent desizing and coating steps. The present invention, hence, provides a novel way of treating yarn so that it can be woven into cloth, with permanent retention of the properties provided to the cloth. Furthermore, cloth prepared from yarn as treated herein has an excellent hand suitable for cutting and finishing operations and can be readily pre-shrunk by compressive methods.

We claim:

1. The method of treating predominantly cellulose containing yarn to improve its abrasion resistance, to improve its resistance to crocking and bleeding when dyed and to reduce its shed loss which comprises applying to said yarn an aqueous dispersion containing from 3 to 55% by weight of solids of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a copolymerized monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from 35 to 90% by weight and said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, to deposit from above 2 to 20% by weight of said solids on said yarn and drying said yarn containing said solids to a total moisture content of not more than about 5% by weight, to coagulate, set and obtain a discontinuous coating of said rubbery material on said yarn.

2. The method of treating predominantly cellulose containing yarn to improve its abrasion resistance, to improve its resistance to crocking and bleeding when dyed and to reduce its shed loss which comprises applying to said yarn an aqueous dispersion containing from about 6 to 20% by weight of solids of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a copolymerized monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from about 55 to 70% by weight, and said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, to deposit from about 4 to 14% by weight of said solids on said yarn and drying said yarn containing said solids to a total moisture content of not more than about 5% by weight, to coagulate, set and obtain a discontinuous coating of said rubbery material on said yarn.

3. The method of treating predominantly cellulose containing yarn to improve its abrasion resistance, to improve its resistance to crocking and bleeding when dyed and to reduce its shed loss which comprises applying to said yarn an aqueous dispersion containing from about 6 to 20% by weight of solids of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a copolymerized monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from about 55 to 70% by weight, said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, and said solids having an average particle size of from about .02 to .20 micron, to deposit from about 6 to 8% by weight of said solids on the yarn and drying said yarn containing said solids to a moisture content of not more than about 5% by weight, to coagulate, set and obtain a discontinuous coating of said rubbery material on said yarn.

4. The method according to claim 3 containing the additional step of weaving said coated yarn into a fabric.

5. The method according to claim 4 containing the additional step of dyeing said fabric.

6. The method according to claim 3 containing the additional step of dyeing said yarn prior to applying said dispersion thereto.

7. The method according to claim 3 containing the

additional step of dyeing said yarn after said dispersion has been applied thereto.

8. The method according to claim 3 in which said dispersion additionally contains a dye.

9. The method according to claim 8 in which said dye is an oxidized vat dye, said rubbery material is a copolymer of butadiene-1,3 and acrylonitrile, said solids have an average particle size of about .06 micron and said yarn is cotton and containing the additional steps of heating said dispersion in contact with said yarn for a relatively short period of time, removing said yarn from said dispersion, drying, applying an alkaline solution containing a reducing agent for said dye to said treated yarn, removing said yarn from said alkaline solution and oxidizing said dye contained in said yarn.

10. The method according to claim 8 in which said dye is indigo.

11. Textile material having predominantly cellulose containing yarn having from above 2 to 20% by weight on said yarn of a coagulated, set and discontinuous coating of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a copolymerized monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from 35 to 90% by weight and said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, said coated yarn exhibiting improved abrasion resistance, improved resistance to crocking and bleeding when dyed and a reduction in shed loss and being essentially dry and non-tacky.

12. Textile material having predominantly cellulose containing yarn having from about 4 to 14% by weight on said yarn of a coagulated, set and discontinuous coating of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a copolymerized monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from about 55 to 70% by weight and said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, said coated yarn exhibiting improved abrasion resistance, improved resistance to crocking and bleeding when dyed and a reduction in shed loss and being essentially dry and non-tacky.

13. Textile material having predominantly cellulose containing yarn having from about 6 to 8% by weight on said yarn of a coagulated, set and discontinuous coating of a rubbery material selected from the group consisting of a polymer of a diene monomer and a nitrile monomer and a polymer of a diene monomer and a nitrile monomer with up to 35% by weight of said second named polymer of a monomer selected from the group consisting of styrene, chlorostyrene, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-vinyl pyridine, methyl vinyl ketone and vinylidene chloride, said diene being an open chain conjugated diene hydrocarbon having from 4 to 8 carbon atoms and being present in said polymers in an amount of from about 55 to 70% by weight and said nitrile being selected from the group consisting of acrylonitrile, methyl acrylonitrile, ethyl acrylonitrile and chloroacrylonitrile and mixtures thereof, said coated yarn exhibiting improved abrasion resistance, improved resistance to crocking and bleeding when dyed and a reduction in shed loss and being essentially dry and non-tacky.

14. Textile material according to claim 13 containing additionally a dye.

15. Textile material according to claim 14 in which said dye is a vat dye, said rubbery material is a copolymer of butadiene-1,3 and acrylonitrile and said yarn is cotton.

16. Textile material according to claim 14 in which said dye is indigo.

17. Cotton denim yarn having an essentially dry and non-tacky discontinuous coating covering the surface of said yarn of from about 6 to 8% by weight of a coagulated and set rubbery copolymer of from about 55 to 70% by weight of butadiene-1,3 and the balance acrylonitrile.

18. Cotton denim fabric having an essentially dry and non-tacky weft yarns and warp yarns, said warp yarns containing indigo and an essentially dry and non-tacky, discontinuous coating covering the surface of said warp yarns of from about 6 to 8% by weight of a coagulated and set rubbery copolymer of from about 55 to 70% by weight of butadiene-1,3 and the balance acrylonitrile, said warp yarns not being adhesively bound together.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,840,442 June 24, 1958

Edward Abrams et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 64, after "methyl" strike out the comma; column 4, line 2, for "than" read -- then --; column 9, line 47, after "crocking" strike out the first "the" and insert instead -- of --; column 12, lines 31 and 32, strike out "an essentially dry and non-tacky"; line 52, list of references cited, under "UNITED STATES PATENTS", for "2,483,236 Berglund" read -- 2,482,236 Berglund --; line 57, for "2,628,151 Warmsley et al." read -- 2,628,151 Walmsley et al. --.

Signed and sealed this 21st day of October 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents