United States Patent Office 3,445,177
Patented May 20, 1969

3,445,177

DISCHARGE PRINTING A DIRECT-DYE DYED HALOALKANOL CROSSLINKED CELLULOSE FABRIC AND CREASEPROOFING WITH AN AMINOPLAST

James H. McKesson, Spartanburg, S.C., assignor to Deering Milliken Research Corporation, Spartanburg, S.C., a corporation of Delaware

No Drawing. Filed June 20, 1963, Ser. No. 289,438
Int. Cl. D06p 5/00, 7/00
U.S. Cl. 8—17 2 Claims

This invention relates to printing and more specifically to printing cellulose fabrics which have been modified so as to have an improved configurational memory.

It is well known that fabrics can be formed which have a tendency to return to a predetermined configuration after washing. For example, by applying certain resins to fabrics and curing the resin while the fabric is in a flattened condition, one can obtain a fabric which when allowed to dry in a flat condition has a pressed appearance and requires no ironing. It is also known that fabrics having an improved configurational memory may be obtained by treating a cellulosic fabric with a cellulose cross-linking agent such as those cross-linking agents disclosed in U.S. Patent 2,985,501. More recently cellulosic fabrics with an improved configurational memory have been obtained by combining a cellulose cross-linking treatment with a resin treatment.

In general, however, fabrics which have been treated so as to produce an improved configurational memory cannot be printed by any of the conventional textile coloration methods, that is to say, cellulosic fabrics which have been processed so as to have an improved configurational memory are not suitable for use with conventional dyestuffs such as for instance directs, basics, vats, pigments, naphthols, azoics, sulfurs, reactives and the like. The aforementioned dyestuffs are correspondingly unsuitable for use in any of the well-known printing methods such as discharge printing, both white and color, and direct or simple application printing of cellulosic fabrics having an improved configurational memory.

In discharge printing, it is first necessary to dye the fabric with color that can be readily discharged. The colors employed are mostly direct dyes, diazotized dyes and developed dyes, none of which are very fast to washing. Dyes of this nature will develop streaks, unevenness, color variations and general nonuniformity whenever an attempt is made to place them on a fabric which has been previously treated with any type of finishing operation. It is therefore impossible to conduct discharge printing operations upon a cellulosic fabric which has been subjected to configurational memory imparting treatments and especially those configurational memory imparting treatments which employ the use of cellulose cross-linking agents.

In ordinary application printing such as for instance, pigment printing by means of a roller, unevenness, streakiness and color variations will frequently develop when the printing is carried out upon a fabric which has previously been treated so as to impart a configurational memory to the fabric. The coloration nonuniformities are especially pronounced where a resin treatment has been employed in producing the improved configurational memory.

It is therefore an object of this invention to provide a process for printing cellulose fabrics having an improved configurational memory.

It is another object of this invention to provide a process for printing cellulose fabrics having an improved configurational memory wherein the improved configurational memory was obtained by treating the fabric with a resin.

It is still another object of this invention to provide a process for printing a cellulose fabric having an improved configurational memory wherein the improved configurational memory was obtained by treating the cellulosic fabric with a cross-linking agent and then treating the cellulosic fabric with a resin.

In accordance with this invention it has now been discovered that a cellulosic fabric having an improved configurational memory may be printed in a satisfactory manner if the printing operation is carried out prior to treatment of the cellulosic fabric with a resin. In the event that a discharge printing technique is to be employed on a cellulosic fabric having an improved configurational memory wherein the improved configurational memory was obtained by treating with a cross-linking agent followed by a resin treatment, the ground shade should be applied prior to treatment with the cross-linking agent and the discharge of the ground color should be carried out intermediate the cross-linking treatment and the resin treatment. It should be understood that whether the printing process being employed is a discharge printing process or a direct or simple application printing process that the printing operations are always carried out prior to deposition of a resin on the cellulosic fabric.

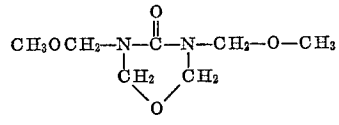
The improved configurational memory cellulosic fabrics to be employed with the printing process of this invention are resin treated cellulosic fabrics and preferably cellulosic fabrics which are treated prior to resin application with an alkali catalyzed cellulose cross-linking agent which results in the cellulosic fibers being cross-linked with linkages of from 3 to 15 carbon atoms in length. The reaction with the cellulose cross-linking agent is conducted with the cellulosic fibers in a moist condition and while the cellulosic fibers are swollen by contact with a basic aqueous solution.

Almost any cellulosic fabric to which resins can suitably be applied can be processed according to this invention, the term "cellulosic" being defined for purposes of this specification and claims to include unmodified cellulose and cellulose modified by etherification or esterification of a portion of the hydroxy groups.

Examples of suitable cellulosic fabrics include fabrics formed from natural cellulose fibers such as cotton and linen fabrics and fabrics formed from regenerated cellulose fibers such as viscose rayon fabrics. If desired, fabrics formed from cellulosic fibers in which the percentage of free hydroxy groups have been replaced by ester or ether groups can be processed according to this invention although it will be understood that the cellulosic fibers should be alkali insoluble, the phrase "alkali insoluble" being defined to mean, in this specification and claims, insoluble in 1% to 5% sodium hydroxide solution. Also, since the new process requires cross-linking of the cellulosic fibers by reaction of a cross-linking agent with free hydroxide groups of the cellulosic fibers, at least some free hydroxy groups must be present in order to obtain a satisfactory degree of cross linkage, but normally cellulosic fibers which contain as few as 1.8 free hydroxy groups per anhydro glycose unit result in sufficient cross linkage for satisfactory results. In view of the above it will be seen that cellulosic fabrics, the fibers of which contain a limited number of acetyl groups, such as cellulose acetate fabrics of a relatively low acetyl content, or fabrics, the fibers of which contain a limited number of methyl ether groups, such as partially methylated cellulose, can be processed according to this invention under proper conditions, but that cellulosic fabrics, the fibers of which have been fully etherified or esterified are not normally suitable for use in the process of this invention.

The resinous materials which can be employed in the process of this invention and which will hereinafter be referred to simply as "textile resins" are low molecular weight (less than 1,000), water soluble, acid or acid salt catalyzed materials which are thermosetting at least in the presence of cellulosic materials as above defined. The

largest class of resins within this group comprises the aminoplast resins formed by reacting compounds such as urea and melamine with formaldehyde, and specific examples of resins within this class include urea formaldehyde resins such as the resin commercially available under the trade name of "Rhonite 610;" methyl ethers of urea formaldehydes such as the resin sold under the trade name of "R–2 Resin;" acrolein urea formaldehyde resins; cyclic ethylene urea formaldehyde resins such as the resin sold under the trade name of "Zset" and the resin sold under the trade name of "R–1 Resin;" trimethylol acetylene diurea; tetramethylol acetylene diurea; melamine formaldehyde resins such as the resins sold under the trade names "Resloom H. P." and and "Resloom L. C."; methylated melamine formaldehyde resins such as the resin sold under the trade name of "M–3 Resin," or the resin sold under the trade name of "M–75 Resin;" copolymers such as a copolymer of melamine formaldehyde and ethylene urea formaldehyde; and the resin known to the trade as Uron which has the formula:



In addition to resins of the above type, one can suitably employ epoxy resins which come within the general group set forth above and specific examples of suitable resins of this class include the diglycidyl ether of ethylene glycol, the triglycidyl ether of glycerol, and the epoxy resin sold under the name of "Eponite 100." Still another class of resins which can suitably be employed are the triazinone resins and any member of this type of resins coming within the above defined group can give satisfactory results according to the process of this invention. Still another resin which can be employed is tris(1-aziridinyl)phosphine oxide which is prepared by reacting three moles of ethyleneimine with one mole of $POCl_3$ and which is known to the trade as "APO Resin" or "Imine I. P. Resin." One need not employ a single resin material but can employ blends of resins of the above type or copolymers where available. Likewise, it is not necessary that the resin be entirely free from water insoluble components since it has been found that dispersed particles of water insoluble materials in the resin solution are not deleterious even though any portion of the resin that is water insoluble does not contribute to the beneficial results obtainable according to this invention. Some of the commercially available resinous materials mentioned above contain small percentages of water insoluble polymeric materials and while an aqueous mixture of such resins can be filtered if desired, equally satisfactory results are generally obtained by employing the unfiltered material.

Suitable acid catalysts for resins of the above types are well known in the art. Urea formaldehyde and melamine formaldehyde resins are best catalyzed by chloride or nitrate salts of hydroxyalkyl amines such as monoethanol amine hydrochloride or 2 amino-2 methylpropanol nitrate. Cyclic ethylene urea formaldehyde resins, acetylene diurea formaldehyde and the uron resins are preferably catalyzed by zinc nitrate or by magnesium chloride. The epoxy resins are preferably catalyzed by acid fluoride salts, such as the catalyst compositions available under the trade names of "Curing Agent 48" and "Curing Agent 20." The above catalyst are all characterized by their ability to furnish hydrogen ions which are necessary for the condensation or etherification reactions taking place during the curing cycle. Generally any amount of catalyst up to about 5% by weight of the solution will give satisfactory results with the preferred range being from about 0.5% to 2% by weight of the resin solution.

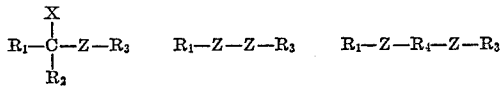
The amount of resin which is applied to the textile fabric according to this invention can be varied within wide limits. It is a general rule that the greater the degree of cross linkage, the smaller the amount of textile resin which can advantageously be employed, and one can obtain results by employing only a relatively small amount of resin on a highly cross-linked cellulosic fabric which are comparable to those obtained by employing a relatively larger amount of textile resin on a cellulosic fabric the fibers of which have been cross-linked to only a slight degree. In most instances, it is desirable to employ only a small amount of the resin material and from about 1% to 5% resin solids on the weight of the fabric generally gives optimum results. Due to the synergistic action of the cross-linking agent and the textile resin, the effectiveness of the textile resin is greatly increased as compared to prior art procedures of resin applications to cellulosic fabrics and satisfactory minimum care characteristics and wrinkle resistance can sometimes be obtained by the procedure of this invention employing as little as 0.5% resin solids, based on the weight of the fabric. At the other extreme, an amount of resin material equal in some instances to as much as 10%, to 15% by weight of the fabric can be employed without imparting an unacceptable hand, but the use of such large amounts of resin is generally not necessary and is not economically desirable.

The textile resins employed according to this invention are, in each instance, water soluble and are applied in the form of an aqueous solution containing the desired amount of catalyst material. Conventional padding equipment is suitable for this operation and with such apparatus the textile fabric can be passed through an aqueous solution of the resin and thereafter extracted, for example by being passed through squeeze rolls, to result in sufficient solution being picked up by the fabric to provide the desired amount of resin solids on the fabric. Following the resin application, the fabric is dried and cured at any suitable curing temperature. The most advantageous curing temperature depends upon the particular resin and catalyst employed, but as a general rule a curing temperature in the range from about 100° C. to 200° C. and preferably between 150° C. and 180° C. is satisfactory. The curing temperature should be maintained for from 10 seconds to 30 minutes with the preferred range being from 30 seconds to 5 minutes depending on the temperature, amount and type of catalyst, and the particular resin compound.

Any cellulose cross-linking agent which results in cross-linkages of from 3 to 15 carbon atoms in length can be employed in the process according to this invention, the phrase "cellulose cross-linking agent" being defined to mean a compound having two or more "connective groups" or in other words, groups which are capable or potentially capable of reacting with the hydroxy groups of cellulose to form ether linkages. Normally the cross-linking agent will have only two connective groups as above defined but in some instances the agent may suitably have as many as four connective groups. In saying that the cross-linking agent results in cross-linkages having from 3 to 15 carbon atoms, it is not intended to exclude the possibility that the linkages formed by the cross-linking agent contain elements other than carbon, such as for instance oxygen, nitrogen, sulfur, silicon, or other polyvalent elements known to form stable organic linkages. Likewise, the cross-linkage may contain substituent groups or side chains and examples of substituent groups which may be present include keto groups, hydroxy groups, halogen groups, and methyl groups. It should also be emphasized that the cross-linking agents while spoken of as having two or more reactive groups, need not possess groups, as it is initially employed in the process of this invention, which are capable of reacting directly with hydroxy groups since the reactive groups can suitably be transformed in situ as a result of the action of the catalyst to give connective groups capable of reacting with cellulose to give a polyether cross-linkage.

Cross-linking agents suitable for use herein may further

be defined as being agents of the type which are capable of being represented by one of the following formulae:



wherein X represents halogen, R_1, R_2 and R_3 represent, in each instance, a member selected from the group consisting of hydrogen and mono-valent, non-functional radicals, R_4 represents a divalent connecting radical and Z, in each instance, represents a divalent radical selected from the group consisting of those capable of being represented by one of the formulae:



wherein R_5 and R_6, in each instance, represent hydrogen or a monovalent, non-functional radical, and X represents halogen.

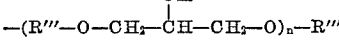
R_1, R_2, R_5 and R_6 in the above formulae, in each instance, preferably represent hydrogen since such compounds are the most readily prepared but they can in one or more instances represent lower alkyl groups such as methyl or ethyl, hydroxyalkyl groups such as hydroxymethyl or hydroxyethyl, monocyclic aryl groups such as phenyl or tolyl, cycloalkyl groups such as cyclohexyl, haloalkyl groups such as chloromethyl and chloroethyl, or R_1 and R_3 can together represent a divalent connecting radical such as a methylene or an ethylene radical. The only requirement is that R_1, R_2, R_5 and R_6 must not be such as to prevent the compound from reacting with at least one hydroxy group in two different cellulose molecules. R_4 can represent any divalent connecting group but in most instances will represent either an alkylene group such as methylene, ethylene or propylene, a hydroxyalkylene group such as hydroxypropylene or a group of the formula

$$—R—Y—R'—Y—R''—$$

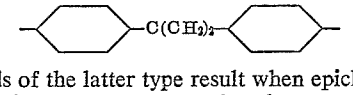
wherein Y represents oxygen or sulfur, R and R'' represent lower alkylene groups such as methylene or ethylene and R' represents any divalent connecting radical as illustrated by a lower alkylene group, a lower hydroxyalkylene group such as 2-hydroxypropylene, a monocyclic aryl radical such as phenyl or tolyl, a radical of the formula

$$—C_2H_4(O—C_2H_4)_n—$$

wherein *n* is an integer of from 1 to about 20 or a radical of the formula



wherein *n* represents an integer of from 1 to about 5 and R'' represents a divalent hydrocarbon radical as illustrated by



Compounds of the latter type result when epichlorohydrin is reacted with less than an equal molar quantity of a dihydric alcohol or phenol. It should also be mentioned that when a cross-linking compound correspondingly to one of the formulate in the preceding paragraph contains two Z groups, the groups may be the same or different. Specific illustrative examples of suitable cross-linking compounds are: 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol, 2,3-dibromo-1-propanol, m-di(β,γ-epoxypropoxy)benzene, 1,3-di(β-hydroxy-γ-chloropropoxy)-2-propanol, 1,2-di(β-hydroxy-γ-chloropropoxy)ethane, 1,2-di(β,γ-epoxypropoxy)ethane, 1,2;3,4-diepoxybutane, 1,2;5,6-diepoxyhexane, 1,5-dihydroxy - 2,4 - dichloro-cyclohexane and 2,6-dichloro-3,4,5-trihydroxy-5-hydroxymethylheptane. The preferred cross-linking compounds are 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol, and mixtures of the two.

The amount of the alkali catalyzed cross-linking agent reacted with the cellulosic fabric may be varied within relatively wide limits but according to the process of this invention only a small degree of cross-linkage is necessary. In some instances satisfactory results can be obtained by reacting a cellulosic fabric with only enough of the alkali catalyzed cross-linking agent to theoretically result as few as 0.0003 cross-link per anhydro glucose unit, the phrase "anhydro glucose unit" being used in a generic sense to include instances where the hydroxy groups of the cellulosic material are in part etherified or esterified, and in most instances the reaction of the fabric with an amount of the cross-linking agent capable of resulting in more than 0.08 cross-link per anhydro glucose unit is not desirable. Best results are generally obtained when the fabric is reacted with an amount of the alkali catalyzed cross-linking agent theoretically capable of providing from 0.001 to 0.01 cross-link per anhydro glucose unit. The cross-linking agent or mixture of cross-linking agents is preferably applied in relatively pure form, or in other words, without the use of a solvent or diluent, but due to the small degree of cross-linkage necessary in accordance with this invention, the cross-linking agent can be employed in an organic solvent or in most instances even in the form of an aqueous solution.

The basic material employed as a catalyst for the cross-linking reaction is preferably an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide but other basic materials such as sodium silicate and quaternary ammonium bases as illustrated by trimethylphenylammonium hydroxide and tetramethylammonium hydroxide can also be employed with less satisfactory results. The basic catalyst for the cross-linking reaction is employed in the form of an aqueous solution of a concentration which provides an active concentration on the fabric of from 1% to 20% and preferably from 5% to 15% by weight. For example, when the basic solution is applied to dry fabric, the concentration of the basic solution is preferably from 5% to 15% by weight. The basic solution may be applied to the fabric either before or after the cross-linking agent is applied and if precautions are taken to prevent excess reaction of the cross-linking agent with water, the basic catalyst and the cross-linking agent can even be applied to the fabric simultaneously. Generally, it is preferred that the basic catalyst be applied prior to the application of the cross-linking agent by means of conventional padding equipment which permits the fabric to be immersed in an aqueous solution of the base and thereafter squeezed or extracted to remove excess basic solution. Alternatively, the basic catalyst solution can be applied by means of sprays, Scotch rolls, or in instances where the cross-linking agent is applied first, the fabric can simply be immersed in an excess of the basic solution of a proper concentration and the reaction allowed to take place during the time the fabric is so immersed.

As previously stated, the cellulosic fabric with which this invention is concerned is a cellulosic fabric which has been subjected to a cross-linking treatment and a resin treatment. Where the printing technique employed is a direct or simple application printing technique, the general procedure followed is to cross-link the cellulosic fabric, wash and dry the fabric, print the fabric, develop the printed color, wash and dry again, apply resin and cure and then subject the fabric to a final washing and drying operation.

The following specific examples of direct or simple application printing are given for purposes of illustration and should not be considered as limiting the spirit or scope of this invention.

EXAMPLE I

A 180 cotton sheeting is immersed into a freshly prepared aqueous solution containing 5% divinyl sulfone and 2% sodium hydroxide and the cloth is thereafter squeezed between rubber rolls to remove excess solution

such that the pickup is about 80%. The wet fabric is rolled into a neat roll, wrapped in polyethylene plastic and aged for 30 minutes. It is then neutralized with dilute acetic acid, thoroughly washed and dried.

A printing paste is then prepared as follows:

Ahcovat golden yellow RK color index 59105	lbs.	3
British Gum	lbs.	250
Cornstarch	lbs.	80
Potassium carbonate	lbs.	100
Hydrosulfite FS	lbs.	150
Glycerine	gallons	5
Turpentine	gallon	1

The yellow printing composition is then applied to the cross-linked cellulosic fabric by means of engraved copper rolls. The fabric is then steam aged, oxidized, washed and dried. The printed fabric with the color thus developed is again washed and dried and padded with a 3% aqueous solution of dimethylol methyl triazinone resin containing 1% zinc nitrate. The resin padded fabric is then dried and cured for 10 minutes at 150° C. and then subjected to a final washing and drying operation. The finished fabric has a pleasing yellow printed design and is found to have excellent minimum care characteristics.

EXAMPLE II

A plain weave cotton fabric made of 30's yarn and containing 80 picks and 80 ends to the inch is impregnated with an aqueous solution containing 15% 1-3-dichloropropanol-2. The impregnated fabric is squeezed out between rubber rolls to a pickup of 80% and immersed into a hot (90° C.) aqueous solution containing 15% by weight sodium hydroxide and 18% sodium chloride. The fabric is kept retained in said alkaline solution for a period of 1 minute and is thereafter removed and thoroughly washed and dried.

A vat dye printing composition is then prepared having the following ingredients:

Thio Indigo Red B (Colour Index No. 1207)	lbs.	3
British Gum	lbs.	250
Cornstarch	lbs.	80
Potassium carbonate	lbs.	100
Hydrosulfite FS	lbs.	150
Glycerine	gallons	5
Turpentine	gallon	1

The cross-linked cellulosic fabric is printed with the red printing composition by use of screen printing equipment. The color of the printed fabric is developed by passage of the fabric through a vat ager employing circulating steam at temperatures of about 215° F. for periods of from about 7 to about 8 minutes in an air-excluding box. After ageing, the goods are oxidized by treatment with a 1% sodium perborate solution. The sodium perborate solution is then neutralized on the fabric by the addition of acetic acid. The printed fabric is then cleaned by placing in a soap bath at 140° F., the soap bath employing a suitable detergent such as for instance Surfonic N-95 (surface active agent). The printed fabric is then passed into a 2% aqueous solution of melamine formaldehyde resin. The resin impregnated fabric is then squeezed between rubber rolls to wet pickup of about 70% and thereafter air dried and cured for a period of about 10 minutes at a temperature of about 150° C. The fabric is then given a final washing and drying and is found to have a pleasing printed red pattern and to have a high degree of tear strength and crease resistance.

In general when the printing process employed is a discharge printing process, it is necessary to dye the fabric with colors that can be readily discharged prior to treatment of the fabric with the cross-linking agent. The discharge colors applied may be satisfactorily discharged only if discharging operations are conducted prior to treatment of the fabric with a resin. The procedure may therefore be described as follows:

Dye fabric using a discharge ground shade
Wash and dry
Apply cross-linking agent
Wash and dry
Discharge on roller printing or screen printing machine
Wash and dry
Apply resin and cure and then subject the fabric to a final washing and drying operation.

The following specific examples of discharge printing are given for purposes of illustration and should not be considered as limiting the spirit or scope of this invention.

EXAMPLE III

A white discharge composition is prepared having the following composition:

Formopon (sodium sulfoxylated formaldehyde)	lbs.	20
Water	gallons	3½
Ambertex (starch base paste)	gallon	1
Anthraquinone paste	pints	2
Aquaprint White 5154 (white textile color)	lbs.	3½
Vat paste composed of 250 lbs. British Gum, 80 lbs. cornstarch, 100 lbs. potassium carbonate, 150 lbs. sodium hydrosulfite, 5 gallon glycerine and 1 gallon turpentine	gallons	14
Potash composition containing 46¾ parts of calcined potash, 44 parts Formopon (sodium sulfoxylated formaldehyde) and 4¾ parts glycerine	gallon	1

180 cotton sheeting (96 warp threads per inch width and 84 threads per inch of length is dyed using as a ground shade Direct Black 22 color index 35435 (Nyango Fast Black FAM). The dyed fabric is then washed and dried and immersed in an aqueous solution containing 15% 1-3-dichloropropanol-2. The fabric is then squeezed out between rubber rolls to a pickup of 80% and immersed into a hot (90° C.) aqueous solution containing 15% by weight of sodium hydroxide and 18% sodium chloride. The fabric is kept retained in said alkaline solution for a period of 1 minute and is thereafter removed and thoroughly washed and dried. Preselected areas of the black dye are then discharged on a screen printing machine employing the white discharge printing composition given above and the fabric is then vat aged, oxidized and washed and dried. The fabric is then immersed in an aqueous solution containing 4% tetramethylol melamine and 1% of ethanolamine hydrochloride, squeezed out between rubber rolls to a pickup of 75%, dried and cured for 2 minutes at 160% C. The cotton fabric prepared in this manner is found to have a pleasing white printed pattern on a black ground shade and to have excellent wrinkle resistance.

EXAMPLE IV

A color discharge composition is prepared having the following composition:

Formopon (sodium sulfoxylated formaldehyde)	lbs.	20
Water	gallons	3½
Ambertex (starch base paste)	gallon	1
Sulfanthrene Pink FS Color index 73360	lbs.	4
Vat paste containing 250 lbs. British Gum, 80 lbs. cornstarch, 100 lbs. potassium carbonate, 150 lbs. sodium hydrosulfite, 5 gallons of glycerine and 1 gallon of turpentine	gallons	14
Potash composition containing 46¾ parts of calcined potash, 44 parts Formopon (sodium sulfoxylated formaldehyde), 4¾ parts glycerine	gallon	1

An 80 square cotton fabric is dyed using as a ground shade Direct Orange 73 color index 25200 (Rosanthrene Orange RSS Concentrated). The dyed fabric is then washed and dried and then wetted with water until it contains approximately 70% by weight water and then passed through pad box containing a quantity of 15% sodium hydroxide. The cloth is then passed through a

pair of squeeze rolls to remove excess moisture and then passed into contact with the upper peripheral surface of the stainless rolls the lower surface of which is in contact with a quantity of epichlorohydrin. The speed of the roll is adjusted such that approximately 40% by weight of the epihalohydrin is deposited on the fabric. The fabric is thereafter passed through a short tenter frame and wrapped into a tight roll. The roll of material is then wrapped in a sheet of polyethylene plastic and allowed to stand for 18 hours, following which time it is unwound and thoroughly scoured in water. The material is then dried on a tenter frame and unwanted portions of the pink printing are discharged on a screen printing machine employing the color discharge composition previously given. The fabric is then vat aged, oxidized and washed and dried and then padded with a 3% aqueous solution of dimethylol methyl triazinone resin containing 1% zinc nitrate, dried and cured for 10 minutes at 150° C. The fabric is found to have an attractive pink print on an orange ground shade and to have excellent minimum care characteristics.

Having thus disclosed the invention, what is claimed is:

1. A process for the preparation of a discharge printed cellulosic fabric having an improved configurational memory comprising the steps of dyeing said fabric with a direct dye as a ground shade, contacting said dyed fabric under aqueous alkaline conditions with a short chain halogenated hydroxyalkane cross-linking agent, discharge printing the cross-linked celluosic fabric with a mixture including a sulfur salt reducing agent and then impregnating the printed fabric with an acid catalyzed aminoplast having a molecular weight not greater than 1,000 and curing said aminoplast.

2. The process of claim 1 wherein said fabric is impregnated with from about 0.5% to about 10% by weight aminoplast solids based on the dry weight of the fabric.

References Cited

UNITED STATES PATENTS

2,123,152	7/1938	Rivat.	
2,234,889	3/1941	Boulton et al.	8—17 X
2,596,192	3/1952	Womble	117—161 X
2,985,501	5/1961	Gagarine	8—120
3,130,001	4/1964	Fenner et al.	8—17

FOREIGN PATENTS

445,261	4/1936	Great Britain.
589,193	6/1947	Great Britain.
696,282	8/1953	Great Britain.
802,574	10/1958	Great Britain.

OTHER REFERENCES

McMullen et al.: Textile Colorist, p. 460–463 and 542–544, pub. 1931.

Saunders et al.: Polyurethanes Chemistry and Technology, Part II, pp. 735–740. Pub. by InterScience Pub., New York, N.Y., 1964.

DONALD LEVY, *Primary Examiner.*

U.S. Cl. X.R.

8—18, 69