

1

3,508,854

**DYEABLE DEXTRIN-MODIFIED LATEX  
TREATED ARTICLE**

Malcolm R. Sockol, Pittsfield, Mass., and Chester J. Kawa, Naugatuck, Conn., assignors to Uniroyal, Inc., a corporation of New Jersey

No Drawing. Filed Nov. 17, 1966, Ser. No. 594,999

Int. Cl. D06p 5/00, 7/00

U.S. Cl. 8—18

7 Claims

**ABSTRACT OF THE DISCLOSURE**

The invention relates to a rubber coated textile fabric comprising a textile fabric substrate and an elastomeric polymer film coating thereon wherein the polymer film contains a dextrin dye acceptor which renders the elastomeric polymer film dyeable with the identical textile dyes which are capable of dyeing the textile fabric substrate.

This invention relates to a dyeable latex compound which is usually applied to the back of textile articles and in particular relates to the addition of dextrin, to a latex of an elastomeric polymer which latex is usually applied to the back of a textile fabric substrate and cured, wherein the dextrin renders the cured latex film dyeable with the identical textile dyestuffs used to dye the textile fabric substrate.

In accordance with the present invention, a layer of compounded latex which contains dextrin is applied by any suitable means to a dyeable substrate such as the back of a textile fabric, and said layer is dried and cured to a film whereupon both the textile fabric and substrate and latex film are dyed simultaneously in one dye bath. A "latex" is a dispersion of synthetic rubber or natural rubber in an aqueous medium. The terms "compounding a latex" or "compounded latex" used in this specification describe the selection of additives and their incorporation into the latex of the synthetic or natural rubber so as to give a homogeneous mixture ready for subsequent processing steps. In accordance with the present invention, the latex film and the textile fabric substrate both absorb ordinary textile dyes from the dye solution. The dye is absorbed and fixed by both physical and chemical attraction into the textile fabric substrate and the cured latex film due to the dextrin, and as a result, the dyes in the textile fabric substrate and cured latex film are fast to washing (leaching), light, and crocking. Thus the present invention provides a novel method so that both a textile fabric substrate and a cured latex film which has been applied thereon are dyed simultaneously in the same dye bath to the same color intensity.

Latex coatings are applied to numerous textile fabrics in order to (1) increase the weight of the goods, (2) to prevent seam slippage, (3) to improve the "hand" and (4) to reduce edge tear. It has been the experience in the prior art that when latex or latex compounds, usually white to off-white in color, are applied to dyed pieces of fabric, the latex film can be detected when viewing the fabric's "face," that is, when viewing the fabric from the non-coated side. This detection of the latex through the substrate is called the "grinning effect" because the white color of the latex compound shows a sharp contrast with the colored face of the fabric. One method which has been used commercially to reduce the "grinning effect" is

2

the use of a pigmentation process. In a pigmentation process, the latex is colored with pigment so that the color of the latex will approximate or correspond to the face shade of the textile fabric substrate which is to be dyed after the latex is applied thereon. The latex compound is applied to the back of the textile fabric substrate and is dried and cured. The textile fabric containing the pigmented latex film is dyed. The color of the pigmented latex corresponds to the textile fabric so that relatively no "grinning effect" from the pigmented latex film occurs. This process has a number of undesirable features. Among them are: (1) An individual latex compound must be pigmented to the color to which the fabric will eventually be dyed. (2) An excess of latex compound which has been pigmented to match a particular face shade is often wasted since it cannot be used on fabrics that will be dyed eventually a different color. (3) The pigmentation of the latex does not eliminate the dyeing process since the textile still has to be dyed to a specific color. (4) Woven fabrics that contain more than one class of fibers may be cross-dyed (e.g., in a given fabric one class of fibers may be dyed one color and another class of fibers may be dyed a different color), and since the latex which is pigmented to only one shade or color is applied to a fabric, an undesirable contrast is often present in many cases due to the latex showing through the face of the light colored cross-dyed fabric.

Elastomeric latices are extremely difficult, if not impossible to dye with most conventional textile dyes since they lack dye receptive sites. It was because of this lack of dyeability that the above noted pigmentation process was developed. We have performed extensive tests to determine whether latices of elastomeric polymers can be modified to become dyeable by the addition of dye acceptor compounds to said latices, and if so, exactly which dye acceptor compounds work effectively when incorporated into the various latices. The results of these tests have shown that when certain cellulosic or cellulosic derivative compounds such as hydroxy-ethyl or hydroxy-methyl cellulose or well-known dye acceptor compounds such as polyvinylpyrrolidone are added to latex and an attempt is made to dye the latex with conventional textile dyes, a number of adverse effects result such as: (1) leaching out of the dye acceptor into the dye bath, (2) thickening or coagulation of the latex compound before or during application unless an excess of stabilizer is used (stabilizers detract from the coating characteristics of the latex), (3) certain dyes are preferentially absorbed and other dyes are not absorbed at all. Certain cationic type starches can be added to a latex without causing the latex to thicken, but these starches will not absorb the type of textile dyes which are used in the present invention. Other possible dye acceptors which could conceivably be used such as the various sugars having a similar composition to dextrin, are not satisfactory dye acceptors since, due to their solubility, they leach out of the compounded latex film into the dye bath when the latex is being dyed.

In addition to the adverse effects stated above, another difficulty associated with the use of polyvinylpyrrolidone in latex is that the modified latex does not age properly. Specifically the latex film is not light fast, which means that after exposure to an ultraviolet radiation source for a relatively short period of time, such as about 20 hours, the color of the latex fades. Normal industry trade requirements are 60-80 hours without an appreciable break in color. This fading effect indi-

cates that the polyvinylpyrrolidone is not a commercially acceptable dye acceptor. None of the abovementioned phenomena occur when dextrin is used as the dye acceptor.

The present invention provides a novel method for dyeing any of the cured latex films disclosed herein by incorporating dextrin into the compounded latices. Dextrin possesses the right combination of properties including (1) good dye receptivity with most of the classes of dyes in textile-dyeing, (2) relatively low solubility when incorporated into the latex to resist leaching by the dye bath and (3) not affecting the chemical and mechanical stability of the latices in which it is used. The use of dextrin in the compounded latex provides an efficient method of reducing the "grinning effect" problem. By simply coating the back of the textile fabric substrate with a latex compound containing dextrin, the latex is dyeable with the same dyestuffs that are used to dye the textile fabric substrate during the dyeing step. Thus in the present invention the compounded latex film is dyed simultaneously with the textile fabric substrate in a single dyeing process. This method eliminates the need for pigmenting individual latex compounds for each desired fabric color. It also eliminates waste of the latex compound, unnecessary use of needed storage space, and inventory problems since only one latex compound has to be made up and coated onto the textile which can be dyed then to any desired color.

It is therefore an object of this invention to provide a dyed textile article having a cured latex coating on the back of a textile fabric substrate which is capable of being dyed to substantially the same intensity as the fibers in the textile fabric substrate.

Another object is to provide a latex compound, suitable for coating textile fabric substrates, which is colored to the same intensity as the fabric and which is fast to light and washing.

In the present invention the substrate or base layer consists of any type of woven or non-woven textile fabric or material which can be dyed with various common textile dyes. The textile fabric used can be a woven, tufted or knitted fabric made from cotton, rayon, rayon-acetate, polyester or nylon such as is used in clothing, upholstery, carpet, carpet backing, draperies, curtains, etc. Alternatively a non-woven textile material can be used such as felt, matting, or fabric which is made by the use of a resin binder to hold the fibers together or a needle punching method.

Any conventional latex of an elastomeric rubber polymer may be modified by the addition of dextrin and applied to the surface of any of the aforementioned substrates. An elastomeric polymer is a polymeric material having special properties such as being amorphous when unstretched but developing crystallinity upon stretching. It must be used above its glass transition temperature to be elastic. The elastomeric polymers used in the present invention are inherently high polymers. The useable polymers possess the characteristic of stretching and retracting rapidly and high strength and modulus while stretched, and recover on release of the stress.

Typical examples of the latices of elastomeric polymers which are used in the present invention are the following: styrene-butadiene rubber (SBR); carboxylated styrene-butadiene rubber; natural rubber; butyl rubber, which is generally a copolymer of isobutylene and 1-2% of a diolefin such as isoprene or butadiene; nitrile rubber, which is generally a copolymer of butadiene and acrylonitrile; a carboxylated nitrile rubber, which is generally a carboxylated copolymer of butadiene and acrylonitrile; neoprene rubber (the polymer of 2-chloro-1,3-butadiene), also known as polychloroprene; and acrylic polymers such as polymeric acrylate and methacrylate esters. Acrylic polymers are dyed by a limited number of dye classes in the unmodified form in a latex film, but the addition of dextrin affords dyeability with all of the

classes of dyes mentioned in this specification. Certain additives generally are incorporated into the latices of the elastomeric polymers cited above so that the natural and synthetic rubber latices which are used in this invention have been compounded with the usual ingredients necessary for curing or vulcanization, prevention of oxidation discoloration, embrittlement and aging. In addition, antifoaming or defoaming agents are used, as well as auxiliary chemicals to control wetting and penetration of latex into the textile article. These compounds can be varied selectively to obtain whatever specific properties are desired in the particular latex chosen to be used. The elastomeric polymers are present in an amount between about 25% and 98% based upon the total weight of compound solids in the film and they are preferably present in an amount between about 40% and 97% based upon the total weight of compound solids in the film.

Dextrin, which provides dyeability when incorporated into the latex in accordance with the present invention is a carbohydrate intermediate product produced from starch by hydrolysis due to the action of dilute acids, diastase, ferments or dry heat. The process of making dextrins by breaking down the long molecules of starch is called "dextrinization." Dextrin is an amorphous, odorless powder which is colored white, yellow or brown. The color of the dextrin is determined by the degree of dextrinization with the white dextrin having a low degree of dextrinization and the brown colored dextrin having a high degree of dextrinization. The degree of dextrinization also determines the solubility of the dextrin in water. Thus the dextrin (white) having a low degree of dextrinization is insoluble in water whereas the dextrin (brown) having a high degree of dextrinization is soluble in water. The yellow dextrin has a solubility product value in between the solubility product of the white dextrin and the brown dextrin. Dextrin is soluble in alcohol, does not give the blue iodine reaction of starch, and it is not fermentable. Methods for making dextrin such as is used in the present invention and methods for characterizing it are found in J. A. Radley, "Starch and Its Derivatives," vol. II, 3rd ed., Chapman & Hall Ltd., London (1953), pp. 107-125.

In the present invention we have found that it is particularly advantageous to use between about 1 and 15 parts and preferably between about 5 and 10 parts of dextrins prepared from tapioca starch, wheat starch, potato starch, corn starch, and rice starch per 100 parts of dry weight of latex solids. Thus we use between about 1.0% and 15% of dextrin dye acceptor based upon the weight of latex solids, and preferably between about 5% and 10% of dextrin based upon the weight of latex solids. The dextrin powder which possesses a dark yellow or brown color may not be as satisfactory as the white dextrin powder since the dark color of the dextrin may affect the color of the latex into which it is incorporated, and therefore affect the true color of the dye. We prefer to use the white colored dextrin products having low dextrinization as opposed to the dark dextrin products having a high degree of dextrinization because the water solubility is less in products having a low degree of dextrinization, and therefore the leaching out of the dextrin having a low degree of dextrinization from the latex into the dye bath is reduced since the dextrin with a low degree of dextrinization is relatively insoluble in the dye bath. Dextrin made from tapioca starch such as National Starch Company product number 18-5311 provides extremely satisfactory dyeing results when incorporated into the latex as a dye acceptor. Other preferred dextrins are sold under the trademarks Nadex 772 and Nadex 791. An optional step which may be included in this invention if it is desired to use a lesser amount of dextrin with a low degree of dextrinization is to add a mixture of between

about 1 and 10 parts by weight of a melamine formaldehyde resin, between about 0.25 and 2.50 parts of glyoxal ( $C_2H_2O_2$  also known as oxaldehyde), and between 0.1 and 1.0 parts of  $ZnCl_2$  or  $MgCl_2$  to between 10 and 100 parts of dextrin. The exact proportions of the melamine formaldehyde resin, glyoxal and  $ZnCl_2$  or  $MgCl_2$  added to the dextrin will depend on the water solubility of the particular dextrin used. We have found that the addition of these compounds to pure dextrin greatly reduces the tendency of dextrin with a high degree of dextrinization to leach out of the latex into the dye bath. This is a convenient way to be able to use some of the lesser preferred dextrans having a high degree of dextrinization in the present invention even though they are more water soluble than the dextrans with a low degree of dextrinization. Also the addition of the above noted mixture to dextrin with a low degree of dextrinization results in the use of less dye acceptor than that amount of pure dextrin which is ordinarily required to obtain the same depth of shade. The dextrin containing mixture is added to the latex or latex compound and mixed therein prior to coating the textile fabric substrate. The melamine formaldehyde resin is cured during the elastomeric polymer curing step.

The method of obtaining a dyeable latex treated textile in accordance with the present invention involves the following steps in sequence. Initially, the compounded latex applied to the textile fabric substrate may be compounded in a "single batch" in a suitable mixer by adding a dextrin paste, which is dextrin powder mixed with a suitable amount of water to facilitate dispersion of the dextrin in the latex, to a mixture of latex and desired additives including dispersants, vulcanizers, defoamers, thickeners and extenders (fillers) using the general proportions indicated below in Table II.

Alternatively, a "pre-compounded" latex containing the desired additives and dextrin which has been previously mixed, is added to a mixture of water, filler, extender, dispersant and thickener ingredients just prior to use. This pre-compounding method is preferred because many commercial enterprises maintain their own compounding facilities and therefore need only add the dextrin-containing pre-compounded latex to the extender, thickener, filler and water mixture, or vice versa, to obtain the desired latex composition. This separate compounding method requires less storage space for the latex compound and reduces the transportation cost since water and filler form a large percentage of the weight of the latex compound.

As noted previously the dextrin may be mixed with melamine-formaldehyde resin, zinc or magnesium chloride and glyoxal and added to the "single batch" or "pre-compounded" latex. A typical formula for a dextrin dye composition containing melamine-formaldehyde, zinc chloride and glyoxal which can be added to the "single batch" or "pre-compounded" latex if desired is given in Table I.

TABLE I

Ingredient	Function	Dry parts <sup>1</sup>	
		General	Preferred
(1) Dextrin acceptor.....	Dye acceptor.....	10-100	12
(2) $NH_4LH$ .....	pH stabilizer.....	( <sup>2</sup> )	pH 9
(3) Melamine formaldehyde resin.....	A cross-linking resin.....	1-10	1.0
(4) Zinc chloride.....	Catalyst.....	0.25-1.00	0.25
(5) Glyoxal.....	Cross-linking agent.....	0.25-2.50	0.75

<sup>1</sup> The dry parts are based upon 10-100 parts of dextrin.

<sup>2</sup> To adjust to a pH of 7 to 11.

A typical formula for the latex compound used in the present invention is set forth in Table II as follows:

TABLE II

Ingredient	Dry Parts <sup>1</sup>	
	General	Preferred
(1) Water.....	( <sup>2</sup> )	( <sup>3</sup> )
(2) Filler dispersants.....	0.1-1.0	0.1-0.3
(3) Alkali salt of polymeric carboxylic acid.....	0.2-1.0	0.2-0.5
(4) Extender.....	0-300	100-105
(5) Latex.....	100-105	102-105
(6) Dye acceptor (can be pure dextrin, or a modified dextrin as shown in Table I).....	1-15	5-10
(7) Thickener.....	0-4	( <sup>4</sup> )

<sup>1</sup> Based upon total dry weight of latex compounded solids in the film.

<sup>2</sup> To form 25% to 70% total solids.

<sup>3</sup> To form 35%-50% total solids.

<sup>4</sup> To desired coating viscosity.

The composition shown in Table II is blended to obtain a homogeneous dispersion of the ingredients.

After the latex compound is blended, it is applied to the textile fabric substrate by means of wet rollers, spraying or any known manner for applying coatings to substrates. As an example, the latex coating may be applied to the back side of the textile fabric substrate as it passes over a roller, one surface of which dips into a latex bath upon rotation.

After the application of latex to the back surface of the textile fabric, the textile fabric substrate containing the layer of compounded latex is passed into an oven at a temperature of between about 230° F. and 350° F. to dry and cure the latex. This step evaporates the water from the latex, coagulates the elastomeric polymer and cures the elastomeric polymer thereby giving a latex film capable of being dyed. This step also cures the melamine formaldehyde resin if it is used in the compounded latex to insolubilize the dextrin dye acceptor. The textile fabric substrate with the film of latex thereon can be dyed by any method of exhaustion dyeing.

The dextrans used in the present invention have the ability of absorbing or attracting and fixing dyestuff molecules in the latex film using all of the classes of textile dyestuffs which are used ordinarily in dyeing regenerated or modified celluloses, cellulose, cellulose acetate, polyester, and nylon commonly used in the trade. Among these dyestuffs are the direct dyes including direct and developed, after-treated direct; basic, sulfur, azoic, vat reactive dyes such as, cellulose fiber reactive (e.g., Procions); chrome, dispersed dyes including, dispersed base diazotized; developed and acid type dyes. The following example illustrates the invention.

#### EXAMPLE

A latex compound containing dextrin was applied to various textile fabric substrates indicated in Table III by passing the textile fabric substrates over a roller which has one surface immersed in a latex bath, and upon rotation the latex is carried along the surface of the roller until it is deposited on the back of each sample of the

textile fabric substrate. Each of the resultant products was cured in an oven at the temperature indicated. The coated fabric was then dyed with the dyestuffs shown in Table III for 1 hour at 200° F. The concentration of dye in the dye bath was varied in each case to between about .1 and 5% on weight of textile substrate and latex backing in order to obtain the same intensity of color in the latex back as in the textile substrate. Table III exemplifies the method used. The latex on each of the textile fabric substrates listed in Table III was dyed to the same color intensity as the dyed textile fabric.

meric film coating, said film being formed by applying to said textile substrate a compounded latex comprising between about 100 and 105 parts of a curable elastomeric polymer, between about 1 and 15 parts of dextrin based upon 100 parts of dry elastomer polymer, and water, subsequently drying and curing said compounded latex which has been picked up by said substrate.

2. The dyed latex coated textile fabric as defined in claim 1 in which the elastomeric polymer is selected from the group consisting of styrene-butadiene rubber; carboxylated styrene-butadiene rubber, natural rubber, butyl

TABLE III

Textile fabric substrate	Type of latex	Latex, parts by weight (dry)	Type of Dextrin (commercial product used)	Dextrin parts by weight (dry)	Curing temp. of latex, ° F.	Dye used
Rayon and acetate.	SBC <sup>1</sup>	100	Nadex 791	5	260	Solantine Fast yellow R.L., C.I. No. 29,025.
Do.	SBC <sup>1</sup>	100	do.	5	260	Setacyl Blue BN C.I. No. 61,505.
Do.	SBC <sup>1</sup>	100	Nadex 772	7	260	Fastusol Orange LGGA CF C.I. No. 40,215.
Do.	SBC <sup>1</sup>	100	do.	7	260	Acetamine Red BE C.I. No. 11,210.
Do.	Natural rubber	100	Nadex 791	7	270	Paranol Fast Blue 4GL C.I. No. 34,200.
Do.	do.	100	National Starch Product 18-5311	7	270	Do.
Do.	do.	100	Nadex 772	6	280	Eastman Fast Yellow 4RLF.
Do.	SBR <sup>2</sup> "2000"	100	National Starch Product 18-5311	10	300	Super Brilliant Blue 3GLST.
Do.	Natural	100	do.	10	325	Sirius Red F3B, C.I. No. 35, 780.
Do.	SBC <sup>1</sup>	100	do.	10	260	Fast Orange, UF26.
Do.	Neoprene 842A <sup>3</sup>	100	do.	10	240	Cibacete Blue, Green C, C.I. No. 62,500.
Do.	do.	100	do.	10	240	Celanthrene Brilliant Blue FFS, C.I. No. 61,505.
Nylon and rayon.	Rohm & Haas AC-33 Acrylic emulsion <sup>4</sup>	100	do.	10	250	Wool Red-Brown 5244.
Do.	do.	100	do.	10	250	Diazo Black AW.
Cotton	SBC <sup>1</sup>	100	do.	10	260	Anthraquinone Vat Black BED 5%.
Do.	SBC <sup>1</sup>	100	do.	10	260	Naphthol A.S. 5%, C.I. No. 37,505.
Nylon rayon.	SBC <sup>1</sup>	100	do.	5	270	Irgalan Yellow 2GL Extra 2%, 2GL Orange RL 3%.
Cotton acetate.	SBC <sup>1</sup>	100	do.	7	270	Procion Green M-2BS.
Do.	SBC <sup>1</sup>	100	do.	7	270	Procion Brilliant Red M-5BS.
Do.	SBC <sup>1</sup>	100	do.	7	270	Procion Brilliant Yellow M-4GS.

<sup>1</sup> SBC is carboxylated butadiene-styrene rubber.

<sup>2</sup> SBR is styrene-butadiene rubber.

<sup>3</sup> Neoprene 842A-A polychloroprene latex of approximately 50% solids and a particle size of 50-100 millimicrons.

<sup>4</sup> Acrylic emulsion-A polyacrylic and polymer latex of 46% solids.

We have determined that the above mentioned dyes can be mixed in one dye bath if a cross dyeing effect is desired. In this case the total concentration of the dyes exceeded 5% but the individual concentration of each dye used in the mixture of dyes did not exceed 5%.

Having thus described our invention what we desire to claim and protect by Letters Patent is:

1. In a dyed rubber coated textile fabric comprising, (A) a textile fabric substrate, and (B) an elastomeric polymer film coating thereon, wherein both fabric and elastomeric polymer film coating thereon are dyed to substantially the same shade in a single dyebath with textile dyes, the improvement wherein said film comprises (a) between about 25% and 98% of a cured elastomeric polymer based upon the total weight of compound solids in the film, in admixture with as a dye acceptor (b) between about one part and 15 parts of dextrin based upon 100 parts of dry rubber of said elasto-

rubber, nitrile rubber, carboxylated nitrile rubber, neoprene rubber, and acrylic polymer.

3. The dyed latex coated textile fabric as defined in claim 2 in which the textile dye used to dye said article is selected from the group consisting of direct, basic, sulfur, azoic, vat, reactive, dispersed, developed and acid type dyes.

4. The latex coated textile fabric as defined in claim 1 in which the compounded latex film contains a mixture having between about 1 and 10 parts of dextrin, between about 0.25 and 2.50 parts of glyoxal per 10 to 100 parts of dextrin and between about 0.1 and 1.0 parts of zinc chloride per 10 to 100 parts of dextrin.

5. In a method of preparing a dyed rubber coated textile fabric comprising applying a compounded latex containing between about 25% and 98% of an elastomeric polymer based upon the total weight of compound solids to a textile fabric substrate, drying and vulcanizing

said latex thereon to form an elastomeric film, and subjecting said latex coated textile fabric to a subsequent dyeing treatment with a textile dye, the improvement comprising incorporating into said compounded latex as a dye acceptor between about 1 part and 15 parts of dextrin based upon 100 parts of elastomer polymer whereby said elastomeric film and said textile fabric substrate are dyed to substantially the same shade in a single dyebath.

6. A method of preparing a latex coated textile fabric as defined in claim 5 in which the elastomeric polymer is selected from the group consisting of styrene-butadiene rubber, carboxylated styrene-butadiene rubber, natural rubber, butyl rubber, nitrile rubber, carboxylated nitrile rubber, neoprene rubber, and acrylic polymer.

7. A method of preparing a latex coated textile fabric as defined in claim 6 in which the textile dye is selected from the group consisting of direct, basic, sulfur, azoic, vat, reactive, dispersed, developed and acid type dyes.

## References Cited

## UNITED STATES PATENTS

3,138,431	6/1964	Swiggett	8—18
2,155,326	4/1939	O'Brien	8—91

## FOREIGN PATENTS

493,915	10/1938	Great Britain.
---------	---------	----------------

## OTHER REFERENCES

10 F. Marchionna: Latex and Rubber Derivatives, vol. 11, The Rubber Age, New York, 1937, pp. 251-252.

R. J. Noble: Latex in Industry, 2d ed., Rubber Age, New York, 1953, pp. 169, 289, 644.

15 NORMAN G. TORCHIN, Primary Examiner

J. E. CALLAGHAN, Assistant Examiner

U.S. Cl. X.R.

8—91