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3,685,953

DRY HEAT REACTION OF QUATERNIZED EPOXIDES AND QUATERNIZED CHLOROHYDRINS WITH HYDROXYLATED TEXTILES

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Int. Cl. D06m *13/34*
U.S. Cl. 8—115 9 Claims

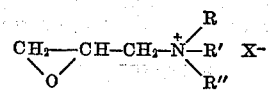
ABSTRACT OF THE DISCLOSURE

Hydroxylised polymers with modified dyeing properties and having hydroxyl groups replaced at least partially by quarternary ammonium groups are provided. These polymers may be made by impregnating a hydroxylised polymer with an aqueous solution containing an epoxypropyl quarternary ammonium salt or a precursor thereof.

The present invention relates to polyhydroxylised polymers, such as cellulose or insolubilised polyvinyl alcohol, bearing quaternary ammonium functional groups and having improved dyeing properties, and to a both simple and economic process for obtaining these polymers.

It is known that the fixation of functional groups with a basic character, such as amine groups, on polyhydroxylated polymer fibres such as cellulose or cellulose derivative fibres confers special properties on the fibres, including a considerable modification of their dyeing affinity. Numerous processes have been tried and have not lead to an industrial application because of certain disadvantages, such as the deterioration of the treated products, the high cost of the treatment, due either to the price of the products, themselves, or to poor useful yields, or even to the complexity of the method used.

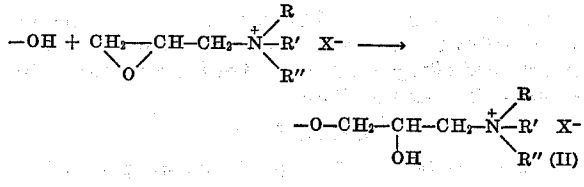
The invention provides a process for treating a hydroxylised polymer usually of a textile nature to modify its dyeing properties, particularly its affinity to fibroreactive dyes, wherein: the hydroxylised polymer is impregnated with an aqueous solution comprising an epoxypropyl ammonium salt of formula



(I)

where R, R′ and R″ are lower alkyl radicals and X⁻ is an anion, for example sulphate, sulphonate and halide, and a strong base as fixation catalyst, particularly alkaline metal hydroxides such as potassium and sodium hydroxides, at a concentration of 0.5 to 10% by weight, preferably 0.5 to 4% by weight; excess water is removed from the impregnated polymer; the polymer is dried at 80 to 140° C., preferably 120° C.; and the polymer is rinsed with water. In practice the concentration of the epoxypropyl ammonium salt in the aqueous solution corresponds to the content of nitrogen required in the final treated polymer.

The reaction can be written as follows:



(II)

(where —OH represents the polyhydroxylised polymer), Formula II being that of a polyhydroxylised polymer bearing quaternary ammonium groups, according to the invention.

Instead of using an epoxypropyl ammonium salt of Formula I directly, a precursor compound of the salt, for example the corresponding chlorohydrin can also be used.

The mode of treatment is generally as follows:

A textile material to be treated is impregnated with an aqueous solution of the quaternary ammonuium salt, at a concentration corresponding to the content of nitrogen requisite for the final product, taking into account the yield and the rate of removal of excess water; the fixation reaction is catalysed by strong bases, particularly alkaline metal hydroxides, such as sodium hydroxide and potassium hydroxide, at the relatively low concentration of 0.5 to 10% by weight, preferably of about 0.5 to 4%, in the aqueous solution. The impregnated material is squeezed out to a retention as low as possible (generally 90%), then dried in a ventilated atmosphere at 80–140° C., preferably 120° C. Continuing this heat treatment a few minutes after complete dryness is often favourable to terminate the fixation reaction. A rinse with water is then sufficient to eliminate any catalyst remaining on the treated textile material.

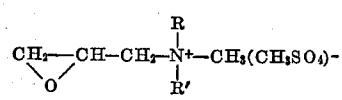
No important result is obtained with a concentration of strong base lower than 0.5%. No additional advantage is obtained with a concentration of strong base greater than 4%. With a concentration of strong base gretae than 10%, the hydoxylised polymer deteriorates and in the case of sodium hydroxide alkali-cellulose is formed. In addition, at a temperature lower than 80° a poor yield is obtained and at a temperature higher than 120° no additional advantage is obtained.

Futhermore, in the chosen treatment conditions, there is obtained fo amounts of fixed nitrogen varying from 0.1 to 0.5%, reproducible fixation yields varying from 60 to 85% in relation to the deposited active product. This is at least unexpected, because with epoxyamines, which are related compounds, a treatment in the conditions according to the invention has only given low fixation yields. In this sphere, it has been possible to establish the following facts.

(a) In a general way, the fixation yields are always better for small amounts of fixed nitrogen.

(b) The yield increases when the amount of excess water removed from the treated material decreases.

(c) The best yields wee obtained in the scale of products tried, with products of the general formula:



where R and R′ are alkyl chains having two or more carbon atoms.

When the three substituents R, R′ and R″ are identical, a heat treatment which is too long can cause a loss of nitrogen and a drop in yield by destruction of the quaternary ammonium for example when the three substituents are methyl groups trimethylamine may be liberated.

The textile material thus treated can then be transformed into spinnable soluble derivatives either in the form of acetate or in the form of xanthate in the case of cellulose.

For polyvinyl alcohol, the treatment can be envisaged:

either on already insolubilised fibres cold by thermal pretreatment;

or again on the final products acetalysed at the handling stage.

The products treated in accordance with the invention exhibit a considerable improvement in their dyeing affinity, and this starting from an amount of nitrogen of 0.1%. Particularly, such an improvement is manifested by:

(1st) A cold fixation until exhaustion of the bath of acid dyes for wool, as well as metalliferous 2/1 complex dyes.

(2nd) A very appreciable increase of the affinity for direct dyes with improvement of fastness to water and to neutral or weakly alkaline washing.

(3rd) A great increase of the affinity for dyes of the soluble phthalocyanine type (for example Pandurane of Durand-Huguenin) and sulphuric esters of vat dyes of the Indigosol type.

(4th) A medium increase of the affinity for vat dyes and naphthols.

(5th) A fixation of fibro-reactive dyes of the type derived from chlorinated cyanide or the like in a neutral bath, with a better yield and better exhaustion of the bath.

For cotton threads and fabrics, this treatment allows the great improvement of the finish of articles containing numerous "buttons" resulting from a low ripeness of the cotton used.

As for the spinnable soluble derivatives of these polyhydroxylised polymers, such as cellulose triacetate, dyeing and printing with the different types of dyes cited above becomes possible, but a vehicle which allows accessibility of the polymer structure to the dye giving it a certain enlargement should be added to the dyeing bath solution.

Fibres and films of triacetate and secondary acetate of cellulose can also be dyed, after enlargement treatment, for example, by soaking in a mixture 50/50 by volume of water and acetone, by a large number of dye categories such as direct dyes, fibro-reactive dyes, acid dyes, metalliferous 2/1 complexes for wool, dyes of the soluble phthalocyanine type and dyes which are diazotizable on fibre. Furthermore, the affinity for plasto-soluble dyes is increased in many cases. This is also applicable to the other spinnable or film-forming derivatives of the polyalcohols, such as esters or ethers.

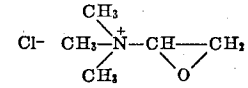
According to a variant of the invention an aqueous paste comprising a non-hydroxylised thickener (for example oil, trimethyl cellulose, or sodium or potassium polyacrylate), 0.5 to 4% of a strong mineral base such as sodium hydroxide and a quaternary ammonium salt of Formula I is applied to an area of a hydroxylised fabric, and then the fabric is subjected to heat treatment at about 100 to 120° C. conveniently by hot air and preferably for 5 to 10 minutes. The fabric may be printed locally or coated on one side with the aqueous paste. After washing a locally modified fabric is obtained. Dyeing the locally modified fabric, depending on how the dye affects the unmodified area of the fabric may result in the unmodified areas being of a different shade or of a different colour to the modified areas. If one side of the fabric has been coated, the final product is a fabric having sides of different colour intensity or of different colours.

Another advantage of the present invention is that the fabrics can be dyed continuously or semi-continuously by fibro-reactive dyes in a neutral bath solution. The impregnation bath solution may be prepared by simple dissolution of the dye in water without further addition of any alkaline ingredient or other. This tends to stabilize and lengthen the life of the bath solution. It suffices to full the fabrics in the bath solution then to evaporate or roll up the pieces and to allow the impregnation bath to act a little while, at a moderate temperature (40–50°) avoiding any drying, thus migration of the dye. This also constitutes another aspect of the present invention.

The invention is illustrated in the following examples.

EXAMPLE 1

A cotton fabric more specifically 25 g. of 130 g./m.² cotton poplin, was fulled in an aqueous solution containing 1% sodium hydroxide and the necessary quantity of epoxypropyl trimethyl ammonium chloride:



so that the concentration of active product (60%), calculated on the epoxy function, was such that a squeezing-out at 100% deposited 1% nitrogen on the sample. This sample kept at the initial dimensions was treated for 10 minutes at 120° C. in a current of hot air.

After rinsing and drying, the cotton fabric had a corrected amount of nitrogen of 0.55%, corresponding to a useful yield of the active product of about 55%.

The presence of a strong base to catalyse the fixation of the epoxy ammonium salt is absolutely necessary, as test A, which follows, shows. Furthermore, when the operation is effected in a full bath, and not by impregnation followed by a heat treatment to dryness as described above, the fixation yield of the active product is very low as test B shows.

Test A

A sample of bleached 130 g./m.² cotton poplin was treated in a full bath in an aqueous solution with 5% epoxypropyl trimethyl ammonium chloride not containing any fixation catalyst: the ratio of the bath was 1/35. The whole was kept for 8 hours at 50° C. avoiding the evaporation of the bath. After rinsing and drying the sample has a content of nitrogen practically identical with that of the untreated fabric i.e. 0.2%. There is, therefore, no reaction in the conditions of the test.

The sample is not dyed by Procion Red G in a neutral medium or by Sulfacide Blue 2 RL.

Test B

The test in the full bath was repeated with an aqueous solution containing 1% sodium hydroxide and 5% epoxypropyl trimethyl ammonium chloride.

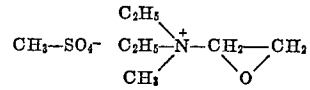
After rinsing and drying, the cotton fabric had a corrected amount of nitrogen of 0.21%, which corresponds to a useful yield of the active product of only 18%.

EXAMPLE 2

The process according to Example 1 was repeated, except that the treatment temperature was 100° C. instead of 120° C. The useful yield of the active product was 48%.

EXAMPLE 3

A cotton fabric was treated in the conditions given in Example 1, but the active product is epoxypropyl diethylmethyl ammonium methyl sulphate:



The fixation yield of the deposited nitrogen was 80%.

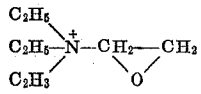
EXAMPLE 4

Example 3 was repeated but varying the concentration of the active product in such a manner that the amount of deposited nitrogen was 0.5%. The fixation yield of the active product was then 90%.

EXAMPLE 5

In the conditions of Example 1, but using as salt of

quaternary ammonium epoxypropyl diethylmethyl ammonium epoxypropyl diethylmethyl ammonium iodide:



The fixation yield was 80%.

EXAMPLE 6

A cotton fabric treated in the conditions of Example 1, with an amount of fixed nitrogen of 0.4%, was dyed in Rouge Diazol Lumiere 8B, a direct dye. It was ascertained that 1% of the dye gave the same intensity of tone as 3% on the untreated fabric. The firmness indices to water, checked in accordance with the E.C.E. code were as follows:

Deterioration	4–5
Scouring on cotton	4–5

while for the untreated fabric, these indices were

Deterioration	2–3
Scouring on cotton	1

EXAMPLE 7

Samples of cotton fabric treated in the conditions of Example 1 with an amount of fixed nitrogen of 0.4% were dyed in neutral aqueous solutions of fibro-reactive dyes (2% of Procion Red G and Procion Brilliant Blue RS). After 15 minutes of dyeing at ambient temperature, then at a temperature increasing from 25° to 60° in 30 minutes, the samples came out with an intensity of tone corresponding to the shade necessitating at least 4% of dye on fabric not modified in the usual dyeing conditions. A control fabric put into the same baths came out barely dyed.

The dyeings obtained did not show any appreciable variation in firmness on relation to standard dyeings, with the same dyes, at the same height of tone on unmodified cotton fabric.

EXAMPLE 8

Samples of fabrics of cotton and of polynosic fibres were treated in the conditions of Example 1 with an amount of fixed nitrogen of 0.3%. They were then dyed by means of the following dyes:

Diazamine Lumiere Red
Sulfacide Blue 2 RL
Neutrichrome Orange RLL
Pandurane Blue B.

It was ascertained that the affinity for these dyes was very high, while the non-modified cotton exhibits little or no affinity for the same dyes.

EXAMPLE 9

The conditions of Example 4 were used to treat a fabric of acetalysed polyvinyl alcohol fibres (Vinylal). The fixation yield was only 25%.

The final fabric containing 0.125% of fixed nitrogen proved to possess a very increased affinity for direct dyes, acid dyes, metalliferous 2/2 complexes and fibro-reactive dyes in a neutral medium.

EXAMPLE 10

A cotton fabric was treated in the conditions given in Example 1 with an amount of fixed nitrogen of 0.5%. After treatment, this fabric was acetalysed in heterogenous phase by a known process, until an amount of combined acetic acid of 55%.

The resulting samples of fabric could be dyed by the following dyes after a pre-soaking in a 50/50 mixture of acetone/water.

Procion Red G
Procion Brilliant Blue RS showing synthesis of the dye
Acétoquinone Blue Green
Acétoquinone Pure Blue R

Orangé Neutrichrome RLL
Bleu Sulfacide Blue 2 RL
Pandurane Blue B
Diazol Blue Lumiere R

EXAMPLE 11

A paste of linters having a degree of polymerisation of 865 was first treated in accordance with the process of Example 3 then acetylised in accordance with a known process in homogenous phase in a medium of methylene chloride. After precipitation by petroleum ether and washing there was obtained a product having the following characteristics:

Amount of nitrogen, 0.4%
Amount of combined acetic acid, 58.6%
Intrinsic viscosity in metal-cresol, 2.07 ml./g.
Soluble in methylene chloride, chloroform, symmetrical tetrachloroethane, acetic acid, and meta-cresol.

Starting from a solution in methylene chloride containing 10% ethyl alcohol, it was possible to manufacture films and fibres. These products could be dyed with the same dyes as listed in Example 10 above, according to the same process.

EXAMPLE 12

Two fabrics manufactured starting from two samples of cotton of the Detapine variety, one with a good maturity and the other of very low ripeness, were treated in the conditions of Example 1, but with an amount of fixed nitrogen of 0.3%.

Samples of treated and untreated fabrics placed end to end were dyed on a Jigger in Naphtasol TR/Solid Red Base TR and in micro powder Solanthrené Blue FRS.

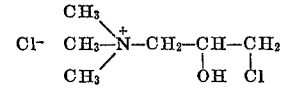
In the two cases it was ascertained that the treated fabric had a distinctly increased affinity: thus, the cotton fabric of very low ripeness, treated, dyes in a shade of deeper colour than the cotton fabric of good ripeness, not treated.

Furthermore, the bad finish of the fabrics of low maturity, which bad finish is due to the presence of numerous "buttons" of "dead cotton" standing out more clearly after dyeing, is found to be distinctly improved by the treatment in accordance with the invention.

EXAMPLE 13

In this example, instead of using an epoxy ammonium salt as in the preceding examples, there was used the corresponding chlorohydrin considered as the precursor of epoxy ammonium. In these conditions, it is necessary to add to the sodium hydroxide at 1% an additional quantity of NaOH to neutralise the chlorine of the chlorohydrin. Operating by impregnation and heat treatment to dryness, there are obtained fixation yields comparable with those obtained with the epoxy ammonium salts.

A sample of cotton poplin of 130 g./m.² was fulled in an aqueous solution containing 2% soduim hydroxide and 6% (chloro-3-hydroxy-2)-propyl trimethyl ammonium chloride



and squeezed out to a dryness of 100%.

The sample kept at the initial dimensions was treated for 10 minutes at 120° C. in a current of hot air.

After rinsing and drying, the cotton fabric had a corrected amount of nitrogen of 0.22%, which corresponds to a useful yield of the ammonium of about 55%.

The treated fabric is strongly dyed by Rouge Procion G in a neutral medium or Sulfacide Blue 2 RL.

The dyes mentioned herein are designated by the following classification numbers of the Color Index:

Naphtazol TR: CI Azoic Coupling Component 8 CI 37525
Solid Red Base TR: CI Azoic Diazo Component II CI 37085
Solanthrene Blue FRS: CI Vat Blue 4 CI 69800
Procion Red G: CI Reactive Red 5
Procion Brilliant Blue RS: CI Reactive Blue 4
Neutrichrome Orange RLL: CI Acid Orange 121
Acetoquinone Blue Breen R: CI Disperse Blue I CI 64500
Sulfacide Blue 2 RL: CI Acid Blue 47 CI 62085
Pandurane Blue I: CI Mordant Blue 77
Diazol Lumiere Blue R: CI Direct Blue 71 CI 34140
Diazamine Luminere Red 5 B: CI Direct Red 117 CI 28230
Diazol Lumiere Red 8 B: CI Direct Red 81 CI 28160.

We claim:

1. A process for treating textiles of cellulose, regenerated cellulose or insolubilised polyvinyl alcohol, each having free hydroxy groups, to modify its dyeing properties, particularly its affinity for fibro reactive dyes, which process comprises:

(a) impregnating the cellulose, regenerated cellulose or insolubilised polyvinyl alcohol with an aqueous solution of an epoxypropyl ammonium salt selected from the group consisting of epoxypropyl trimethyl ammonium chloride, epoxypropyl diethylmethyl ammonium methyl sulphate, and epoxypropyl diethyl methyl ammonium iodide, and precursors chlorohydrin thereof, at a predetermined concentration to obtain a nitrogen concentration of about 0.1 to 0.5% by weight of the final product, wherein said aqueous solution contains a strong mineral base as a fixation catalyst at a concentration of about 0.5 to 10% by weight;

(b) removing excess water from the impregnated cellulose, regenerated cellulose or insolubilised polyvinyl alcohol;

(c) drying the impregnated product to complete dryness at from 80° C. to 140° C.; and

(d) rinsing the totally dried product with water;

this combination of steps causing the epoxypropyl ammonium salt to be chemically affixed directly to the cellulose, regenerated cellulose or insolubilised polyvinyl alcohol at the level of the free hydroxy groups thereof.

2. A process according to claim **1**, wherein the strong mineral base is an alkaline metal hydroxide.

3. A process according to claim **2**, wherein the alkaline metal hydroxide is selected from the group consisting of potassium and sodium hydroxides.

4. A process according to claim **1**, wherein the strong mineral base is at a concentration of 0.5 to 4.0% by weight in the aqueous solution.

5. A process according to claim **1**, wherein the impregnated product is totally dried at 120° C.

6. A process according to claim **1**, wherein the cellulose, regenerated cellulose or insolubilised polyvinyl alcohol is in the form of thread.

7. A process according to claim **1**, wherein the cellulose, regenerated cellulose or insolubilised polyvinyl alcohol is in the form of fabric.

8. A process for treating a fabric of cellulose, regenerated cellulose or insolubilised polyvinyl alcohol to locally modify its dyeing properties, which process comprises:

(a) applying to an area of the fabric an aqueous paste containing an epoxypropyl ammonium salt selected from the group consisting of epoxypropyl trimethyl ammonium chloride, epoxypropyl diethylmethyl ammonium methyl sulphate and epoxypropyl diethylethyl ammonium iodide, and precursors chlorohydrin thereof a strong mineral base as a fixation catalist, and a non-hydroxylised thickener;

(b) drying the treated fabric to complete dryness at from about 100° to 120° C.; and

(c) washing with water.

9. The process of claim **1**, wherein drying step (c) is carried out for a maximum of about 30 minutes.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

8—31, 100 IE

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,685,953 Dated August 22, 1972

Inventor(s) Georges Cuvelier, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 29, "gretae" should read -- greater -- ; line 36, "fo" should read -- for -- ; line 48, "wee" should read -- were -- . Column 4, line 36, "0.2%" should read -- 0.02% -- . Column 5, line 2, "epoxypropyl diethylmethyl ammonium" should be cancelled; line 5,

line 5, "-CH_2-CH_2" should read -- -CH_2-CH-CH_2 --.

line 6, "C_2H_3 " should read -- CH_3 -- ; line 73, "showing synthesis of the dye" should read -- (See Chemical Abstracts, 1968, Volume 68, Page 968s, and 1967, Volume 67, Page 100984a, and U. S. Patent No. 3,133,921, showing synthesis of the dye) -- . Column 6, line 2, "Bleu" should be cancelled. Column 7, line 14, "Blue I" should read -- Blue 3 -- ; lines 32-33, "precursors chlorohydrin" should read -- chlorohydrin precursors -- . Column 8, lines 27-28, "precursors chlorohydrin thereof" should read -- chlorohydrin precursors --; line 28, before "a", first occurrence, insert -- , -- .

Signed and sealed this 22nd day of May 1973.

(SEAL)
Attest:

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Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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