

## [54] PRODUCTION OF TEXTILE FINISHES

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[58] Field of Search..... 260/555 R, 68, 70 R, 70 A, 260/553 CD

## [56]

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## [57]

## ABSTRACT

A process for the production of textile finishes based on ethylene glycol, formaldehyde, glyoxal and urea, particularly for finishing union cloth containing cellulose.

4 Claims, No Drawings

## PRODUCTION OF TEXTILE FINISHES

The invention relates to a process for the production of textile finishing agents for fabrics consisting of or containing cellulose.

In the finishing of union cloth based on cellulose and particularly on mixtures of cotton and synthetic fibers, exceptionally high standards are required. The cloth, after finishing, should exhibit not only a high degree of wet and dry crease resistance but also a pleasant soft handle. The finish also has to be fast to chlorine and in the case of a colored cloth the coloration must not be affected by the finishing agent.

It is known that impairment of color fastness can be avoided by using N-dimethylol compounds of 4,5-dihydroxyethylenurea and also some carbamates. Dimethylol-4,5-dihydroxyethylenurea finishes do not however impart fastness to chlorine, whereas dimethylolcarbamates may provide adequate fastness to chlorine in some circumstances, although they usually result in more than average damage to the cellulose fiber.

It is known from German Laid-open Specification No. 1,469,382 that cellulosic textiles can be treated with an aqueous solution of an acetal from formaldehyde and glycol, a catalyst mixture and an additive acting as a buffer, for example melamine-formaldehyde, dimethylolethylenurea or dimethyloldihydroxyethylenurea. This method has the disadvantage that the said additives are injurious to the achievement of a finish which is fast to chlorine.

It is known from Swiss Pat. No. 399,407 that a mixture of acetal resins, for example reaction products of formaldehyde with monohydric or polyhydric aliphatic alcohols, dimethylolalkylenurea and methylolaminotriazine compounds can be used as a finishing agent. Such mixtures have however a marked negative effect on the shade and fastness of dyed textiles.

It is an object of the invention to provide a textile finishing agent not having the said disadvantages.

Another object of the invention is to provide a finishing agent for textiles consisting of or containing cellulose which combines high resistance to hydrolysis and good fastness to chlorine with a pleasant handle and does not cause any shade change in colored goods.

Other objects of the invention will be evident from the following detailed description.

We have found a process for the production of a textile finishing agent in which ethylene glycol and formaldehyde are reacted in a molar ratio of from 1:1.5 to 1:2.5 in the presence of an acid and then the mixture is reacted with the same molar amount of 0.3 to 0.4 mole of each of glyoxal and urea based on 1 mole of ethylene glycol at a pH of from 6 to 7 so that after the reaction from 5 to 15 percent of free formaldehyde is contained in the solution.

Textile finishing agents prepared by the said process may be used in an outstanding way for finishing cellulose cloth or union cloth containing cellulose in order to obtain a good, soft and smooth hand, good fastness to chlorine of the finish and a high degree of wet and dry crease resistance without affecting the shade and color fastness. The new agents have also proved to be suitable on union cloth containing other native cellulose fibers or regenerated cellulose fibers instead of cotton.

The surprising superiority over prior art finishing agents is not completely understood because the chemical processes taking place during the preparation of

the solution are not quite clear. It is therefore advisable that the process conditions specified such as molar ratios, pH, and sequence of addition should be adhered to as closely as possible.

5 Ethylene glycol and formaldehyde are reacted in a molar ratio of from 1:1.5 to 1:2.5, preferably from 1:2.0 to 1:2.5, in the presence of an acid, conveniently within a period of from 1 hour to 4 hours at a temperature of from about 80° to 100°C.

10 The acid used is a medium strength or strong acid, i.e. one having a dissociation constant K or  $K_1$  of at least  $10^{-4}$ . It is preferred to use a mineral acid, particularly sulfuric acid or aqueous hydrochloric acid; p-toluenesulfonic acid, for example, may however also be used. The amount of acid is advantageously chosen so that a pH of from 0.4 to 1.5 is maintained during the reaction of glycol with formaldehyde.

15 The reaction mixture is then adjusted to a pH of from 6 to 7 with alkali, preferably with aqueous caustic soda solution or an aqueous sodium carbonate solution. The preferred pH range is from 6.2 to 6.8.

20 Glyoxal and urea are then added to the mixture in the same molar amounts of 0.3 to 0.4 based on the ethylene glycol. The mixture is thereafter conveniently kept for 25 about three to five hours with or without stirring at about 30° to 50°C.

25 If desired the solution may then be adjusted to the optimum end pH for the textile finishing which is from 6.5 to 6.8. It is essential that under the said conditions from 5 to 15 percent of free formaldehyde is present.

30 The ethylene glycol used is advantageously employed in the form of a high percentage product having a water content of not more than 10 percent. Glyoxal and formaldehyde may be used in the form of their commercially available aqueous solutions or in the form of their polymerized products. Urea may be used in solid form or also as an aqueous solution.

35 The solution obtained may be used as a finishing agent by all methods used for the application of N-methylol compounds to textile materials; these are methods in which the material to be finished is impregnated with a solution or dispersion of the finishing agent and an acid or potentially acid catalyst and reacted with the finishing agent with the formation of acetal bonds between the cellulose molecules of the textile material and the finishing agent; this reaction may be carried out either in the wet condition of the textile material or a partial or complete drying of the textile material may be carried out between the impregnation and the chemical reaction.

40 The new finishing agents are used in known manner, preferably in the form of aqueous impregnating liquors. The concentration of finishing agent depends in the usual way on the effect aimed at. It is generally from 50 to 200 g/liter. The material to be treated is impregnated with the impregnating liquor in the usual way, preferably by padding. The impregnated material is freed from excess impregnating liquor by a known method, for example by squeezing. The impregnated fibrous material 45 may be dried and then heated in the presence of an acid or potentially acid catalyst to a temperature of up to 210°C, preferably at from 130° to 180°C. The reaction is generally over under these conditions within one minute to six minutes. The fibrous material, during drying or thereafter, may be mechanically shaped, for example by compression, crimping, ironing, calendering, embossing or pleating. After the reaction the fibrous

material has a high dry crease recovery angle; moreover the shape imparted to the fibrous material is fixed therein in a washproof manner.

The treated material may be washed, rinsed and dried by conventional methods.

Furthermore the very advantageous possibility is available of leaving the impregnated and squeezed material wet or drying it to a moisture level of from 10 to 35 percent based on the weight of the amorphous regions contained in the cellulose, i.e. in the case of native cellulose, for example cotton, to a moisture level of from 3 to 10.5 percent, in the case of regenerated cellulose to a moisture level of from 6 to 21 percent, in each case based on the whole of the cellulose component and then storing it at room or elevated temperature, preferably at a temperature of not more than 50°C without appreciable loss of water in the presence of an acid and/or potentially acid catalyst. Instead of drying the wet material to the said moisture content, it may also first be dried completely and then moistened again to the said content. In a method which has proved to be very suitable the controlled moistening is carried out by impregnating the dry textile material with an inert non-aqueous liquid which contains the small amount of water necessary and also the catalyst or catalysts. The reaction with the cellulose under these conditions generally requires from 5 to 20 hours or even less at temperatures above 50°C. This embodiment of the process makes it possible to finish fibrous material consisting of or containing cellulose in a simple and reliable way in a single operation so that it has a high to very high wet crease recovery angle to 140° or more and an average dry crease recovery angle of 110° or more. It is possible by varying the process conditions to adapt the level and difference between wet and dry crease recovery angles to the particular requirements.

Acid and potentially acid catalysts are generally known and conventional for the purpose of creaseproof finishing. Examples are inorganic and organic acids such as sulfuric acid, hydrochloric acid, phosphoric acid, boric acid, formic acid, acetic acid, oxalic acid, tartaric acid, maleic acid, and salts which have an acid reaction or which form acids by the action of heat and/or by hydrolysis, for example ammonium salts and amine salts of strong acids, magnesium chloride, zinc chloride and zinc nitrate. Mixtures of two or more catalysts may also be used. It is preferable to use magnesium chloride, zinc nitrate and zinc chloride for the process of deferred curing. The reaction of the finishing agents to be used according to the invention is carried out in the presence of these catalysts as already stated above. This may be effected by applying the catalysts, preferably in the form of aqueous solutions, to the material to be finished before or after impregnation of the same. It is preferred however to add the catalysts direct to the impregnating liquor containing the finishing agent. The concentration of the catalysts is chosen within the conventional range for the particular finishing method used. Catalyst concentrations of from 1 to 40 g/liter have generally proved to be suitable for finishing at high temperature and deferred cure and, based on the weight of finishing agent, amounts of catalyst of from 4 to 60 percent, preferably from 20 to 40 percent, whereas for finishing in a swollen condition of the fiber, i.e. in the presence of a considerable amount of water, and at lower reaction temperature it may be

necessary, as already known, to use strongly acid catalysts in a concentration of up to 20N.

Conventional water-repellent, softening, leveling, wetting and finishing agents such as particularly polymer solutions or dispersions may be used together with the new finishing agents. Examples of water-repellents are the known paraffin wax emulsions containing aluminum or zirconium and also preparations containing silicones and perfluorinated aliphatic compounds. Examples of softeners are oxyethylation products of high molecular weight fatty acids, fatty alcohols or fatty acid amides, high molecular weight polyglycol ethers and their esters, high molecular weight fatty acids, fatty alcohol sulfonates, stearyl-N,N-ethylenurea and stearyl amidomethylpyridinium chloride. Examples of leveling agents are water-soluble salts of acid esters of polybasic acids with ethylene oxide or propylene oxide adducts of long chain oxyalkylatable base materials. Examples of wetting agents are salts of alkyl naphthalenesulfonic acids, alkali metal salts of sulfonated diethyl succinate and the adducts of alkylene oxides to fatty alcohols, alkylphenols, fatty amines and the like. Examples of finishing agents are cellulose ethers or esters and alginates, and also solutions or dispersions of synthetic polymers and polycondensates, for example of polyethylene, polyamides, oxyethylated polyamides, polyvinyl ethers, polyvinyl alcohols, polyacrylic acids or their esters and amides and also the corresponding polymethacrylic compounds, polyvinyl propionate, polyvinylpyrrolidone, copolymers, for example those of vinyl chloride and acrylic esters, of butadiene and styrene or acrylonitrile or of  $\alpha$ -dichloroethylene,  $\beta$ -chloroalkylacrylic esters or vinyl- $\beta$ -ethyl ethers and acrylamide, or the amides of crotonic acid or maleic acid or of N-methylolmethacrylamide and other polymerizable compounds. These additional auxiliaries are generally used in amounts of from 0.3 to 4 percent, preferably from 1 to 2.5 percent, based on the weight of the dry textile material; in special cases these amounts may however be exceeded.

The finishing agents of the invention give finishes on union cloth and cellulose cloths which have a very high resistance to hydrolysis and good fastness to chlorine. In particular a pleasant handle is imparted to the cloth. It may be emphasized that the agents are also suitable for colored materials because no variations in shade occur during the finishing.

The following Examples illustrate the invention. The parts and percentages specified are by weight. Parts by weight bear the same relation to parts by volume as the kilogram to the liter.

#### EXAMPLE 1

55 A mixture of 620 parts of ethylene glycol and 1,672 parts of 40 percent formaldehyde solution has 14 parts of 50 percent sulfuric acid added to it and the whole is heated to refluxing temperature while stirring for 1 hour. After cooling to about 50°C a pH of 6.5 is set up with concentrated caustic soda solution. 5,200 parts of 60 40 percent glyoxal solution and 218 parts of urea are then added. The whole is stirred for another 2 hours at 30° to 35°C and then a final pH of 6.5 to 6.8 is set up.

#### EXAMPLE 2

65 620 parts of ethylene glycol is heated under reflux with 678 parts of paraformaldehyde and 9 parts of concentrated sulfuric acid for ninety minutes while stirring.

A pH of 6.5 is set up and then 535 parts of glyoxal and 222 parts of urea are added to the reaction mixture and the whole is heated for another 2 hours at 35°C while stirring. After filtration 2,050 parts of finishing agent is obtained.

	(I)	(II)
untreated cloth	35 kg	35 kg
finished cloth	22 kg	24 kg
one chlorination	23 kg	18 kg
three chlorinations	23.5 kg	7.5 kg
five chlorinations	20.0 kg	destroyed

### EXAMPLE 3

The superiority of the finishing agent as regards resistance to chlorine (measured as the tear resistance of the impregnated cloth) is demonstrated.

A mixture of:

I. 150 parts of the product of the invention prepared as described in Example 1 (50 percent aqueous solution) and

30 parts magnesium chloride hexahydrate; and for comparison

II. 150 parts dimethylolglyoxalmonoureine (50 percent aqueous solution) prepared by reaction of urea, glyoxal and formaldehyde in the ratio 1:1:2; and

22 parts magnesium chloride hexahydrate is made up in each case to 1 liter of solution.

Pure cotton cloth is impregnated with this solution in each case. The liquor pick-up is 70 percent. After the impregnated cloth has been dried condensation is carried out for about 5 minutes at 155°C.

The tear resistance (measured on a strip of 50 mm × 200 mm) indicates the resistance of the finish in the case of one or more chlorinations as follows:

We claim:

1. A process for the production of a textile finishing agent wherein ethylene glycol and formaldehyde are reacted for a period of from 1 to 4 hours in a molar ratio of from 1:1.5 to 1:2.5 at a temperature of from 80° to 100°C in the melt or an aqueous solution in the presence of an acid having a dissociation constant K or K<sub>1</sub> of at least 10<sup>-4</sup> and sufficient to bring about a pH range 10 in the reaction medium of from 0.4 to 1.5, and the resulting mixture is reacted at a temperature of from 30° to 50°C for a period of from 3 to 5 hours with an equal molar amount of from 0.3 to 0.4 mole, based on 1 mole of ethylene glycol, of each of glyoxal and urea at a pH 15 of from 6 to 7 which is brought about by the addition of alkali or sodium carbonate so that from 5 to 15 percent of free formaldehyde is contained in the solution 20 after the reaction.

2. A process as claimed in claim 1 in which ethylene 25 glycol and formaldehyde are used in a molar ratio of from 1:2.0 to 1:2.5.

3. A process as claimed in claim 1 in which the acid is a mineral acid.

4. A process as claimed in claim 1 wherein the reaction 30 in the second stage takes place at a pH of from 6.2 to 6.8.

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UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 3,862,224

DATED : January 21, 1975

INVENTOR(S) : Harro Petersen et al

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

In the Heading, insert -- [73] Assignee: Badische Anilin & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany --.

Signed and Sealed this  
Thirty-first Day of August 1976

Attest:

**RUTH C. MASON**  
*Attesting Officer*

**C. MARSHALL DANN**  
*Commissioner of Patents and Trademarks*