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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,243,350**
(22) 1998/07/17
(43) 1999/01/22

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(51) Int.Cl.[6] D06M 13/192, D06M 13/207
(30) 1997/07/22 (1362/CAL/97) IN
(30) 1997/07/22 (1361/CAL/97) IN
(30) 1998/01/31 (9802032.4) GB
(30) 1998/01/31 (9802031.6) GB

(54) **TRAITEMENT DE TISSUS**
(54) **TREATMENT OF FABRICS**

(57) Une matière cellulosique fibreuse est traitée par application d'une solution aqueuse à base d'un acide polycarboxylique et d'un acide hydroxycarboxylique, notamment un acide carboxylique aromatique ortho-hydroxylé, comme l'acide salicylique, ou d'un sel, comme un sel de métal alcalin, de métal alcalino-terreux ou d'ammonium, en guise de catalyseur d'estérification; le tissu est séché et chauffé pour activer l'estérification par réticulation de l'acide polycarboxylique et de la cellulose de la matière cellulosique fibreuse de façon à produire un tissu avec des propriétés améliorées au niveau des faux plis et (ou) de l'infroissabilité et (ou) de la résistance au rétrécissement et (ou) de la facilité de séchage. Comme la méthode présente l'avantage de ne pas nécessiter de dérivés de formaldéhyde, son application et les matériaux traités ne libèrent pas de formaldéhyde lors de leur fabrication ou de leur utilisation, et les catalyseurs ne contiennent pas et n'utilisent pas de composés phosphorés.

(57) Fibrous cellulosic material is treated by applying an aqueous solution including a polycarboxylic acid crosslinking agent and a hydroxycarboxylic acid, particularly an aromatic ortho-hydroxy carboxylic acid, especially salicylic acid or salt particularly alkali metal ammonium or alkaline earth metal salts, as an esterification catalyst, drying the fabric and heating it to promote crosslinking esterification of the polycarboxylic acid and the cellulose of the fibrous cellulosic material to give fabric with improved wrinkle and/or crease and/or shrink resistance and/or smooth drying properties. The method has the advantage that it does not use formaldehyde derivatives and thus the operation of the method and treated materials do not release formaldehyde during manufacture or use and the catalysts do not contain or use phosphorus containing compounds.

Abstract

Treatment of Fabrics

Fibrous cellulosic material is treated by applying an aqueous solution including a polycarboxylic acid crosslinking agent and a hydroxycarboxylic acid, particulalry an aromatic *ortho*-hydroxy carboxylic acid, especially salicylic acid or salt particularly alkali metal ammonium or alkaline earth metal salts, as an esterification catalyst, drying the fabric and heating it to promote crosslinking esterification of the polycarboxylic acid and the cellulose of the fibrous cellulosic material to give fabric with improved wrinkle and/or crease and/or shrink resistance and/or smooth drying properties. The method has the advantage that it does not use formaldehyde derivatives and thus the operation of the method and treated materials do not release formaldehyde during manufacture or use and the catalysts do not contain or use phosphorus containing compounds.

Treatment of Fabrics

This invention relates to a method of imparting wrinkle and/or crease and/or shrink resistance and/or smooth drying properties to fabrics made from cellulosic fibres or yarns or blends containing cellulosic fibres or yarns. More particularly it relates to such a method of treatment which does not involve the use of formaldehyde or formaldehyde derivatives or phosphorus containing compounds.

Many commercial processes for imparting wrinkle, crease and/or shrink resistance and/or smooth drying properties to cellulosic fabrics, particularly cotton textiles, are known. The treated fabrics and garments made from them retain their dimensions and smooth appearance in use and also during machine wash and tumble dry processes.

Commercially, such properties can be imparted to cellulosic fabrics by a finishing treatment with resinous compositions. The most commonly used resins for such finishing are based on formaldehyde derivatives such as formaldehyde-urea or substituted urea addition products such as DMEU and DMDHEU. Such resins are believed to function by promoting crosslinking of the cellulose in the fabric thereby imparting the desired properties. In recent years, efforts have been made to develop crosslinking agents which do not include formaldehyde or its derivatives to remove the possible evolution of formaldehyde during manufacture, storage and/or use of cellulose, particularly cotton fabrics, treated with formaldehyde addition products.

Non-formaldehyde crosslinking agents which have been suggested previously include polycarboxylic acids as disclosed by Gaghiardi and Shipee, American Dyestuff Reporter 52, 300 (1963). Rowland *et al.*, Textile Research Journal 37, 393 (1967), disclosed the use of partially neutralized polycarboxylic acids with base prior to the application to the fabric in a pad, dry and heat cure treatment, elaborated US Patent 3526048. Canadian Patent No 2097483 describes rapid esterification and crosslinking of fibrous cellulose in textile form using boric acid or derivatives as crosslinking catalyst.

Welch *et al.* in US Patents 4975209, 4820307, 4936865 and 5221285 disclose the use of alkali metal salts of phosphorus containing acids, particularly sodium hypophosphite as crosslinking esterification catalysts in the treatment of cellulosic materials. The use of sodium hypophosphite has several disadvantages: it is expensive, relatively high levels are needed in practice and it tends to cause shade changes in fabrics dyed with sulphur dyes or certain reactive dyes. In addition, phosphorus containing effluents can promote algal growth and/or eutrophication of downstream water bodies such as streams and lakes.

The present invention is based on the discovery that certain hydroxycarboxylic acids and/or their salts, particularly alkali metal salts at lower concentration show accelerating effect on esterification and crosslinking of cellulose by polycarboxylic acids. The use of such catalysts can enable the provision of a treatment method that uses neither formaldehyde derivatives or phosphorus compounds, but can give adequately rapid esterification and crosslinking of cellulosic in fibres to provide effective wrinkle, crease or shrink resistance or smooth drying properties to materials made from such cellulosic fibres. Thus, in this invention fibrous cellulosic material is treated with a polycarboxylic acid in the presence of a hydroxycarboxylic acid curing catalyst at elevated temperature. The process can be carried out by impregnating the material with a solution containing the polycarboxylic acid and the curing catalyst followed by heat treatment to produce esterification and crosslinking of the cellulose with the polycarboxylic acid.

The present invention accordingly provides, a method of treating fibrous cellulosic textile material which comprises:

a applying to the cellulosic textile material an aqueous solution including at least one polycarboxylic acid as a crosslinking agent for the cellulose and a hydroxycarboxylic acids or a salt as an esterification catalyst,

b drying the textile material and heating it to promote crosslinking esterification of the polycarboxylic acid and the cellulose of the cellulosic textile material.

In referring to the material as being "cellulosic", we mean that the major part of the fibre forming components of the material is cellulose. Thus, the term includes purely cellulosic materials such as cotton and cellulose-rich blends particularly cellulose-rich polyester blends, such as polycotton materials. Typically, the material contains from 30 to 100% of cellulosic fibres. Typical cellulosic fibre materials which can be included in fabrics treated according to this inventions include cotton, flax, rayon, jute, hemp and ramie. It can also be a synthetic cellulosic fibre material such as rayon, particularly viscose rayon or solvent derived rayon commonly called lyocell fibre. The cellulosic material can be a blend of fibres of cellulosic materials with non-cellulosic materials and in particular includes blends of cellulosic fibres, particularly cotton, with polyester, particularly polyethylene terephthalate polymer or related copolymers. The textile can be a woven (including knitted) or non-woven textile, but as crease resistance is particularly important in clothing, the textile will usually be a clothing textile material.

The term "formaldehyde free" means that the process does not release formaldehyde during the treatment of the fabric with the resin or during subsequent manufacture of garments or their use including washing and wearing. The term "wrinkle or crease resistance" means that a treated fabric is less likely to be wrinkled or creased after being worn or after a laundering operation than it would if it had not been so treated.

The invention uses polycarboxylic acids as cellulose crosslinking agents to improve the wrinkle resistance, shrinkage resistance and smooth drying properties of cellulosic fibre containing textile without the use of formaldehyde or agents that release formaldehyde. Some such polycarboxylic acids are known from the literature. Suitable polycarboxylic acids for use in the method of this invention include aliphatic, including open chain and alicyclic, polycarboxylic acids, and aromatic polycarboxylic acids. Desirably the polycarboxylic acid includes at least 3, particularly at least 4 and often more carboxylic acid groups per molecule.

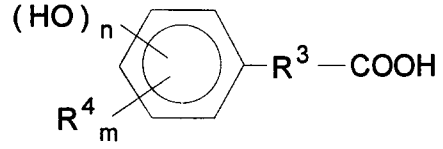
Particularly suitable aliphatic polycarboxylic acids include acids in which at least two carboxylic acid groups are separated by 2 or 3, more usually 2, carbon atoms and desirably where the polycarboxylic acid includes a plurality of such arranged pairs of carboxylic acid groups. Where such an aliphatic acid includes an ethylenic double bond, it is very desirable that it is positioned α,β- to a carboxylic acid group; such an aliphatic acid may include a hydroxyl group on a carbon atom also carrying a carboxylic acid group; and further the aliphatic chain or ring may include one or more oxygen and/or sulphur atoms. Suitable aromatic acids include those where at least two carboxylic acid groups are attached to adjacent aromatic ring carbon atoms.

Examples of suitable aliphatic polycarboxylic acids include maleic acid, methylmaleic (citraconic) acid, citric acid, itaconic acid, 1,2,3-propanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid (commonly known as BTCA), all *cis*-1,2,3,4-cyclopentanetetracarboxylic acid, oxydisuccinic acid, thiodisuccinic acid; oligo- and/or poly-maleic acid and/or anhydride (as described in GB 2295404 A and WO 96/26314 A and abbreviated "OMA") and suitable aromatic polycarboxylic acids include benzene hexacarboxylic acid and trimellitic acid.

The amount of crosslinking agent used will typically be from 1 to 10%, particularly from about 2 to about 7%, by weight based on the dry fabric weight. The particular concentration of crosslinking agent used in the treating solution will depend upon the degree of cross linking desired, the proportion of cellulosic fibres in fabric being treated and the solubility of the crosslinking agent. Typically, the concentration is from about 1 to 20%, more usually 2 to 10% particularly from 0.5 to 7 and especially about 5%, by weight of the solution.

The curing catalyst used in this invention is one or more hydroxycarboxylic acid(s). The curing catalyst can be aliphatic, aromatic. Suitable aliphatic compounds include mono-carboxylic mono-hydroxyl acids, in particular of the formula (I): $H\text{-}R^1\text{-}CH(OH)\text{-}R^2\text{-}COOH$ (I) where each of R^1 and R^2 is a direct bond or a C_1 to C_4 alkylene group, in particular where R^1 is a direct bond, such

that the total number of carbon atoms in the acid molecule is from 2 to 6 (??). Examples include hydroxyacetic acid (glycollic acid), glyoxalic acid (di-hydroxyacetic acid) and 4-hydroxybutyric acid. Suitable aromatic compounds include mono-carboxylic hydroxy acids in which at least one of the carboxyl and hydroxyl groups is directly attached to the aromatic ring. Desirably, the carboxyl group and at least one hydroxyl group are directly attached to the aromatic ring. The ring may also carry inert substituents such as one or more C_1 to C_4 alkyl group(s), but desirably, not more than two such groups are attached to the aromatic ring. Particular aromatic acids are of the formula (II):



(II)

where

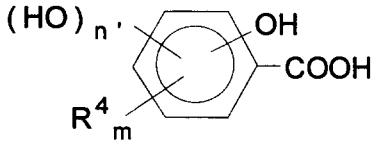
R^3 is a CH_2 group, or, and desirably, a direct bond;

n is from 1 to 3, particularly 1 or 2;

each R^4 is independently a C_1 to C_4 alkyl group; and

m is 0, 1 or 2.

Among aromatic acids, those where the carboxylic acid group and a hydroxyl group are directly attached to the aromatic ring and are positioned substituted *ortho*- to each other on the ring are particularly useful. Very desirable such '*ortho*-acids' are those of the formula (III):



(III)

where

m and R^4 are independently as defined for formula (II) and n' is 0 or 1.

Examples include 3-hydroxybenzoic acid, 4-hydroxy- benzoic acid and 2-hydroxyphenylacetic acid and examples of suitable *ortho*-acids include 2-hydroxybenzoic acid (salicylic acid), 2,4-dihydroxybenzoic acid (b-recorcylic acid), 2,4-dihydroxy- 5-methylbenzoic acid (orcinylic acid) and the cresotic acids, especially 2-hydroxy-3-methylbenzoic acid, 2-hydroxy-4-methylbenzoic acid and 2-hydroxy-5-methylbenzoic acid.

The hydroxycarboxylic acid catalyst can be used as the free acid or as a salt, particularly an alkali metal, ammonium or alkaline earth metal salt, or a mixture of the free acid and a salt or salt(s). The salt forming cations are particularly of potassium, sodium, ammonium, magnesium, calcium or a mixture of these cations. It is not clear whether the free acid form or the salt form of the curing catalyst is the more active component of the catalyst. The form present will depend on the acidity of the solution used for the treatment of the textile and the effect of the drying and heating steps. We

have found that the textile is advantageously treated using a moderately acidic solution, typically having a pH of from 2 to 6, usually not more than 4.5, more usually from 2.5 to 4 and especially about 3. Under such conditions, the curing catalyst may be present as the neutral free acid, as acid anions or a mixture depending on the acidity of the catalyst. Aromatic 2-hydroxy- carboxylic acids (*ortho*-acids) typically have acidities in aqueous solution such that both the neutral free acid and the acid anions are present at significant concentrations (relative to he overall concentration of the catalyst) at pH values of about 3.

In making up treatment solutions, it will often be convenient to start by dissolving a readily water soluble metal or ammonium salt and subsequently adjusting the pH of the solution rather than to try to dissolve what may be a sparingly soluble free acid at the use pH directly.

The amount of hydroxy aromatic acid catalyst used will typically be from 1 to 100%, more usually 1 to 50%, desirably 2 to 30% and especially 5 to 20%, by weight of the polycarboxylic acid crosslinking agent. Expressed as a percentage based on (the dry weight of) the material being treated, the amount will typically be from 0.1 to 10%, more usually from 0.2 to 3%, particularly 0.5 to 2% by weight. The concentration used in the treatment solution is typically from 0.1 to 10%, more usually from 0.2 to 5%, particularly from 0.3 to 2%, by weight of the solution.

The action of the hydroxy aromatic acid catalysts used in this invention seems to go beyond the effect that might be expected of a simple catalyst. We do not know why this may be, but suspect that because the hydroxy aromatic acid catalysts have at least two potentially reactive sites, they may be acting to form further cross links by reacting with the cellulose and/or with the polycarboxylic acids used as cellulose crosslinking agents. The precise mechanism by which the effect arises is not critical to the invention.

The catalysts used in this invention can be used alone or in combination with other catalytic materials. In particular they can be used in combination with organic or inorganic sulphonic or sulfinic acids or salts. In such combinations, suitable organic or inorganic sulphonic or sulfinic acids or their salts include inorganic sulphonic acids i.e. compounds including the group SO_3H (or SO_2OH), particularly halosulphonic and amidosulphonic acids, particularly those of the general formula: XSO_2OH where X is Cl, F or NH_2, respectively chlorosulphonic and fluorosulphonic acids and amidosulphonic acid (taurine); and organic sulphonic acids which typically have the general formula: RSO_2OH where R is an organic group, particularly an alkyl or cycloalkyl group, an unsaturated straight or branched chain hydrocarbyl, particularly alkenyl group, or an unsaturated cyclic or arene group. especially suitable organic catalysts inlcude the alkane sulphonic acids and

their alkali metal salts e.g. methane, ethane, propane, butane, pentane and hexane sulphonic acids, camphor sulphonic acid, isethionic acid (2-hydroxyethane sulphonic acid), methane- di-sulphonic acid and trifluoromethanesulphonic acid. Other useful curing catalysts include arene and alkyl arene sulphonic acids such as benzene, *p*-hydroxybenzene, *p*-toluene and dodecylbenzene sulphonic acids, naphthalene-1- and napthalene-2-sulphonic acids and 1,3-benzene and 2,6-naphthalene disulphonic acids and benzene sulphinic acid.

Sulphonic or sulfinic acid catalysts can be used as the free acids or as salts, particularly an alkali metal, ammonium or alkaline earth metal salts, or a mixture of free acid and salt(s). The salt forming cations are particularly of potassium, sodium, ammonium, magnesium, calcium or a mixture of these cations. It is not clear whether the free acid form or the salt form of this type of catalyst is the more active form. The form present will depend on the acidity of the solution used for the treatment of the textile and the effect of the drying and heating steps. At the moderately acid conditions typically used in this invention, it is likely that any sulphonic or sulfinic acid catalysts used will be present mainly as the (electrically) neutral free acid.

When the catalyst system includes a sulphonic or sulfinic acid catalyst, the amount of this additional catalyst used will typically be from 10 to 200%, more usually 25 to 150%, desirably 50 to 120%, by weight of the polycarboxylic acid crosslinking agent. Expressed as a percentage based on the (dry weight of the) textile being treated, the amount will typically be from 1 to 30%, more usually from 2 to 20%, particularly 2.5 to 10% by weight. The concentration used in the treatment solution is typically from 0.1 to 20%, more usually from 0.2 to 10%, particularly from 0.5 to 7%, by weight of the solution.

The use of sulphonic or sulfinic acids as a reaction catalyst in the preparation of fibrous cellulosic textile materials having improved crease and wrinkle resistance is the subject of a co-pending application claiming priority from Indian Patent Application No 1361/CAL/97 and GB Patent Application No 9802031.6 and filed as Application No (Applicant's reference CPW 50525).

The treatment is typically carried out by first impregnating the cellulosic or cellulosic containing textile materials with an aqueous treating solution containing the crosslinking agent and the curing catalyst, and removing excess liquid e.g. using wringers, with these steps being repeated, if necessary, to obtain the desired liquid pick up. The material is then dried to remove the solvent and then cured, e.g. in an oven, typically at about 150 to 240°C, usually from 160 to 200°C for a time of from 5 seconds to 30 minutes, usually 1 to 5 minutes to promote the esterification and crosslinking of the cellulose by the polycarboxylic acid. Typically the pick up of treatment solution is from 30 to 120%, more usually from 50 to 100%, particularly about 80% of the dry weight of the untreated textile.

We have confirmed the presence of cellulose ester carbonyl groups in cellulosic textile material treated according to the invention by FT-IR (Fourier transform infra red) spectroscopy. The absorption band of the carbonyls of cellulose esters in infra red spectra has been reported and in the range of 1720 to 1750 cm^{-1} (Zhbankov, P.G., "Infrared spectra of cellulose and its derivatives", Consultant Bureau, New York, 1968, pp 315-316). Our observations show an absorption peak at about 1720 to 1735 cm^{-1}.

The treatment solution containing the crosslinking agent and the curing catalyst forms part of the invention which accordingly specifically includes an aqueous solution of at least in one polycarboxylic acid cellulose crosslinking agent, particularly at a concentration of from 1 to 20% by weight of the solution, and at least one hydroxycarboxylic acid esterification catalyst, particularly at a concentration of from 0.2 to 10% by weight of the solution. The invention further includes an aqueous solution of at least in one polycarboxylic acid cellulose crosslinking agent, particularly at a concentration of from 1 to 20% by weight of the solution, at least one hydroxycarboxylic acid esterification catalyst, particularly at a concentration of from 0.2 to 10% by weight of the solution and at least one organic or inorganic sulphonic or sulfinic acids or a salt esterification catalyst, particularly at a concentration of from 0.2 to 10% by weight of the solution.

The invention further includes cloth treated by the method of the invention and in particular, a cellulosic textile material, which may be woven (including knitted) or non-woven, which carries residues of at least in one polycarboxylic acid cellulose crosslinking agent esterified to hydroxylic sites in the cellulose and residues of at least one hydroxycarboxylic acid esterification catalyst. In this aspect, the invention also includes a cellulosic textile material, which may be woven (including knitted) or non-woven, which carries residues of at least in one polycarboxylic acid cellulose crosslinking agent esterified to hydroxylic sites in the cellulose, residues of at least one hydroxycarboxylic acid esterification catalyst (which may be bound chemically to the textile or to residues of at least in one polycarboxylic acid cellulose crosslinking agent), and at least one hydroxycarboxylic acid esterification catalyst, particularly at a concentration of from 0.2 to 10% by weight of the solution

In these aspects of the invention particularly desirable features are as described for the method of the invention.

The following Examples illustrate the invention. All parts and percentage are by weight unless otherwise stated.

Materials

BTCA 1,2,3,4-butanetetracarboxylic acid

OMA oligo-maleic acid

Surf Commercial proprietary domestic detergent *ex* Hindustan Lever

Test Methods

Wrinkle recovery angles (WRA)

were determined by ATCC Test Method 66-1990 Wrinkle recovery of fabrics: Recovery angle method. The wrinkle resistance of woven textiles is represented by the wrinkle recovery angles; the greater the WRA the greater the wrinkle resistance of the fabric. Results are reported in degrees.

Example 1

This Example illustrates the use of salicylic acid (introduced as sodium salicylate) as a curing catalyst for the durable press finishing of cotton fabric using BTCA.

Cotton cloth test pieces (10 inches square; ca. 25x25 cm;) were thoroughly wetted by immersion in a treatment bath containing an aqueous solution (80 ml) of BTCA (5 g) and sodium salicylate (0.5 g) as curing catalyst at a pH adjusted to 3. The wetted cloth was passed between the rolls of a wringer and the process repeated twice to give an overall pick up 80% by weight of the treatment solution based on the dry weight of the untreated cloth. The test pieces were stretched on a rack and dried in an air forced draft oven at 85°C for 5 minutes. The dried test pieces were then treated in an air draft oven at 180°C for 2 minutes.

The measured WRA was 278°. Treated test pieces had a WRA of 256° after immersion for 5 minutes with 1% Surf solution, followed by rinsing with water and air drying.

Example 1C

Example 1 was repeated, but substituting sodium benzoate (5 g) for the sodium salicylate used in Example 1 and gave a WRA (before washing) of 261°.

Example 2

Example 1 was repeated but substituting oligomaleic acid (OMA) for the BTCA used in Example 1 and gave a WRA (before washing) of 255°.

Example 3

Example 1 was repeated, but substituting sodium 3-hydroxybenzoate (1 g) for the sodium salicylate used in Example 1 and gave a WRA (before washing) of 276°.

Example 4

Example 1 was repeated, but substituting sodium 4-hydroxybenzoate (1 g) for the sodium salicylate used in Example 1 and gave a WRA (before washing) of 276°.

Example 5

Example 1 was repeated, but substituting sodium 2-hydroxyphenylacetate (1 g) for the sodium salicylate used in Example 1 and gave a WRA (before washing) of 274°.

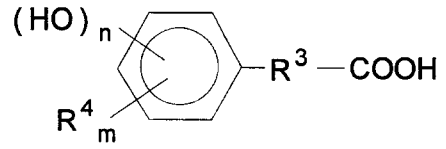
Claims

1 A method of treating fibrous cellulosic textile material which comprises:

a applying to the cellulosic textile material an aqueous solution including at least one polycarboxylic acid as a crosslinking agent for the cellulose and a hydroxycarboxylic acids or a salt as an esterification catalyst,

b drying the textile material and heating it to promote crosslinking esterification of the polycarboxylic acid and the cellulose of the cellulosic textile material.

2 A method as claimed in claim 1 wherein the esterification catalyst is a mono-carboxylic hydroxy acid of the formula (II):



(II)

where

R^3 is a CH_2 group, or, and desirably, a direct bond;

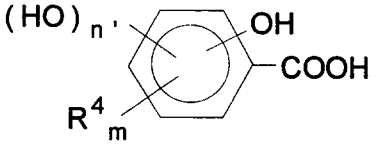
n is from 1 to 3, particularly 1 or 2;

each R^4 is independently a C_1 to C_4 alkyl group; and

m is 0, 1 or 2,

and/or a salt thereof.

3 A method as claimed in claim 2 wherein the catalyst is an aromatic hydroxycarboxylic acid of the formula (III):



(III)

where m and R^4 are independently as defined for formula (II) in claim 2 and n' is 0 or 1 and/or a salt thereof.

4 A method as claimed in either claim 2 or claim 3 wherein the catalyst is one or more of 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2-hydroxyphenylacetic acid 2-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,4-dihydroxy5-methylbenzoic acid 2-hydroxy-3-methyl-benzoic acid, 2-hydroxy-4-methylbenzoic acid and 2-hydroxy-5-methylbenzoic acid and/or a salt thereof.

5 A method as claimed in any one of claims 1 to 4 wherein the polycarboxylic acid crosslinking agent includes at least two carboxylic acid groups are separated by 2 or 3 carbon atoms.

6 A method as claimed in any one of claims 1 to 5 wherein the polycarboxylic acid is one or more of maleic acid, methylmaleic acid, citric acid, itaconic acid, 1,2,3-propanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, all *cis*-1,2,3,4-cyclo- pentanetetracarboxylic acid, oxydisuccinic acid, thiodisuccinic acid, oligo- and/or poly-maleic acid and/or anhydride, benzene hexacarboxylic acid and trimellitic acid.

7 A method as claimed in claim 1 wherein the polycarboxylic acid is 1,2,3,4-butane tetra-carboxylic acid and/or oligo- and/or poly-maleic acid and the catalyst is 2-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid (β-recorcylic acid), 2,4-dihydroxy- 5-methylbenzoic acid 2-hydroxy-3-methylbenzoic acid, 2-hydroxy-4-methylbenzoic acid, 2-hydroxy-5-methyl-benzoic acid or a mixture or a salt thereof.

8 A method as claimed in any one of claims 1 to 7 wherein the amount of polycarboxylic acid crosslinking agent used is from 1 to 10% by weight based on the dry fabric weight.

9 A method as claimed in claim 8 wherein the amount of polycarboxylic acid used is from about 2 to about 7% by weight based on the dry fabric weight.

10 A method as claimed in any one of claims 1 to 9 wherein the amount of hydroxycarboxylic acid catalyst used is from 1 to 100% by weight of the polycarboxylic acid crosslinking agent.

11 A method as claimed in claim 10 wherein the amount of hydroxycarboxylic acid used is from 2 to 30% by weight of the polycarboxylic acid crosslinking agent.

12 A method as claimed in claim 11 wherein the amount of hydroxycarboxylic acid used is from 5 to 20% by weight of the polycarboxylic acid crosslinking agent.

13 A method as claimed in any one of claims 1 to 12 wherein the heating step is carried out at a temperature of from 150 to 240°C.

14 A method as claimed in claim 13 wherein the temperature is from 160 to 200°C.

15 A method as claimed in any one of claims 1 to 14 wherein the heating step is carried out for a time of from 5 seconds to 30 minutes.

16 A method as claimed in claim 15 wherein the time is from 1 to 5 minutes.