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COMPLETE SPECIFICATION

Hemi-Acetals, their preparation and use

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new class of hemi-acetals and to their preparation and use. More particularly, the invention relates to new hydroxy-containing hemi-acetals, to their preparation and to their use particularly in the treatment of textiles.

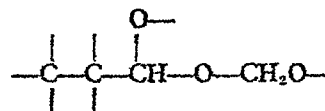
Cellulosic fabrics, such as cotton and rayon, have rather poor resilience, that is they are easily creased or wrinkled when crushed or otherwise subjected to localised physical force. In addition, many of these fabrics have poor dimensional stability as exemplified by poor resistance to shrinkage. In order to overcome these shortcomings, it has been common practice to treat the fabric with a resin, such as a urea- or melamine-formaldehyde resin, that could be subsequently insolubilised within the fabric fibres. The results with these materials have not been entirely satisfactory, particularly with white goods. For instance, the materials impart chlorine-retentive properties which cause discoloration on exposure to heat. Furthermore, often large amounts of resin are needed to obtain the desired crease recovery. This makes the treatment uneconomical as well as, in many instances, affecting the feel of the fabric. In addition, many of the fabrics treated with such resins tend to lose their strength and are easily torn and furthermore, have poor washability, that is the resin is easily lost from the fabric after a few washings with soap and water.

Similar problems have been found in the preparation of paper products. Ordinary paper

when wet loses its strength and is easily torn. In order to overcome this shortcoming, it has also become common practice to treat the paper with nitrogen-containing resins, such as urea- or melamine-formaldehyde resin, that can be subsequently cured to form an insoluble resin. While this method has imparted some improvement in wet strength, it still fails to give a product having the properties required for many commercial applications, for example an acceptable wet strength. In addition, the improvement in wet strength is only temporary and is readily lost after short periods of exposure to water. This defect is particularly serious as it prevents continued use of the paper or use for applications such as food wrappers or containers. Also the paper treated in this manner generally loses its customary feel, becomes quite brittle and loses some of its absorbency. Furthermore, paper treated in this manner may have poor resistance to acids and alkalis and therefore may not be able to be used when the paper is to be contacted with these chemicals.

Related problems are also found with other fibrous materials such as leather. In this instance it is highly desirable to find materials that give the leather a permanent tanning effect rather than one that is lost after exposure to moisture, acids and alkali.

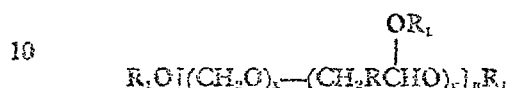
It has now been discovered that these disadvantages can be largely overcome by the use of the new hemi-acetals provided by the process of the present invention. These new products comprise organic compounds possessing in the molecule at least one and preferably two or more hemi-acetal groups of the general skeleton:



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and at least one and preferably a plurality of alcoholic hydroxy groups. The main chain containing the said hemi-acetal group may be acyclic or cyclic and may contain aliphatic or cycloaliphatic carbon atoms and oxygen atoms.

The process of the invention more specifically provides new hydroxy-containing hemi-acetals having the general structural formula:



wherein R is an alkylene radical, preferably containing from 1 to 3 carbon atoms, x and y are each integers of 1 to 5, preferably of 1 to 3, n is an integer of at least 2, and preferably 2 or 3, and R₁ is hydrogen or an alkyl group, at least one of the R₁ groups being hydrogen; alternatively, two of the —OR₁ groups may be removed and the remaining radicals joined together through an oxygen atom to form a cyclic structure or a carbonyl group.

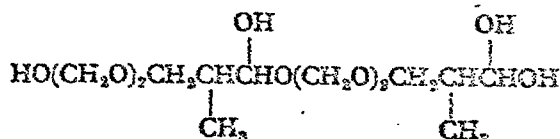
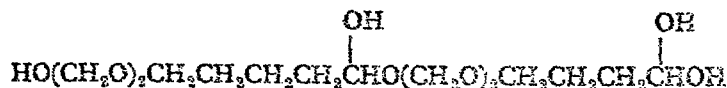
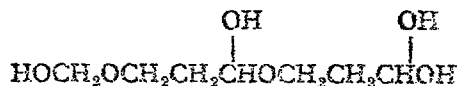
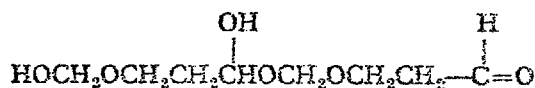
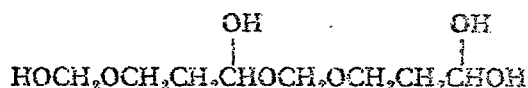
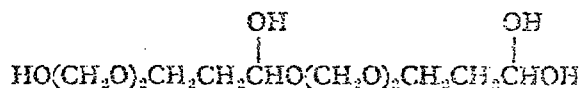
According to the present invention a process for preparing hydroxy-containing hemi-acetals comprises reacting under acidic conditions:

(1) an aldehyde in which there is attached to

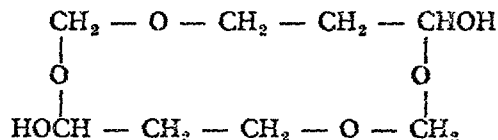
the alpha or beta carbon atom relative to the aldehyde group a hydroxyl, alkyl-sec-amino, primary amino or mercapto group, or an aliphatic carbon-carbon unsaturated linkage is attached to the said alpha or beta atom, for example acrolein, and (2) a dissimilar aldehyde containing no reactive group other than the aldehydic group, for example, formaldehyde. Preferably the aldehydes defined under (1) and (2) are present in a molar ratio of at least 1:1 and preferably the reaction is carried out in the presence of water and/or one or more alcohols as hereinafter defined as liquid medium.

The invention also provides a process for use in the treatment of fibrous materials, such as, for example, textile fabrics, paper and leather, in which the fibrous material is treated with a product of the process of the invention. This process especially comprises impregnating the fibrous material with an aqueous medium containing a product of the process of the invention and an acidic catalyst and then heating the treated material to effect cure.

Particular examples of the hemi-acetals prepared by the process of the invention include, among others, those represented by the following structural formula:

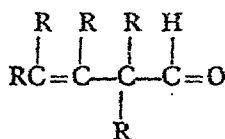
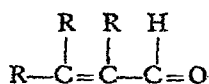
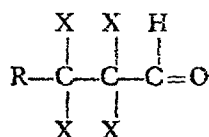


and cyclic hemi-acetals such as



The new products of the process of the invention are prepared by reacting formaldehyde with a dissimilar aldehyde as hereinbefore defined under acidic conditions. Preferred aldehydes to be reacted with formaldehyde include such aliphatic polyaldehydes as hydroxyadipaldehyde and succinaldehyde, and aldehydes such as, for instance, 2-hydroxypropionaldehyde, 3-hydroxypropionaldehyde, 3-aminopropionaldehyde, 2-hydroxybutyraldehyde, 3-hydroxybutyraldehyde, 3-mercaptopropionaldehyde, 3-mercaptopropionaldehyde, 3-aminopentanal, 3-mercaptopentanal, 2-mercaptohexanal, 2-aminododecanal, 3-hydroxycyclohexanal, acrolein, methacrolein, crotonaldehyde, alpha-phenylacrolein, alpha-cyclohexylacrolein, 2-pentenal, 3-hexenal, 2-decenal, 2-cyclohexenal and 2-hydroxy-3-mercapto-tetradecanal.

The preferred members of the above group of aldehydes may be exemplified by the following formulae:



wherein each R represents hydrogen or an aliphatic or cycloaliphatic hydrocarbon group containing up to 12 carbon atoms, and each X represents a hydroxyl, mercapto, primary amino, or alkyl-sec-amino group or represents the same as R, at least one, and preferably one or two, of the X groups representing one or more of the four functional groups specified above.

The ethylenically unsaturated aldehydes are particularly useful in the process of the present invention because of their outstanding properties in the treatment of textile fabrics. Thus preferred products are prepared by reacting formaldehyde with an alpha, beta-ethylenically unsaturated monoaldehyde or a beta, gamma-

ethylenically unsaturated monoaldehyde, such as acrolein, methacrolein, crotonaldehyde or alpha-cyclohexylacrolein.

The second aldehyde reactant to be employed in the process of the present invention is preferably formaldehyde but may be any dissimilar aldehyde containing no reactive group other than the aldehydic group. Examples of such unsaturated mono- and polyaldehydes include formaldehyde, and formaldehyde precursors, such as formalin, paraformaldehyde, trioxene and methylal; acetaldehyde; butyraldehyde; pentanal; hexanal; octanal; dodecanal; cyclohexanal; 2,4-dimethylcyclohexanal; glyoxal; succinaldehyde; 1,8-octanedial, benzaldehyde, adipaldehyde and 3,5-diethylhexanal. Preferably the aldehyde contains up to 12 carbon atoms and is an aliphatic or cyclo-aliphatic saturated mono-, di- or tri-aldehyde.

The use of formaldehyde or a precursor thereof is especially preferred in the process of the invention, for the products obtained thereby are particularly suitable for the treatment of cellulosic textiles.

The relative quantities of the two aldehydes employed in the process of the invention may vary between certain limits. Thus, the functional aldehyde, for example acrolein, and the non-functional aldehyde, for example formaldehyde, may be conveniently combined in molar ratios between 8:1 and 1:8. Particularly outstanding results are obtained when the two aldehydes are combined in molar ratios between 4:1 and 1:4 and more preferably between 1:1 and 1:2.

The reaction between the two aldehydes is carried out in an acidic medium. It is preferred to have the reaction medium at a pH between 0.5 and 6, and especially between 0.5 and 3. When expressed on a normality basis, it is preferred to use reaction media having a normality between 0.05N and 1N. The acidic medium can be obtained by the addition of an acidic or acid-forming material; for example, sulphuric acid; oxalic acid; an alkane sulphonic acid; phosphoric acid; an amine phosphate; an acid-acting salt, such as zinc chloride, magnesium chloride, stannic chloride, aluminium chloride or zinc nitrate; or an acid clay. The concentration of the acidic material employed and the amount added depends on the particular ingredient selected and the acidity desired. It is generally preferred to use a moderately strong acid, such

as sulphuric acid in a concentration between about 20% to 98% by weight, particularly between 20 and 60%.

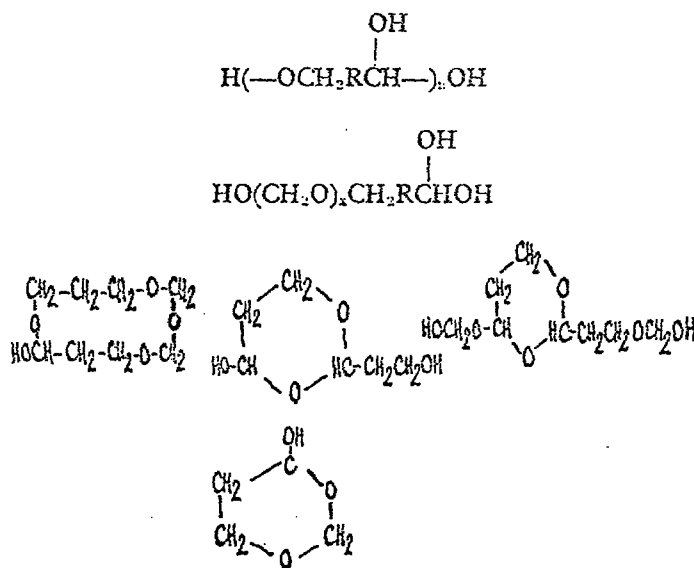
When the product is to be used for cloth treatment, it is sometimes preferred to use the acid-acting salts such as magnesium chloride and zinc nitrate as the catalyst. The catalyst may then be retained in the product and used as a further catalyst in the subsequent reaction with the cloth using the product contained in the original reaction medium.

The reaction of the two aldehydes is conducted in the presence of liquid medium comprising water and/or one or more alcohols such as aliphatic, cycloaliphatic and heterocyclic alcohols. The use of water is particularly desirable as the reaction product may then be used directly in the reaction medium for the treatment of textiles as noted herein-after.

The reaction temperatures employed may vary over a wide range. As the reaction is exothermic, cooling should generally be employed to reduce the temperature. The preferred temperature is between about 0° C and 80° C, and particularly between 10 and 50° C. Any suitable pressure may be employed.

After the reaction has been completed, the reaction mixture is preferably neutralised by the addition of suitable basic materials, and then any excess reactants are preferably removed. This removal may be carried out, for example, by distillation or extraction with suitable solvents, such as petroleum ether or chloroform.

If desired, further processing steps may be employed to favour the production of the cyclic materials over the linear products. Thus, by use of ether extraction followed by azeotropic removal of water with benzene until substantially all the water has been removed, it is possible to greatly increase the formation of the cyclic hemi-acetal structures as shown above. The products obtained from the process of the invention may also contain small quantities of other materials which for most applications are not harmful and in many instances add to the effectiveness of the utilisation. Thus, there may be small amounts of materials having a structure similar to those previously described by a generic formula but wherein x is 0 or n is 1; for example compounds having the structural formulae



wherein R represents an alkylene radical, preferably containing from 1 to 3 carbon atoms, x is an integer of 1 to 5, preferably of 1 to 3 and n is an integer of at least 2 and preferably 2 or 3. If not desired, these compounds may be removed by such methods as extraction or distillation, but for cloth treatment there is normally no need to remove such materials.

The new condensation products prepared by the process of the invention are generally substantially colourless and fluid liquids, though they may be viscous liquids or semi-solids. Their molecular weights are normally between 150 and 250. In general the products are not

very stable in the presence of acids or alkalis and ~~decompose~~ on heating. Because of these characteristics, it is preferred to maintain and use the material in the solution as formed.

The products of the process of the invention surprisingly react like aldehydes in many instances but do not have their disadvantages, such as strong odour and high toxicity. The new materials have been found to be particularly outstanding for treating fibrous material as they impart improved properties thereto. Textile fabrics treated with the new materials have greatly improved crease resistance in both wet and dry state. Furthermore, this improvement is accomplished by the use



decomposed

only very small amounts of the new hydroxy-containing hemi-acetals and without causing a loss of other desired properties, such as feel and strength. A further advantage is that the treated fabric is normally non-chlorine retentive and can therefore be subjected to bleaching and application of heat without discoloration.

Woollen fabrics treated with an aqueous solution of the new condensation products have improved shrink resistance and resistance to matting. The new products are also useful in imparting improved resistance to fraying, pilling and improved dyeability to the synthetic type fabrics, such as those of the polyamide and polyester type.

The new hemi-acetals are also of particular value in the treatment of other fibrous materials, such as paper and leather. They are particularly effective as wet strength agents for sulphite and Kraft paper and as tanning agents for cowhide, calfskin and goatskin. They may also be used in the preparation of non-woven fabrics from synthetic and natural materials.

Furthermore, the hemi-acetals produced by the process of the present invention are also useful as insolubilising agents for starch, such as cereal, corn, rice, wheat, root, potato and tapioca starches and as insolubilising agents for casein and other albuminous materials. They are also of value as cross-linking agents for hydroxy-containing materials, such as cellulose derivatives, cellulose ethers and cellulose esters such as ethyl and methyl cellulose, cellulose acetate and propionate, and cross-linking agents for hydroxy-containing polymers such as polyvinyl alcohol, hydrolysed copolymers of vinyl acetate and alpha-olefins and polyallyl alcohols.

The new hemi-acetals may also be used to produce resinous materials by reaction with polyhydric alcohols such as pentaerythritol, di- and polypentaerythritols, and then reacting the resulting product with a polyisocyanate, such as, for example, an arylene diisocyanate.

The new hemi-acetals also find use in the preparation of new phenolic derivatives by condensation with phenols. Such materials may be subsequently reacted with epichlorohydrin in the presence of an alkali to form new epoxy resins.

The hemi-acetals produced by the process of the present invention may be used for the treatment of wood, as tissue fixing agents, as embalming fluids and as agents for use in medical pathological work and also as intermediates for the preparation of fungicides and insecticides and as intermediates for the preparation of oil-soluble derivatives for use in lubricating and fuel oil compositions.

The products of the process of the invention are preferably employed in an aqueous

medium and in combination with acidic curing agents. However, other media such as solvents or mixtures of water and solvents may be used as well as other types of curing agents. Suitable solvents include, for instance, alcohols such as ethanol, butanol, isopropanol, acetone, dioxane, diacetone alcohol, esters, ethers and ether esters of glycol and glycerol, ethylene dichloride, benzene and toluene, and mixtures thereof.

Sometimes it is desirable to employ the products in an aqueous emulsion or suspension. Suitable emulsifying agents include the ionic and non-ionic agents, such as, for example, the mono-oleate of sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene ethers of alkylphenols, carboxymethylcellulose, starch, gum arabic, aryl and alkylated aryl sulphonates, such as cetrl sulphonate, cetyl sulphonate and sulphonated mineral oils, and mixtures thereof. The emulsifying agents are generally employed in amounts varying from 1.0% to 10% by weight and more preferably from 1% to 5% by weight.

The amount of the product employed in an aqueous medium for treatment of the fibrous materials depends chiefly on the amount of product to be deposited on the fibrous material and this in turn depends on the number of applications and the pick-up allowed per application. When the solution is applied but once, with a 90% to 100% pick-up by weight of the fabric in the dry state, a concentration between about 0.5% and 25% by weight will ordinarily suffice. Preferred concentrations range from about 1.5% to 4% and particularly 2%. If less than 80% pick-up is permitted, the concentration may, in some instances, go as high as 30% to 50%.

The curing agent employed may be any acidic catalytic material, such as an organic or inorganic acid, for example, oxalic, lactic, succinic, acetic, maleic, phosphoric, boric, sulphonic, perchloric, persulphuric, p-toluene-sulphonic or sulphuric acid. Alternatively the curing agent may be one or more metal salts such as, for example, zinc fluoroborate, copper fluoroborate, zinc persulphate, cupric arsenite, cupric chlorate, cupric chromate, cupric dichromate, cupric fluorosilicate, cupric nitrate, zinc nitrate, cupric sulphate, cobaltic chlorostannate, cobaltous fluoroborate, cobaltous fluorosilicate, cobaltous sulphite, chromic sulphate, chromic nitrate, lead borate, lead chlorate, lead phosphate, barium chlorate, barium phosphate, magnesium fluorosilicate, magnesium chloride, magnesium perchlorate, magnesium nitrate, magnesium fluoroborate, magnesium sulphate, manganese sulphate, manganese fluoroborate, cadmium arsenate, cadmium borate, cadmium perchlorate, cadmium phosphate, aluminium arsenate, aluminium chlorate, aluminium nitrate,

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aluminium fluoroborate, nickel phosphate, nickel selenate, nickel sulphate, silver sulphate, silver nitrate, silver thiosulphate, stannic fluoroborate, strontium chlorate, titanium sulphate, vanadium sulphate, zinc chlorate, 5 zinc fluorosilicate, zinc permanganate, zinc phosphate, zinc sulphate, zirconium sulphate, aluminium phosphate, aluminium sulphate, vanadium nitrate, vanadium sulphate, 10 vanadium fluoroborate, vanadium selenate, bismuth phosphate, ferric phosphate, ferric pyrophosphate, ferric sulphate, ferrous sulphite, ferrous perchlorate, mercuric arsenate, mercuric chromate, mercuric sulphate, mercurous chlorate, mercurous fluoroborate, nickel fluoroborate or nickel arsenate. 80

The amount of the curing agent used depends upon the product selected and the method of cure. Generally, the amount used is 20 between 0.1% and 15% based on the weight of the condensation product. The metal salts and boron trifluoride complexes are preferably employed in an amount between about 25 0.1% and 8% and the organic acids and inorganic acids are preferably employed in an amount between 0.1% and 10% by weight of the product. 85

The solution employed to treat the fibrous material may also contain a plasticiser to improve flexibility, though this should not be present in such a proportion as to render the finished materials soft or sticky at tempera- 30 tures and humidities to which they would be exposed. It is found, however, that the substances employed in the present invention yield products which are sufficiently flexible for most purposes without the use of plasticisers. Among plasticisers that may be 40 used according to the present invention may be mentioned organic and inorganic derivatives of phenols, for example, diphenylol propane and triphenyl and tricresyl phosphate, sulphonamides, sulphonylides, alkyl 45 phthalates, for example, diethyl phthalate and glycol phthalates, diethyl tartarate, derivatives of polyhydric alcohols, for example, mono-, di- and tri-acetin, and products obtained by condensing polyhydric alcohols with themselves or with aldehydes or ketones. The 50 compositions may also contain natural resins, for example, shellac, rosin, and other natural resins and synthetic or semi-synthetic resins, for example, ester gum, polyhydroxy- 55 polybasic alkyd resins, phenolaldehyde and urea-aldehyde resins. 100

The new products may also be used in combination with polyepoxides, such as, for example, glycidyl ethers of polyhydric alcohols or phenols. 60 Textile-softening agents, and particularly those of the cationic-type such as stearamidoethyl diethyl methyl quaternary ammonium methyl sulphate, the trimethyl ammonium methyl sulphate of monostearylmetaphenylene- 65 diamine, s-di-1-(2-palmitamidoethyl) urea monoacetate and palmityl amine hydrochloride, and mixtures thereof, may also be added in varying amounts to improve the feel of the treated fabrics. Other examples of suitable materials to which the compounds of the invention may be applied include polyethylenes, acrylics and silicone-treated fibres. 70

The application of the solution containing the product to the fibrous material may be 75 effected in any suitable manner, the method selected depending upon the results desired. If it is desired to apply the solution only to one surface of the material, as, for example, when it is desired to treat the back only of a fabric having a face of artificial or natural silk and a cotton back, the application may be effected by spraying as a liquid or gas or by means of rollers, or the composition may be spread upon the surface by means of a doctor blade. When, however, it is desired to coat both surfaces of the material, or if the material is to be thoroughly impregnated with it, the material may be simply dipped in the solution or run through conventional-type padding rollers. The solutions may also be applied locally to the material, for example, by means of printing rollers or by stencilling. 80

The amount of the product to be deposited on the fibrous material depends upon the properties to be imparted, to the finished material and the use to which this is to be put. If treated material is a fabric used for dresses and shirts, the amount of the products deposited will generally be between 1% and 20% by weight of the fabrics. If stiffer materials are required such as for shoe fabrics and draperies, still higher amounts of resins, such as of the order of 25% to 50% by weight may be deposited. If the material is paper and the property to be imparted is wet strength, the amount of material deposited may be from 0.1% to 15% by weight. In determining the amounts of product deposited, it should, of course, be remembered that the presence of the product in a few instances causes a slight decrease in tear strength of the material and the amount deposited should be balanced between the desired properties and the desired tear strength. 95

If the desired amount of the product deposited is not obtained in one application, the solution can be applied again or as many times as desired in order to bring the amount of the condensation product up to the desired level. 100

After the desired amount of solution has been applied, the treated material is preferably dried for a short period to remove some or all of the dispersing liquid, such as water or alcohol. This is generally accomplished by exposing the wet material to hot gas at temperatures ranging from 50° C to 80° C. The drying period depends largely on the amount of pick-up permitted during the application 125 130



sticky

the solution, and the concentration of the condensation product. In most instances, drying periods of from 5 to 30 minutes should be sufficient.

5 The dried material is then exposed to relatively high temperatures to accelerate the cure. Temperatures used for this purpose generally range from 100° C to 200° C, and more preferably from 100° C to 150° C. At 10 these preferred temperature ranges the cure can generally be accomplished in from 3 to 10 minutes. Exposures of less than 3 minutes, for example 1 minute, may probably be used in continuous, commercial processing.

15 After curing, it is desirable in most cases to wash the treated material to remove any soluble materials. A perborate wash is particularly desirable.

20 The above-described process may be utilised for the treatment of any fibrous material. This includes textile material, such as woven fabrics, non-woven fabrics, threads, yarns, cord, and string, paper, leather, and films. These materials may be prepared from 25 natural or synthetic materials, such as cotton, linen, natural silk and artificial silk, such as silk obtained from cellulose acetate or other organic esters or ethers of cellulose, viscose rayons, jute, hemp, animal fibres, such as 30 wool, hair, as well as synthetic materials which include, among others, those prepared from acrylonitrile, vinylidene cyanide polymers, polyamides, polyester - polyamides, and polymers prepared from corn protein and 35 formaldehyde. As in the above-noted addition polymers, this includes the homopolymers as well as copolymers and terpolymers, such as, for example, those prepared from 85% 40 acrylonitrile and 15% vinyl acetate, from 60% vinyl chloride and 40% acrylonitrile and from 85% vinylidene chloride and 15% vinyl chloride. Other synthetic fibres include those prepared from polyethylenes and polypropylenes, polyurethanes, mineral fibres such 45 as glass fibres and alginic materials such as alginate rayon.

50 The papers employed in the process of the invention include those prepared from wood, cotton, linen, hemp, jute, mulberry, straw, bamboo, cane fibres or mixtures thereof, by

any of the known processes such as the sulphate, sulphite or soda process.

The leather employed is preferably cowhide, calfskin or other hides commonly employed in the preparation of leather goods. 55

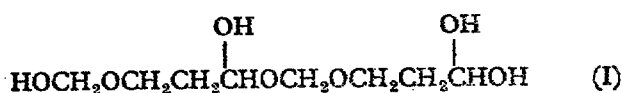
The fibrous materials treated may be colourless or may be dyed, printed or otherwise coloured to the desired shade. It is also possible to first subject the colourless material to the process of the invention and then apply 60 the desired dye, pigment or other colouring material.

The product treated as noted above may be utilised for any of the conventional applications, such as in the manufacture of dresses, 65 drapes, upholsteries, shoe fabrics, carpets, coats, shirts, uniforms, shoes, towels, cords, construction paper, wrapping paper and containers.

70 The invention will now be illustrated by the following Examples in which all quantities are expressed on a weight basis. In the Examples the wrinkle recovery values are reported as the sum of average warp and fill 75 measures; the tear strength values were determined by the Trapezoid Method ASTM D—39—49. The dry crease recovery values were determined on cloth dried at 250° F, and the wet crease recovery values by soaking the 80 fabric in water for 30 minutes and then blotting before testing and all tests were carried out at 50% relative humidity at 78° F.

EXAMPLE 1.

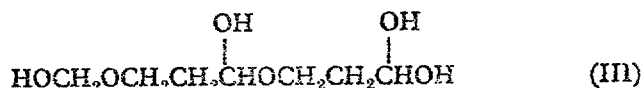
85 To a solution of 1 mol of formaldehyde in 11 parts of 50% sulphuric acid there was added 1 mol of freshly distilled acrolein. The mixture had a normality of about 0.76. The temperature was allowed to rise to about 35— 40° C. The mixture was cooled and held at 90 room temperature for about 12 hours. The mixture was then neutralised with sodium hydroxide and filtered. Analysis of the resulting product by infra-red, molecular weight, functionally and carbon and hydrogen 95 analysis indicated that the solution contained hydroxy-containing hemi-acetals of the formula:



and



Small amounts of each of the following were also present:



and



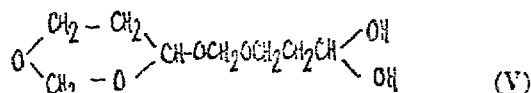
5 The above solution was combined with water to form a solution having 2% solids, there was added 3% of a 50% aqueous solution of magnesium chloride, and the combined mixture used to pad cotton fabric. The
10 impregnated sheet was then dried at 250° F for 5 minutes and cured at 300° F for 5 minutes. The finished product was washed with sodium perborate and rinsed three times in warm water, framed to dimensions and
15 dried at 250° F. The material had a dry crease recovery of 250 (W + F) and had 76% retention of original strength. The scorch test gave a value of 79% reflectance (81% before test) as compared to 80% (82% before test)
20 for the control.

When the padding process was repeated using solutions containing 4, 5, 6, 8, 9 and

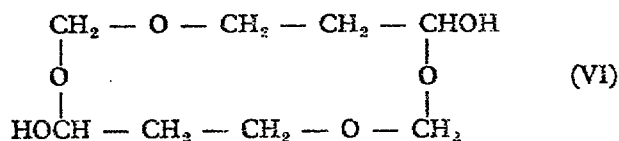
10% solids respectively similar results were obtained.

EXAMPLE 2.

The reaction of formaldehyde and acrolein in the presence of sulphuric acid was carried out by the process of Example 1 except that the temperature of the mixture was not allowed to rise above 35° C. After several hours at room temperature the acid was neutralised by the addition of a saturated solution of sodium sulphate and the mixture then extracted with ether. The ether was removed under vacuum followed by azeotropic distillation with benzene. The resulting product was a clear fluid liquid. Analysis as in Example 1 indicated that the liquid contained a mixture of hydroxy-terminated hemi-acetals of the formulae



and



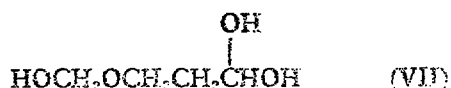
5 Parts of the liquid hydroxy-terminated hemi-acetals prepared as above were combined with water to form a 5% solution and
45 10 parts of a 10% aqueous solution of zinc nitrate added as catalyst. Bleached cotton cloth was padded with the above solution by means of a Butterworth 3-roll laboratory
50 padder. The cloth after padding showed an 80% wet pick-up. The impregnated cloth was then dried at 250° F for 5 minutes and cured at 300° F for 5 minutes. The finished product was washed with sodium perborate solution,
55 rinsed three times in warm water and then framed to dimensions and dried at 250° F. The cloth treated in this manner had the same appearance, feel and hand as before the treatment and had excellent shrink, scorch and
60 wet and dry crease resistance. The material

had a dry crease recovery value (W and F) of 243 compared to a value of 162 for an untreated sample of the material. By the AATCC Scorch Test the cloth had a reflectance of 79% (81% before test) compared to a value of 80% (82% before test) for the untreated cloth. The excellent resistance to laundering was shown by the fact that the fabric treated in the above-described manner could be washed 20 or more times without material change in the high crease recovery values.

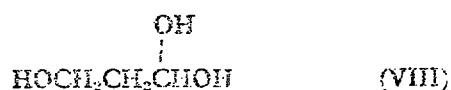
EXAMPLE 3.

To a solution of 4 mols of formaldehyde (300 ml of formalin solution) in 22 parts of 50% sulphuric acid there was added 1 mol of freshly distilled acrolein. The mixture had a normality of 0.78. The temperature of the

ixture was kept below 35° C for 24 hours. The solution was then saturated with sodium sulphate and the mixture extracted with ether. The ether was removed under vacuum to give a clear fluid liquid. Analysis as in Example 1 indicated that the liquid contained a predominate amount of the hydroxy-terminated hemi-acetal of the formula I (as shown in Example 1); smaller amounts of each of the following compounds were also present:



and



EXAMPLE 4.

This Example illustrates the preparation of a hydroxy-terminated hemi-acetal from glyceraldehyde and formaldehyde using sulphuric acid as a catalyst.

To a solution of 1 mol of formaldehyde as a Formalin solution in 20 parts of 50% sulphuric acid there was added 150 ml of an aqueous solution containing 1 mol of glyceraldehyde. The mixture had a normality of about 0.8. The temperature of the mixture was kept below 35° C for 36 hours. A saturated solution of sodium sulphate was then added to neutralise the acid and the mixture extracted with ether. The ether was removed under vacuum to give a clear fluid liquid hydroxy-terminated hemi-acetal.

The above product was applied to cloth as shown in Example 1. The resulting product had improved crease resistance.

EXAMPLE 5.

Example 1 was repeated with the exception that hydroxy acrylaldehyde was employed in place of acrolein. A similar product was obtained and cloth treated in the same manner had similar properties.

EXAMPLE 6.

Examples 1 to 4 were each repeated three times replacing the sulphuric acid catalyst by each of the following in turn: phosphoric acid, nitric acid and an amino hydrogen phosphate. In each instance similar results were obtained.

EXAMPLE 7.

This Example illustrates the preparation of a condensation product from acrolein and formaldehyde using sulphuric acid as the catalyst, and the superior results obtained by using the condensation product as a crease-proofing agent for cotton fabric.

To a suspension of 3.7 mol of formaldehyde in the form of para-formaldehyde in 150 parts of 30% sulphuric acid there was added 1 mol of freshly distilled acrolein. The mixture

had a normality of about 0.8 and a pH of about 1. The temperature rose from 14° C to 40° C. The mixture was cooled and then held at room temperature for 12 hours by cooling. The mixture was filtered and the clear filtrate neutralised with calcium oxide. The product was then extracted with ether (chloroform was also suitable) to give a white fluid non-volatile product possessing free OH group and having the following analysis: C, 44.0%; H, 8.2%; OH value, 0.981 eq/100g; carbonylic value, 1.749 eq/100g.

5 Parts of the reaction product prepared above were combined with water to form a 5% solution and 5 parts of a 50% aqueous solution of magnesium chloride were added as catalyst.

Bleached cotton print (80 x 80 count) cloth was then impregnated with the above-described solution by means of a Butterworth 3-roll laboratory padder. The cloth after padding showed an 80% wet pick-up. The cloth was then impregnated, dried, cured, washed with sodium perborate solution, rinsed in warm water and then framed to dimensions and dried by the method described in Example 2.

The cloth treated in the above-described manner had the same appearance and feel as before the treatment and had excellent shrink, scorch and wet and dry crease resistance. The material had a dry crease recovery value (W and F) of 243 compared to a value of 162 for an untreated sample of the material. By the AATCC Scorch Test the cloth had a reflectance of 79% (81% before test) compared to a value of 80% (82% before test) for the untreated cloth. The excellent resistance to laundering was shown by the fact that the fabric treated in the above-described manner could be washed 20 or more times without material change in the high crease recovery values.

The chlorine retention of the fabric was demonstrated in the following manner. Cotton fabric was placed for 10 minutes in a hypochlorite solution containing 0.4% available chlorine using a bath to cloth ratio of 30:1 and maintained at 140° F. The fabric was then rinsed six times for 5 minutes at 100° F and dried as smooth as possible. A hot iron at 400° F was placed on the cloth for 30 seconds. The cloth was then examined to determine the extent of the discoloration and degradation. A dark colour indicates charring due to chlorine retention. It was found that the fabric treated by the above-described process had substantially the same colour as before the treatment, while a related fabric treated with urea-formaldehyde resin was highly discoloured.

EXAMPLE 8.

The treatment of cloth by the method of Example 7 was repeated with the exception that the catalyst employed was 10 parts of a

10% aqueous solution of zinc nitrate. In this instance, the resulting fabric had a crease recovery value of 237.

EXAMPLE 9.

5 To a suspension of 1 mol of formaldehyde in the form of para-formaldehyde in 150 parts of 30% sulphuric acid there was added 1 mol of freshly distilled acrolein. The temperature rose from 21° C to 44° C. The mixture was cooled and the temperature held at room temperature for 12 hours by cooling. The mixture was neutralised with sodium hydroxide and then filtered.

15 The above product, without extraction as in the previous Examples, was combined with water to form a solution having 2% solids, there was added 3% of a 50% aqueous solution of magnesium chloride and the combined mixture used to pad cotton fabric as in Example 7. The impregnated sheet was then dried, cured, and washed with sodium perborate and rinsed as in Example 2. The cloth treated in this manner had the same appearance and feel as before the treatment but had excellent shrink and crease recovery both wet and dry. The material had a dry crease recovery of 250 (W + F) and had 76% retention of original strength. The scorch test gave a value of 79% reflectance (81% before test) as compared to 80% (81% before test) for the control.

When the above padding process was repeated using solutions containing 4, 5, 6, 8, 9 and 10% solids respectively similar results were obtained.

EXAMPLE 10.

To a suspension of 1 mol of formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 2 mols of freshly distilled acrolein. The mixture had a normality of about 0.8 and a pH of about 1. The temperature rose to 35° C and then was held at room temperature for 14 hours with cooling. The mixture was filtered and the clear filtrate neutralised with calcium oxide. The product was then extracted with ether and chloroform to give a white, fluid, non-volatile water-soluble product possessing free OH groups and having the following analysis: C, 52.7%; H, 27.8%; OH value, 0.45 eq/100g; carbonylic value, 0.82 eq/100g.

5 Parts of the reaction product prepared above were combined with water to form a 5% solution and 10 parts of a 10% aqueous solution of zinc nitrate added as catalyst. Bleached cotton print cloth was padded with the above solution and the impregnated fabric was then dried, cured and washed as in Example 2.

The cloth treated in the above-described manner had the same appearance and feel as before the treatment, and had excellent crease recovery and shrink and scorch resistance. The material had a crease recovery value of 244 as compared to a value of 162 for an un-

treated sample. The treated cloth also had no chlorine retentive properties as shown by a test as described in Example 7.

EXAMPLE 11.

Results similar to those shown in Example 10 were obtained when the zinc nitrate was replaced in the padding bath shown in Example 10 with each of the following catalysts: magnesium chloride, zinc fluoroborate, magnesium perchlorate and magnesium sulphate.

EXAMPLE 12.

To a suspension of 1 mol of formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 2 mols of freshly distilled acrolein. The temperature rose to 38° C and then was held at room temperature for 16 hours with cooling. The mixture was then neutralised with sodium hydroxide and filtered. The above product, without extraction as in Example 10 was combined with water to form a solution having 2% solids. 5 Percent of zinc nitrate as a 10% aqueous solution was then added as catalyst.

Bleached cotton print cloth was padded with the above solution and the impregnated fabric dried, cured and washed as in Example 2. The finished cloth had a dry crease recovery of 260 (W + F). The scorch test gave a value of 78% reflectance (81% before test) as compared to 80% (82% before test) for an untreated sample.

Similar results were obtained when the above padding process was repeated using magnesium chloride as the catalyst. In this instance the product had a crease recovery value of 240 and retained 80% of its original strength.

EXAMPLE 13.

To a suspension of 4 mols of formaldehyde in 150 parts of 50% sulphuric acid there was added 1 mol of acrolein. The temperature rose to 40° C and was kept there with cooling for about 18 hours. The mixture was filtered and the clear filtrate neutralised with sodium hydroxide and saturated with sodium sulphate. The product was filtered and extracted with ether, dried and stripped to give a water-soluble white non-volatile syrup having free OH groups. 10 Parts of the reaction product prepared above were combined with water to form a 10% solution and 5 parts of zinc fluoroborate added as catalyst.

Bleached cotton print cloth was padded with the above solution and the impregnated fabric was then dried, cured and washed as in Example 2. The cloth treated in the above-described manner had the same appearance and feel as before the treatment, and had good shrink and crease resistance.

EXAMPLE 14.

A 5% solution of the condensation product prepared in Example 7 containing 5% zinc nitrate as catalyst was used to pad sheets of rayon gabardine cloth. The impregnated cloth



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was dried at 60° C and cured at 300° F for 5 minutes. The rayon cloth treated in this manner was quite soft and had increased wrinkle resistance, good washability and excellent shrink resistance.

EXAMPLE 15.

This Example illustrates the use of the condensation product shown in Example 10 for the treatment of woollen fabric to impart shrink resistance.

A 5% solution of the condensation product prepared in Example 10 containing 5% magnesium chloride as catalyst was used to impregnate a sheet of woollen fabric by means of a 3-roll laboratory padder. The impregnated cloth was dried at 60° C and cured for 15 minutes at 160° C. The woollen fabric treated in this manner had the same appearance as before the treatment and had good strength and improved shrink resistance.

EXAMPLE 16.

This Example illustrates the use of the condensation product shown in Example 7 for the treatment of paper.

Pieces of unbleached Kraft paper were treated with a 10% solution of a condensation product prepared as in Example 7 and containing 5% zinc nitrate as catalyst. The sheets were impregnated by means of the laboratory padder as shown in that Example. The treated sheets were dried and heated for 5 minutes at 300° F. The resulting sheets had the same feel and appearance as before the treatment and displayed excellent resiliency, good fold endurance, good absorbency and high wet tensile strengths and burst strengths.

EXAMPLE 17.

This Example illustrates the use of the condensation product in treating paper in the beater stage.

Unbleached Kraft paper pulp was beaten in a beater in the usual manner and made into an 0.6% water suspension. A portion of the aqueous solution of a condensation product prepared as in Example 7 containing 5% zinc nitrate was added to the paper pulp suspension so as to give a solution having 3% condensation product based on the weight of the paper pulp. This suspension was then made into a paper sheet and the sheet dried for a few minutes at 60° C. The dried sheet was heated for 5 minutes at 300° F. The resulting sheet appeared as normal paper but displayed excellent resiliency, good fold endurance, good absorbency and good wet strength.

Similar results were obtained by replacing the zinc nitrate catalyst with each of the following: magnesium chloride, zinc fluoroborate, magnesium perchlorate and zinc sulphate.

EXAMPLE 18.

Pieces of acetone dehydrated hide, amounting to about 15 parts, were placed in a 5%

solution of a condensation product prepared as in Example 7 and zinc nitrate as the curing agent. The hide in contact with this solution was gently agitated at room temperature. The hide was then removed, dried and heated to cure the condensation product. The leather had good resistance to detanning by treatment with acids and alkali.

EXAMPLE 19.

To a suspension of 1 mol formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 1 mol of aldol (2-hydroxybutyraldehyde). The temperature rose to about 40° C. The mixture was cooled and held at room temperature for 12 hours by cooling. The mixture was then neutralised with calcium oxide and the product filtered.

The above solution containing the condensation product of formaldehyde and the 2-hydroxybutyraldehyde was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

EXAMPLE 20.

To a suspension of 1 mol of glutaraldehyde in 150 parts of 30% sulphuric acid there was added 1 mol of freshly distilled acrolein. The temperature rose to about 30° C, and then the mixture was cooled to room temperature and kept there for about 16 hours. The resulting mixture was neutralised with calcium oxide and the product filtered.

The above solution containing the condensation product of glutaraldehyde and acrolein was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

EXAMPLE 21.

To a suspension of 1 mol of formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 1 mol of 3-aminopropionaldehyde. The temperature rose to about 50° C and the mixture was cooled to room temperature and kept there for about 12 hours. The resulting mixture was neutralised and filtered.

The above solution containing the condensation product of formaldehyde and 3-aminopropionaldehyde was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

Related condensation products to the above were obtained when the 3-aminopropionaldehyde was replaced by equimolar amounts of each of the following: 2-aminobutyraldehyde, 3-mercaptopropionaldehyde, 3-mercaptopentanal and crotonaldehyde.

WHAT WE CLAIM IS:—

1. A process for the preparation of a hydroxy-containing hemi-acetal which comprises reacting under acidic conditions: (1) an aldehyde in which there is attached to the alpha or beta carbon atom relative to the aldehydic group a hydroxyl, alkyl-sec-amino, primary amino or mercapto group, or an



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was dried at 60° C and cured at 300° F for 5 minutes. The rayon cloth treated in this manner was quite soft and had increased wrinkle resistance, good washability and excellent shrink resistance.

EXAMPLE 15.

This Example illustrates the use of the condensation product shown in Example 10 for the treatment of woollen fabric to impart shrink resistance.

A 5% solution of the condensation product prepared in Example 10 containing 5% magnesium chloride as catalyst was used to impregnate a sheet of woollen fabric by means of a 3-roll laboratory padder. The impregnated cloth was dried at 60° C and cured for 15 minutes at 160° C. The woollen fabric treated in this manner had the same appearance as before the treatment and had good strength and improved shrink resistance.

EXAMPLE 16.

This Example illustrates the use of the condensation product shown in Example 7 for the treatment of paper.

Pieces of unbleached Kraft paper were treated with a 10% solution of a condensation product prepared as in Example 7 and containing 5% zinc nitrate as catalyst. The sheets were impregnated by means of the laboratory padder as shown in that Example. The treated sheets were dried and heated for 5 minutes at 300° F. The resulting sheets had the same feel and appearance as before the treatment and displayed excellent resiliency, good fold endurance, good absorbency and high wet tensile strengths and burst strengths.

EXAMPLE 17.

This Example illustrates the use of the condensation product in treating paper in the beater stage.

Unbleached Kraft paper pulp was beaten in a beater in the usual manner and made into an 0.6% water suspension. A portion of the aqueous solution of a condensation product prepared as in Example 7 containing 5% zinc nitrate was added to the paper pulp suspension so as to give a solution having 3% condensation product based on the weight of the paper pulp. This suspension was then made into a paper sheet and the sheet dried for a few minutes at 60° C. The dried sheet was heated for 5 minutes at 300° F. The resulting sheet appeared as normal paper but displayed excellent resiliency, good fold endurance, good absorbency and good wet strength.

Similar results were obtained by replacing the zinc nitrate catalyst with each of the following: magnesium chloride, zinc fluoroborate, magnesium perchlorate and zinc sulphate.

EXAMPLE 18.

Pieces of acetone dehydrated hide, amounting to about 15 parts, were placed in a 5%

solution of a condensation product prepared as in Example 7 and zinc nitrate as the curing agent. The hide in contact with this solution was gently agitated at room temperature. The hide was then removed, dried and heated to cure the condensation product. The leather had good resistance to detanning by treatment with acids and alkali.

EXAMPLE 19.

To a suspension of 1 mol formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 1 mol of aldol (2-hydroxybutyraldehyde). The temperature rose to about 40° C. The mixture was cooled and held at room temperature for 12 hours by cooling. The mixture was then neutralised with calcium oxide and the product filtered.

The above solution containing the condensation product of formaldehyde and the 2-hydroxybutyraldehyde was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

EXAMPLE 20.

To a suspension of 1 mol of glutaraldehyde in 150 parts of 30% sulphuric acid there was added 1 mol of freshly distilled acrolein. The temperature rose to about 30° C, and then the mixture was cooled to room temperature and kept there for about 16 hours. The resulting mixture was neutralised with calcium oxide and the product filtered.

The above solution containing the condensation product of glutaraldehyde and acrolein was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

EXAMPLE 21.

To a suspension of 1 mol of formaldehyde as a formalin solution in 150 parts of 30% sulphuric acid there was added 1 mol of 3-aminopropionaldehyde. The temperature rose to about 50° C and the mixture was cooled to room temperature and kept there for about 12 hours. The resulting mixture was neutralised and filtered.

The above solution containing the condensation product of formaldehyde and 3-aminopropionaldehyde was applied to white cotton fabric as in Example 9 whereupon similar results were obtained.

Related condensation products to the above were obtained when the 3-aminopropionaldehyde was replaced by equimolar amounts of each of the following: 2-aminobutyraldehyde, 3-mercaptopropionaldehyde, 3-mercaptopentanal and crotonaldehyde.

WHAT WE CLAIM IS:—

1. A process for the preparation of a hydroxy-containing hemiacetal which comprises reacting under acidic conditions: (1) an aldehyde in which there is attached to the alpha or beta carbon atom relative to the aldehydic group a hydroxyl, alkyl-sec-amino, primary amino or mercapto group, or an

- aliphatic carbon-carbon unsaturated linkage; and (2) a dissimilar aldehyde containing no reactive group other than the aldehydic group.
- 5 2. A process as claimed in claim 1, in which the aldehyde defined under (1) is hydroxy adipaldehyde or succinaldehyde.
3. A process as claimed in claim 1, in which the aldehyde defined under (1) is a hydroxy-substituted monoaldehyde.
- 10 4. A process as claimed in claim 1, in which the aldehyde defined under (1) is an alpha,beta-ethylenically unsaturated aldehyde.
5. A process as claimed in claim 4, in which the said aldehyde is acrolein.
- 15 6. A process as claimed in any one of claims 1 to 5, in which the dissimilar aldehyde is formaldehyde.
7. A process as claimed in any one of claims 1 to 6, in which the aldehydes defined under (1) and (2) respectively are reacted in a molar ratio of between 8:1 and 1:8.
- 20 8. A process as claimed in claim 7, in which the molar ratio is between 4:1 and 1:4.
- 25 9. A process as claimed in claim 8, in which the molar ratio is between 1:1 and 1:2.
10. A process as claimed in any one of claims 1 to 9, in which the reaction is carried out in the presence of water and/or one or more alcohols.
- 30 11. A process as claimed in any one of claims 1 to 10, in which the reaction is carried out at a temperature between 0° C and 80° C.
- 35 12. A process as claimed in claim 11, in which the temperature lies between 10° C and 50° C.
- 40 13. A process as claimed in any one of claims 1 to 12, in which the reaction medium has a pH of between 0.5 and 6.
14. A process as claimed in claim 13, in which the reaction medium has a pH of between 0.5 and 3.
- 45 15. A process as claimed in either of claims 13 or 14, in which the reaction is conducted in the presence of sulphuric acid.
16. A process for the preparation of a hydroxy-containing hemi-acetal substantially as hereinbefore described with reference to any one of Examples 1 to 7.
- 50 17. A process for the preparation of a hydroxy-containing hemi-acetal substantially as hereinbefore described with reference to any one of Examples 7, 9, 10, 12, 13 or 19 to 21.
- 55 18. A compound whenever prepared by a process as claimed in any one of claims 1 to 17.
- 60 19. A compound as claimed in claim 18, whenever prepared by the reaction of an alpha, beta-ethylenically unsaturated aldehyde and an alkanedialdehyde.
- 65 20. A compound as claimed in claim 19, in which the alkanedialdehyde is glutaraldehyde.
21. A composition suitable for use in the treatment of fibrous materials which comprises a solution of at least one compound as claimed in any one of claims 18 to 20 in a solvent.
- 70 22. A composition as claimed in claim 21, in which the solvent is water and/or an alcohol.
- 75 23. A composition suitable for use in the treatment of fibrous materials which comprises an emulsion or suspension of at least one compound as claimed in any one of claims 18 to 20.
- 80 24. A composition as claimed in claim 23, in which the emulsion or suspension contains an emulsifying or suspending agent in an amount of 0.1 to 10%, by weight.
- 85 26. A composition as claimed in any one of claims 21 to 25 which also contains a plasticizer.
27. A composition as claimed in any one of claims 21 to 26, which also contains a resin.
- 90 28. A composition as claimed in any one of claims 21 to 27, which also contains a textile softening agent.
29. A process for the treatment of a fibrous material in which the fibrous material is treated with one or more compounds as claimed in any one of claims 18 to 20.
- 95 30. A process for the treatment of a fibrous material in which the fibrous material is treated with a composition as claimed in any one of claims 21 to 28.
- 100 31. A process as claimed in either of claims 29 to 30, in which the treatment is effected by impregnation with an aqueous medium containing an acid-acting catalyst, followed by heating to effect cure.
- 105 32. A process as claimed in any one of claims 29 to 31, in which the fibrous material treated is a textile fabric to which is imparted crease and shrink resistance.
- 110 33. A process as claimed in claim 32, in which the textile fabric is a cellulosic material, or a woollen, rayon or cotton fabric.
34. A process as claimed in any one of claims 29 to 31, in which the fibrous material treated is leather or paper.
- 115 35. A process as claimed in any one of claims 29 to 34, in which the acid-acting catalyst is a metal salt.
36. A process as claimed in claim 35, in which the metal salt is a heavy metal nitrate.
- 120 37. A process as claimed in claim 36, in which the heavy metal nitrate is zinc nitrate.
38. A process as claimed in claim 35, in which the metal salt is a magnesium salt.
- 125 39. A process as claimed in any one of claims 31 to 38, in which the cure is effected at a temperature between 100 and 200° C.
40. A process as claimed in claim 40, in which the temperature is between 100 and 150° C.
- 130



4. A process for the treatment of a fibrous material to improve its properties substantially as hereinbefore described with reference to any one of Examples 1, 2, 4 and 5.

42. A process for the treatment of a fibrous material to improve its properties substantially as hereinbefore described with reference to any one of Examples 8 to 22.

43. A treated fibrous material, whenever obtained by means of a process as claimed in any one of claims 29 to 42. 10

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