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2,739,908

METHOD OF IMPREGNATING TEXTILE FABRIC WITH RESIN

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1 Claim. (Cl. 117—139.4)

The present invention relates to improvements in the treatment of fibrous materials.

An object of this invention is to impart stability to and to reduce the tendency to crease of, or to impart a stable crinkle or crease to, fabrics made from materials such as flax, cotton, hemp, jute, wool, silk, rayon e. g. regenerated fibres from cellulose, proteins, alginates or from cellulose compounds such as acetate rayon, or from synthetic fibres of the various types known under the trade names nylon, Vinyon, Terylene, Saran, by way of example.

The invention may be applied to the fibrous material in the loose state, in the form of rovings or slubbings, yarns, woven fabrics, knitted fabrics, and manufactured garments; in all cases the treatment may be applied to a single fibrous material or to a mixture of one or more of the fibres indicated above.

According to this invention such textile material is treated throughout or in localised areas, either simultaneously or successively, with a product capable of penetrating and becoming insoluble within the fibre structure and with an artificial resin product of higher molecular weight which does not penetrate the fibre structure but is capable of adhering to it. If it is desired to impart a stable crinkle to fibres or to impart stable creases or pleats to fabrics, the material is thereafter crinkled or creased and then treated, for example by heating while in the crinkled or creased condition, to insolubilise the product which has penetrated the fibre structure.

In a preferred form of the invention, such textile material is treated, either simultaneously or successively, with a solution which may be an aqueous solution of a synthetic resin intermediate condensation product which is still crystalloidal and with a solution which may be an aqueous solution of a substance which is colloidal and the so treated textile material is thereafter treated to form the synthetic resins in water-insoluble condition. If the material is to be given stable crinkles or creases, then it is crinkled or creased after treatment with the solution or solutions but before or concurrently with the treatment to form the synthetic resins in water-insoluble condition.

Preferably the substance which is crystalloidal is an amino-aldehyde intermediate condensation product of low molecular weight, e. g. a condensate obtained by the treatment of formaldehyde with an amino compound such as urea in aqueous solution for no more than sufficient time to produce a solution of a crystalloidal methylol compound having a viscosity of less than 10 centipoises, when measured at 20° C. in a solution equivalent to 60 urea-formaldehyde condensate to 40 water. Preferably the substance which is colloidal and is capable of conversion to a synthetic resin is a far-condensed amino-aldehyde condensation product, e. g., a condensate obtained by the treatment of formaldehyde with an amino compound such as urea in aqueous solution for a sufficiently long time to form a non-crystallisable colloid so-

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lution, being a greater length of time than merely to produce a crystallisable methylol compound, and having a viscosity of at least 20 centipoises, when measured at 20° C. in a solution equivalent to 60 urea-formaldehyde condensate to 40 water.

Usually the fibrous material will be treated with the aforementioned condensation products in aqueous solution, treated to remove excess reagents, the impregnated material dried, treated to break down any adhesions between individual yarns or between fibres broken down, if desired treated to produce crinkles or creases e. g. by crimping or pleating, and finally the condensation or resin formation completed by heating in the presence of a catalyst which may be an acid, a mixture of acids, a mixture of an acid and a salt, but preferably in the presence of a substance which is capable of becoming acid (or more acid) or of liberating acid during the treatment, such for instance as ammonium thiocyanate, ammonium dihydrogen phosphate or aluminium chloride.

Materials treated according to this invention resist distortion and alternatively or concurrently, the treated materials tend to recover from distortion; there are also manifold subsidiary advantages in the treated products over the untreated materials. One important advantage is the resilience of the treated material as exhibited in the improved resistance to creasing and the recovery from creasing; at the same time there is a diminished tendency to shrink when washed. Treated materials, moreover, can be made resistant to shrinkage (and to swelling) with less resinous condensation product than is necessary for the best "crease-resisting" effects. In the present invention advantage may also be taken of the resiliency of the textile materials and their resistance to distortion, when so treated, to provide them with crinkles or creases which are stable and resist deformation.

As will be apparent from the foregoing, water-soluble amino-aldehyde condensation products may be made in two forms, corresponding broadly to colloid and crystalloid types. The crystalloid type approximates to a monomeric form and is capable of penetrating textile fibres; it has been used for producing crease-resisting effects. The older colloid type is much more highly condensed and has a higher molecular weight; in general, it will not penetrate textile fibres but remains on the surface. The colloid type when used alone for the treatment of textile materials does not give crease-resisting effects, but has been used as a stiffening agent for textiles and also as a fixing agent for filling and coating materials.

It has hitherto been found that where crease-resistance is required, it is disadvantageous to produce materials with surface resin and the object of treatment in general has been to form the resin within the actual fibre and evenly distributed throughout it.

It has now been found that superior products may be obtained by the use of a suitable mixture of crystalloid and colloid amino-aldehyde condensation products but consisting mainly of the crystalloid type to the extent of about 90% or even more.

Compared with the use of a suitable solution consisting entirely of the crystalloid type with low molecular weight for treatment of fabrics, the use of the mixture offers certain advantages in that the yield of resin in and on the fabric is superior, and furthermore, there is a greater resistance to loss of resin on laundry washing. The tensile strength of the treated fabric is greater and the resistance to abrasion is better; other properties also show an improvement.

The materials treated according to the present invention possess a high degree of recovery from creasing in an atmosphere of high humidity and even in the wet state, this recovery being much greater than of crease-resisting textile materials prepared with crystalloid products alone

and to which the small amount of colloidal resin has not been added. This high degree of recovery is of particular advantage when the materials are deliberately crinkled or creased in accordance with one form of the present invention since it enables materials which have been crimped or pleated to retain their crimps or pleats even when they have been wet. Thus, the material treated as described in the general example hereinafter given, compared with a similar fabric of viscose rayon staple fibre treated with a solution consisting entirely of urea-formaldehyde condensation product of low molecular weight, showed a recovery from creasing at high humidities, and even in wet state, which was much superior, and when the treated material was allowed to dry, it presented a relatively uncrumpled appearance. The material when crimped or pleated before the final heating to 145° C. showed much better retention of the crumps or pleats when wetted and then allowed to dry.

The solution of a urea-formaldehyde condensation product of low molecular weight and a low viscosity of the order of 5 to 6 centipoises capable of penetrating textile fibres may be prepared according to the methods given, for example, in our British Patent No. 449,243.

The more complex solution of a urea-formaldehyde condensation product of a relatively high viscosity of the order of 40 centipoises higher molecular weight and incapable of penetrating textile fibres may be prepared according to the methods given, for example, in British Patent No. 517,011.

The following is a general example of carrying out the invention. Specific examples will be given later herein.

A mixture of the two solutions mentioned above was made consisting of 90 parts by volume of the former (crystalloid) and 7.5 parts by volume of the latter (colloid) was diluted to 50% with water and catalyzed with 1.5% of ammonium dihydrogen phosphate estimated on the volume of liquor.

A plain weave fabric of viscose rayon staple-fibre was impregnated with the solution, centrifuged to remove excess of reagents, and then dried in warm air at a temperature of approximately 40 to 50° C.; during and after the drying process the fabric was subjected to mechanical manipulation so as to break down adhesions between the yarns and between the fibres, and to recover substantially the suppleness of the original cloth. The dried fabric was then heated for three minutes at 145° C. rinsed in soap and water, and dried.

Compared with a similar fabric of viscose rayon staple fibre treated with a solution consisting entirely of a urea-formaldehyde condensation product of low molecular weight, there was a greater yield of resin, the loss in weight on repeated laundry washing was less, and the resistance to abrasion was greater.

Similar effects were obtained with a cotton cloth, and it was also found that the tensile strength was better.

In general, the aim of the invention is to produce improved products which are still soft and supple, with individual fibres free to move, and with good draping properties. With this end in view the amount of colloidal condensation product in the impregnating solution should not, in general, be more than essential for the effect desired. A slight excess imparts a stiff finish with the danger that the treated fabric may be brittle.

For certain purposes, such as the manufacture of laminated stabilised fabrics, it may be desirable to have more than the minimum quantity of colloidal condensation product.

It is also possible to conduct the treatment of the textile material in two stages, first with the crystalloid solution of low molecular weight, followed by the very dilute solution of the colloidal product of high molecular weight.

The invention is not confined to the use of urea-formaldehyde products, but it also includes the use of condensation products of melamine-formaldehyde; again, it also includes the use of a melamine-formaldehyde product of

low molecular weight for the crystalloid product with a urea-formaldehyde product of high molecular weight for the colloid product, and vice versa. Further, the colloid product need not necessarily be of the aminoaldehyde type and it is possible to use compounds such as polyvinyl alcohol (in greater amount than amino-aldehyde) which become fixed at the fibre surface where they form polyvinyl formal with the formaldehyde from the crystalloid product; other colloidal substances capable of reacting with formaldehyde may also be used.

It is believed that the crystalloid product of low molecular weight penetrates the fibre, reduces the swelling capacity of the treated material, stabilises it, and imparts resilience, whereas the colloid product of high molecular weight remains on, or just within, the surface of the fibres sealing the fibres and imparting valuable mechanical properties.

The amount of resin required on the finally treated material for the purposes of the invention is not critical, as distribution is more important than quantity; nevertheless, as a general guide, the improvements in stabilisation, swelling, wet strength and so forth may be obtained with as little as 2 to 5% of resin expressed on the weight of the dry untreated fabric; the full benefits of crease-resistance require rather more and may range up to 10 to 15%. With carefully prepared fabrics and repeated impregnations it is possible to obtain soft and supple fabrics with as much as 30 to 50% of resin mainly within the fibre substance.

It is very surprising and not to be predicted that a combination of these two physical types of amino-aldehyde condensation product, even in suitable proportions, would produce materials with improved resistance to abrasion and improved tensile strength over materials treated in known ways with resinous condensation products. It is also most surprising that such products possess a higher degree of recovery in the wet state than those prepared from crystalloidal resinous products only.

The textile material to be treated must be thoroughly absorbent so as to imbibe the crystalloidal part of the mixture of amino-aldehyde condensation products. With rayon materials it may be advisable to give a preliminary treatment with 6% of NaOH solution; with cotton and linen it may be necessary to mercerise the materials to be treated by the invention in order to obtain the maximum absorptive capacity. Some other textile materials such as acetate rayon or nylon, may require swelling in a suitable swelling agent before treatment. If dried the prepared materials need careful drying before impregnation lest the temperature and other conditions of drying should reduce the absorptive capacity. It may even be desirable to treat the swollen materials in the wet swollen state (when more concentrated impregnating solutions and repeated impregnations may be necessary); fibres which are not swollen by the usual reagents may be swollen in a solvent and transferred by way of a hydroxylic solvent to water before impregnations in the swollen state.

According to the methods of the present invention, it is also possible to incorporate compatible substances in the impregnating solution and so produce combined effects in one operation. Hence, it is possible to incorporate inert fillers such as starch, dextrin and china clay, and also materials such as the colloidal dispersions of silicon compounds, all of which can be rendered fast to washing later. Similar remarks apply to the delustering agents which may be used with rayon such as barium sulphate. Pigments may also be bound to the fibre by means of the resin, and indeed the present invention may also find application in pigment printing.

Where ammonium salts are used as catalysts, it is possible to incorporate latices of natural and synthetic rubber with the reaction mixture; it is also possible to incorporate reagents such as stearaminopyridinium chloride or octadecyloxymethylpyridinium chloride which

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impart water repellent properties. Where salts of certain polyvalent metals are used as catalysts, it is possible to add wax emulsions, for example, combined resistance to creasing and spot proofing come from such use of aluminium acetate as catalyst if the impregnated and dried fabric is steamed to produce the basic acetate or the oxide.

The drying of the impregnated material demands particular care. For the best effects the goods should not be stretched during drying as this not only interferes with the softness of the material but may even produce brittle treated materials by bringing the internal liquor to the surface if undue tension is used. Again, the conditions of temperature and humidity within the drying chamber should, if possible, be such that the water vapour is removed from the fibre as vapour, and steps should be taken to ensure that the crystalloidal product does not diffuse towards the surface or the treated fabric after formation of the resin will be brittle.

The mechanical manipulation of the fabric during and after drying is highly desirable so as to break down the adhesion between fibres and between yarns before resin formation and so produce soft and supple results with the fibres free to move. Suitable devices for this purpose are the jiggling stenter, the scroll breaker, the button breaker or even a simple doctor blade over which the fabric is flexed. Drying may take place on cylinders heated by steam, gas or electricity, on stenters heated by air which may be moist at the entrance (and here a strong air blast may be used to separate the fibres), or in a chamber with radiant heat, infra-red heat or high frequency radiations.

During the drying process it is possible to shrink the fabric; this may be accomplished on a stenter equipped with an over-feed device, or on a special machine for producing controlled compressive shrinkage. Such intermediate shrinkage treatments may be found of great advantage in the treatment of rayon materials.

During or after drying, the impregnated material may be subjected to mechanical distortion subsequently rendered permanent by formation of resin from the condensation products; hence it is possible to crinkle the loose fibres by compressing a mass of fibres to crinkle rovings and yarns in a goffering machine, to over-twist yarns and then impart reverse twist. With fabrics, for example, it is possible to calender them, to Schreiner them, to emboss them, or to produce glazed effects by friction. With many of the machines employed for the above purpose, it is possible to form resin from the condensation product by heat at the same time that the mechanical effect is imparted.

The impregnated and dried fabric may be heated in different ways. When using catalysts which are weakly acid, the time and temperature are of the order of 3 to 5 minutes at 160 to 180° C.; whereas, with stronger acids (or potential acids) the temperature may be reduced to 130 to 150° C.

Where a heated chamber is used for the final resin formation there are advantages in the presence of a certain amount of steam; this not only assists the decomposition of the potential catalyst, if such a catalyst is used, but it also ensures a more efficient transfer of heat to the fabric. Furthermore, the textile material often has a better handle when heated in presence of some steam compared with heating in the dry state.

Linen fabrics which have been treated with urea-formaldehyde condensation products which penetrate the fibre may be subjected to a further process by treatment with caustic soda as described in our British Patent No. 437,361. It may be frequently desirable to subject linen materials treated by the present invention to a similar process. Materials treated according to the present invention lose less resin during such treatment than materials treated by known processes and the recovery from creasing afterwards is superior; similar remarks apply to crease-resisting cotton and rayon material which have been subjected to further treatment with caustic soda.

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Advantages of products treated according to the present invention compared with untreated materials and in many cases as compared with materials treated with crystalloid products alone are the improved resistance to and recovery from creasing, together with decreased shrinkage on laundering. They show an increase in weight, and possess an improved resilience and handle, and they drape better. With rayon fabrics there is an increase in the dry tensile strength and an increase in the wet tensile strength.

Textile materials treated in the above manner swell less than untreated materials and in many cases than materials treated with crystalloid products only in water and in swelling agents; it is thus possible to subject the treated rayon material to alkaline solutions of sodium hydroxide which would otherwise dissolve or disintegrate them. The property of absorbing less water is useful in that more rapid drying of the wet material is possible.

When the process is applied to dyed or printed materials, the colours become faster to washing and many of them become faster to light. Many textile materials are sensitive to oxidation and particularly to photo-degradation, and considerable resistance is imparted by the present invention; furthermore, those dyes which accelerate photo-degradation of cellulosic material are rendered safer by the use of the new process.

Fabrics treated by the present invention, particularly knitted fabrics, are less easily distorted than untreated materials; both woven and knitted treated fabrics are less liable to fray, and woven fabrics are less liable to slip after treatment.

Further advantages which have been noted in the treated materials, as compared with the untreated, are resistance to bacterial decay and to mildew, some resistance to soiling and a readiness to shed dirt; to some extent, the treated materials are also spot-proof.

The following are specific examples of carrying out this invention in two of its preferred forms:

Example 1

(a) 100 gms. urea are dissolved in 200 gms. of commercial formaldehyde solution (40%) which has been neutralised and the mixture is then acidified to pH=4.5 with tartaric acid.

(b) 25 parts of urea, 5 parts of thiourea are dissolved in 75 parts of neutralised formaldehyde (40%). 3½ parts of ammonium hydroxide (density 0.88) are added and the solution refluxed for 3 minutes. 5 parts of boric acid dissolved in 25 parts of water are added and refluxing continued for 1 hour.

7.5 cc. of the mixture prepared as in (b) was added to 90 cc. of the mixture prepared as in (a) and the resulting mixture was diluted to 50%. 3% of ammonium dihydrogen phosphate (estimated on the concentrated liquor) was added and a plain woven cotton fabric impregnated with this liquid, squeezed by passing between the bowls of a mangle and dried at a temperature less than 110° C. The fabric was then heated at 120° C. for two minutes and then lightly washed in 0.5% warm soap solution, well rinsed in water and finally dried.

The finished fabric had much improved resistance to creasing and good resistance to wear.

The material treated according to the above Example 1, when wetted and crumpled and hung up to dry naturally, dried with an almost complete absence of crumples and creases. When crimped or pleated before the final heating to 180° C. it showed high retention of the crimps or pleats with absence of additional unwanted creases.

Example 2

(a) 100 gms. urea are dissolved in 200 cc. of neutralised 40% formaldehyde solution. This neutral solution is allowed to condense for from 3 to 20 hours at room temperature.

(b) 60 parts of urea, 150 parts (by weight) of 40% formaldehyde solution and 6 parts by weight of hexa-

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methylene tetramine are mixed and heated on a water bath until on cooling a test sample no turbidity is produced. The time of heating may be, for example, half an hour to two hours. In one experiment the viscosity of the solution produced was 40 centipoises and its density 34° Tw.

These two solutions were then used to impregnate an all rayon viscose fabric as in Example 1.

The material treated according to the above Example 2 shows similar advantages to the material of Example 1 and can usefully be crimped or pleated before the final heating to 120° C.

I claim:

Process for the improvement of a cellulosic textile fabric which comprises impregnating said textile fabric with a mixture of two aqueous solutions, one of said solutions comprising a crystalloidal thermosetting condensation product formed from formaldehyde and urea said crystalloidal condensation product having a viscosity of from about 5 to about 6 centipoises, the other of said solutions comprising a colloidal thermosetting condensa-

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tion product formed from formaldehyde and urea said colloidal condensation product having a viscosity of at least 20 centipoises, and the quantity of said crystalloidal condensation product being 90 parts to 7.5 parts of said colloidal condensation product, and heating the textile fabric so impregnated in the presence of an acidic catalyst to form thermoset resin from both said condensation products, the amount of said condensation products in said textile fabric when so heated being such that said textile fabric after said heating contains from 2% to 50% by weight of resin calculated on the untreated textile fabric.

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