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SIZING TEXTILES

László Auer, Mansfield, Mass.

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8 Claims. (Cl. 91—70)

This invention relates to sizing textiles; and it comprises relatively permanently sized fabrics carrying adsorbed synthetic resins produced, in situ, in and on the fibers and resistant to laundry detergents; and it also comprises methods of so sizing fabrics wherein the fabric is impregnated with weak, substantially neutral or slightly alkaline aqueous solutions of formaldehyde and a reactant therewith, such as ureas, phenols, etc., or of simple, water-soluble, reaction products of such materials, and then dried and cured in the presence or absence of catalysts, the fabric being sometimes pre-impregnated with benzoic acid, phthalic acid or other acid catalyst difficultly soluble in aqueous liquids and the impregnated fabric being sometimes aged before or after drying; all as more fully hereinafter set forth and as claimed.

Fabrics of cotton, linen, wool, synthetic fiber, etc., are customarily sized sufficiently to prevent limpness while preserving suppleness. Starch preparations are often used. The sizing has other functions, one being the preservation of the fullness of texture, the so-called loftiness and a cementing action in uniting threads. This is particularly important with rayon, in which the threads, and the ultimate fibers, are smooth surfaced. Most of the common sizing materials based on starch do not penetrate the thread and have little influence on the fiber-to-fiber union therein, but they do bond the threads themselves. In practically all cases, the sizing material is between the threads and to this extent interferes with porosity; which is always important in garment cloth. And it is difficult to adjust sizing to preserve the fullness of texture against crushing, preventing wrinkling and creasing. Resistance to creasing depends to some extent on the resilience of the fibers and threads and the prior commercial sizings do not help in this respect.

Another serious difficulty with the sizing materials in use is that most of them do not well withstand washing; they are removed in the laundry to a greater or less extent. Most of the laundry detergents are, like soap suds, alkaline and there are few sizings in use which are highly resistant to these detergents; this being particularly true of those of light color suitable for use in fine garments.

I have found that I can secure better results in the preservation of loftiness by departing from the usual custom of charging the interthread spaces with relatively gross materials; materials with a particle magnitude not less than that of a starch granule and sizing the threads themselves. In the present invention, I produce an adsorbed synthetic resin resistant to detergents formed in situ in and on the threads. So doing, the sizing material is intimately and uniformly distributed and there are no accumulations of coarse particles to interfere with porosity. The total amount of foreign matter added to a textile fabric to secure a wrinkle-proofing result is surprisingly small. With this type of sizing, the threads are bonded together at crossing points without occurrence of intervening layers of appreciable thickness. The normal resiliency of the threads is not interfered with and is, indeed, increased. The gross result is a greater resistance to crushing with no more lessening in suppleness than may be desired. Under pressure the normal textile comes back when the pressure is released; in other words, the fabrics do not crush, crease or wrinkle like fabrics containing sizing as a filler. It is not a question of crushing strength of a layer of sizing.

Many of the synthetic resins are inert in contact with weak alkaline solutions and can be used for my purposes, as they give fabrics which are readily washable and permanent against the action of soapsuds and the detergents used in laundries.

The best resins for my purposes, however, are those produced from formaldehyde with a urea, (urea, urea derivatives, substituted ureas) or formaldehyde and with the various phenols, phenol itself, meta-cresol, and other substituted phenols like p-tertiary-amyl-phenol, etc. With both types, it is possible to produce a mobile water soluble, neutral or weakly alkaline solution which contains nothing of a resinous nature but does produce resin upon heating or when catalyzed by the action of an acid or both. The formaldehyde may be fully or partly replaced in the process by compounds forming formaldehyde in situ, by formaldehyde derivatives, or other similarly acting aldehydes, like hexamethylene tetramine, acet-aldehyde, etc. The dissolved materials of these solutions are not resinous but are resinifiable. If the acid is one of the aromatic series, such as benzoic acid or phthalic acid, it may join in the action and contribute to the resin. Resin formation with both urea-formaldehyde and phenol-formaldehyde, is a progressive action; the materials are water soluble and not at all resinous to begin with and they end up as highly resinified products. In both cases, there are intermediate stages and gradations.

In one embodiment of my invention which I regard as highly advantageous, a fabric, cotton, linen or rayon, is treated with a hot solution of an acid difficultly soluble in water such as benzoic acid or phthalic acid. Neither acid has any great solubility in hot water but the amount which will remain in solution at a temperature of 88° to 90° C. is sufficient for my purposes. From such a solution fabric takes up about the right amount of acid. Cellulose fibers adsorb the acid by an action similar to those occurring in dyeing: the material is taken out of solution and distributed uniformly through the fiber. It may be regarded as in solid solution or as being adsorbed. For the present purposes, the difference is verbal. The solution is applied to the cloth in any of the usual ways, usually by dipping in a bath of aqueous acid, withdrawing and pressing. When the fibers exhaust the bath its acid content must be replenished.

The fabric having been thus "soured," is pressed to get rid of superfluous solution and is then, so to speak, chemicked. A cold solution is prepared containing urea and formaldehyde in about equal proportions by weight and of neutral, or slightly alkaline, character. The amount of the formaldehyde may be however in some cases larger. It is a mobile solution usually containing 7 to 10 per cent urea. Some reaction may take place between the two substances, but it is very slow if any. Such a reaction is not essential for the success of the process. Methylol urea or dimethylol urea are not formed immediately in appreciable quantities. On acidulating, an action begins ultimately producing a resin; rapidity of the action being proportional to the acid concentration, acid used and the temperature.

On treating the soured fabric with this solution, the solutes are taken up by the fabric; entering into reaction where acid is encountered as in diffusing into a thread. The fibers tend to adsorb the solutes as they adsorbed the acids. Taking up of the formaldehyde and urea is fairly quick, so that dipping and wringing suffices. As before, when the bath becomes exhausted it is replenished with formaldehyde and urea. There are also drag-out losses. The acids when encountered by the liquid catalyze reaction but their action is not very quick and with the amount of acid in the fiber described, it is generally advisable, working in the cold, to age the chemicked fabric for 6 to 10 hours. Alternatively, the fabric can be passed over skeleton drums, steam heated, and brought to a temperature of 80° to 90° C. This effects both ageing and evaporation of the water, giving a dry fabric.

At this stage in the action, while there is adsorbed more or less resinous matter in the fabric, the action has not in general progressed quite as far as I desire. I thereafter advance it further by what I may call a curing action; the dry fabric is heated to about 135–140° C. for about 3–5 minutes.

The final effect is also obtainable at room temperature or at temperatures below 135° C. but the lower the temperature the slower the condensation, e. g. at room temperature it takes 2–3 months.

Formaldehyde and urea in the neutral or weakly alkaline solutions enter into a progressive reaction but it is quite slow. It is accelerated by acid and heat. In making plastics and for other purposes, it is quite general to use the formaldehyde and urea in a 2:1 molecular proportion; equal weights of urea and of actual formaldehyde. This is the proportion that corresponds to dimethylol urea but in resinification about a quarter of the formaldehyde is discarded; it vaporizes and is wasted. For this reason, in some cases I found it advantageous to make the solution with a somewhat less proportion of formaldehyde than the 2:1 ratio. Using a 2:1 ratio slows down the mutual reaction considerably, this being one of the reasons it is used. But there is no particular advantage in this in the present action; the solutions may be used as soon as they are made, but standing does not do any harm to the impregnating liquid as at this concentration no insoluble condensates are formed for several weeks at room temperature.

The procedure just described may be varied. It is possible to use a 1-bath process in which souring and chemicking are simultaneous; phthalic acid or benzoic acid being dissolved in the urea-formaldehyde solution previously described and the liquor immediately applied to cloth. More speed and greater care are, however, required than with the 2-bath process described, first souring and then chemicking. Urea and formaldehyde are readily taken up by fibers and, while I do not particularly recommend it, it is possible to operate in reversed order: first chemicking and then souring. In souring, both benzoic acid and phthalic acid have individual advantages and sometimes one is more advantageous than the other; this depending on circumstances. Mixtures of the two acids may be used but are not ordinarily particularly advantageous. Benzoic and phthalic acid have the advantage, being difficultly soluble in cold water of increasing laundry proofness, and of accelerating the condensation moderately, so that no insoluble condensates are formed in the solution during or prior to application. Other water soluble catalysts form water sensitive condensates and are not satisfactorily laundry-proof.

The described process may be applied to any of the ordinary fabrics of carbohydrate nature or to the yarns; to cotton, linen, ramie, etc., and also to the various regenerated cellulose products known as rayon. The fabric may be first mercerized, although this leaves it with more or less residual alkali and may require an increase in the amount or strength of the chemicking bath. To increase adsorption power of the fabric wetting out agents may be added to the baths.

In all details, the above procedure is applicable to a chemicking bath containing equivalent amounts of formaldehyde and a phenol, such as meta-cresol or phenol itself. The character of the products made is, however, somewhat different and the process is better applicable to goods in which slight color is not objectionable.

Goods processed in either way are open-textured, preserve their loftiness well against creasing, wrinkling and crushing, and withstand repeated and drastic washings; they are, so to speak, laundry proof.

Fabrics treated as described can afterwards be sized in ordinary ways and by ordinary materials, where there is utility in so doing; as in stiffening linen by starching.

In the commercial practice of the present invention, the solutions employed in impregnating the fabric may be prepared in various ways. In certain practical embodiments, aqueous solutions of the urea and formaldehyde may be employed. For instance, commercial urea can be dissolved in neutralized commercial formaldehyde solution, the molar ratio of formaldehyde to urea being e. g. advantageously 2:1 and the aqueous solution of urea and formaldehyde so prepared at room temperature, after dilution to the proper concentration, can then be directly used to impregnate the fabric. In other embodiments, these solutions may be so treated as to permit the urea to combine with the formaldehyde to the extent of producing simple, non-resinous, water-soluble reaction products. In the absence of acid catalysts the reaction between urea and formaldehyde is rather slow. In the present invention the urea and formaldehyde solution may be used in any stage of advancement. Reaction is finally completed in the fabric by ageing and curing. Naturally, the further the advancement of the reaction in the liquid used, the less time is required in the later stages of ageing. For instance, the above mentioned solution of urea in aqueous formaldehyde may be heated, even to boiling, for a short time and then cooled before applying it to the fabric. In cooling, it is advantageous to dilute with cold water. In any event, the concentration of the solutions should be so adjusted as to reduce their urea content to below 20 per cent.

Example 1.—A solution of urea is prepared by dissolving 45 parts of urea in 457.5 parts of water having a hardness of 12 German hardness degrees. Separately there is prepared a neutral or slightly alkaline solution of formaldehyde by neutralizing 112.5 parts of commercial aqueous formaldehyde containing 40 per cent actual formaldehyde with 2 parts of concentrated ammonia. The two solutions so prepared are mixed at room temperature and the mixture so obtained may be used for impregnating fabrics, either with or without the addition of wetting out agents.

For impregnating cotton cloth there may be added to the above aqueous solution of urea and formaldehyde, approximately 2 to 3 per cent of sodium salt of sulfated cetyl alcohol. The latter serves as a plasticizer and a wetting out agent. This mixture is then applied to the cotton cloth, the impregnation being carried out at room temperature.

The impregnated cloth is placed on a tinterframe and aged for 4 hours at room temperature. During this time, the urea gradually acts with the formaldehyde to form simple addition products. The aged cloth is then dried at 80° to 90° C. until dry while still under tension. The dried impregnated fabric is then cured by heating to between 125° and 135° C. for 3 to 5 minutes to effect the formation of the resinous sizing, in situ, in and on the cloth; this sizing being substantially insoluble in water and resistant to mild detergents. The drying and curing above mentioned may be effected in a current of warm and hot air, respectively. Also, the curing may be effected by passing the dried fabric between or over hot rolls or drums.

The curing of the dry impregnated fabric may be facilitated by employing acid catalysts to expedite condensation and resinification of the simple reaction products absorbed by the fabric. The following example is illustrative of those embodiments of this invention wherein such acid catalysts are so employed.

Example 2.—In this example, the cotton cloth is pre-impregnated with a suitable acid catalyst prior to impregnation with the aqueous solution of urea and formaldehyde.

A 1 to 5 per cent solution of benzoic acid is prepared by boiling a suitable amount of benzoic acid with water. The cotton cloth is then immersed in the boiling solution until the fabric absorbs the acid catalyst. The pre-impregnated cloth is squeezed between rolls or by other suitable means to remove excess solution and dried.

The dry cloth is then immersed in an aqueous solution of urea and formaldehyde, such as prepared in Example 1, and the impregnation effected at room temperature. After removing the cloth from this solution it may be then dried and cured, as in Example 1, without ageing at room temperature. The cloth having been pre-impregnated with the acid catalyst, the formation of simple addition products from the urea is facilitated and their formation is substantially complete by the time that the free moisture has been evaporated during drying. After the fabric is substantially dry, those reaction products quickly resinify into the final condensation product at the curing temperature in the presence of the acid catalyst. The cloth sized and creaseproofed in the above manner has improved resistance to the usual detergents employed with textile materials.

In the above procedure a wetting out agent may be added either to the benzoic acid bath or to the urea-formaldehyde bath or to both.

In the above example, phthalic anhydrid or phthalic acid may be used in lieu of the benzoic acid for pre-impregnating the cloth with the acid catalyst. These catalysts are substantially insoluble in water and in aqueous solutions at room temperature, but are soluble in hot water and may be advantageously employed. In these processes, the resinifying actions do not become pronounced until the higher temperatures used in the subsequent drying and curing, render the catalyst fully active.

Likewise in Examples 1 and 2, in lieu of the cotton cloth, other fabrics such as rayon, linen, wool, jute, hemp, ramie etc., may be impregnated in like manner. Further, in lieu of the urea and formaldehyde, there may be employed other water-soluble reactants which, in the subsequent operations, are likewise converted into resinous sizings which are resistant to detergents. For instance, thiourea may be employed in lieu of urea and thioformaldehyde in lieu of the formaldehyde.

Instead of employing a simple aqueous solution of formaldehyde and urea as in the above examples, solutions of the simple reaction products thereof may be used for impregnating the cloth. That is, the urea in such solutions may be reacted with the formaldehyde until simple water-soluble reaction products are obtained, this reaction being effected by standing at room temperature for a considerable period of time or by boiling the solution for a few minutes. The following example illustrates the preparation and use in the present invention of aqueous solutions of such simple reaction products.

Example 3.—To 280 liters of 40 per cent formaldehyde solution there are added 6 liters of ammonia solution (0.906 specific gravity) to obtain a substantially neutral aqueous formaldehyde solution. In this neutralized solution, there are dissolved 150 kilograms of urea and then 18.6 liters of the said ammonia solution is added to render the mixture slightly alkaline. The alkaline solution is then heated to boil and is boiled for about 3 minutes to effect limited reaction; the boiling being advantageously under reflux. At this time, substantial amounts of simple reaction products are formed. Then the reaction is checked by cooling; advantageously by diluting the boiling solution with 1100 liters of water, external cooling being also used, if necessary, to check the reaction. The dilute solution so prepared is very suitable for impregnating various fabrics by the method disclosed in Example 1, wherein condensation catalysts are not present. The formation of simple reaction products having been initiated prior to impregnating cloth, a shorter ageing period may be employed.

By also employing a condensation catalyst, the processing may be further expedited. In this modification of the invention, the cloth may be pre-impregnated with the acid catalyst as in Example 2. Or, the catalyst may be added to the impregnation bath at room temperature just prior to the application thereof to the fabric. The following example is a further illustration of such embodiments of the present invention.

Example 4.—In this example the formation of simple reaction products from the urea and formaldehyde is effected as in Example 3, but the checking of the reaction is primarily effected by external cooling, a small amount of diluting water being employed. After the reaction has been checked and a cool dilute solution obtained, this solution may be further diluted by adding an aqueous solution of benzoic acid sufficient to introduce about 1 per cent of benzoic acid into the impregnating bath, then the impregnating solution containing the acid catalyst is applied to the cloth, the water evaporated and the dry impregnated cloth cured.

Also, the fabric sized by the present invention may be further sized with other materials by subsequent operation. The following example is illustrative of such methods.

Example 5.—In this embodiment of the present invention, a slightly acid aqueous solution of urea and formaldehyde is employed for impregnating the fabric; one which has an acidity due to the natural acidity of commercial formalin. To prepare such a solution, 4.5 kilograms of urea are dissolved in 50 kilograms of water and to the solution so obtained there is added 9 kilograms of the commercial formalin, a solution containing 40 per cent of actual formalehyde and having a slight acidity.

Using the above solution, pre-dried rayon fabric is impregnated on the Foulard of the tinter-frame, the material being passed between the rolls thereof which automatically squeeze out the fabric and remove excess solution. The impregnated fabric is then dried on the tinter-frame in a stretched, strained condition, while passing slowly on the heated drums; the drying being continued until the formaldehyde odor has been obviated. Next, the dried material is then heated to 98° C. for approximately 10 minutes to effect condensation and cure the treated fabric.

The rayon fabric so sized with urea resin may be further sized with a mixture consisting of

Orapret WTN, a sulfonated product of fatty material containing softening agents	kg	8
Sodium salt of a sulphated fatty alcohol which is partially aryl substituted	kg	2
Glycerol	do	8
Sodium acetate	grams	50
Water	liter	100

After applying the above sizing composition, the fabric is again dried. After drying it may be sprayed with water and re-dried in a stretched condition on the tinter-frame.

The finished product so obtained is somewhat heavier than the materials sized with urea resin alone, but it is softer, more elastic and its elasticity improves when stored for 1 to 2 months.

In lieu of the above mentioned second sizing composition, other sizing compositions may be used; or that composition may be slightly modified. For instance, in addition to the ingredients mentioned, it may also contain $MgCl_2$ and urea. The addition of free urea prevents formation of free acid or free formaldehyde during laundering or ironing. One per cent urea on the sizing mixture suffices.

In the above method, in lieu of employing pre-dried rayon, there may be used a rayon fabric which has been pre-impregnated with an acid catalyst, such as phthalic acid or benzoic acid, 1 per cent of such catalyst being advantageously present in the solution during the pre-impregnation.

In the above examples, I have employed for impregnation, solutions containing a urea concentration of substantially below 25 per cent, as I have found that with concentrations of 25 per cent or more, it is difficult to obtain open-textured sized fabrics having the desired suppleness. When highly concentrated solutions (heavy sirups) are employed, I find that the fabric becomes undesirably plugged and the final products are relatively stiff; sometimes even brittle. Likewise, if the solution contains solid or solidifiable resins, either in solution or in the form of fine colloidal dispersion, such resinous matter likewise undesirably plugs the pores of the fabric, resin being more or less filtered out by the fabric, rather than being adsorbed by the threads as a permanent sizing.

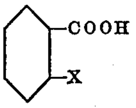
In the commercial practice of this invention, I find that solutions containing 7 to 10 per cent of urea, or the equivalent quantities of other reactants themselves, give highly satisfactory results. With such concentrations, the fiber directly absorbs the size-forming materials and the exhausted solution readily drains from the fabric and upon drying, an open-textured fabric is readily obtained. Briefly, there is no need for eliminating surplus resin, as no such resin exists prior to the drying and sometimes prior to the curing, depending upon the particular conditions employed. The squeezing operations which I sometimes employ are primarily for the purpose of reducing the moisture content to thus facilitate drying. However, when using the more highly concentrated solutions, this squeezing serves to remove the unabsorbed solution of materials and return them to the impregnating bath. Depending upon the character of the sizing desired and the fabric being processed, the conditions employed may be varied, particularly the concentration of the impregnating bath. In some cases, I may employ solutions containing more than 10 per cent of the size-forming materials. However, satisfactory results can be obtained with any of the various types of impregnating solutions with concentrations less than 20 per cent. It is not necessary to use solutions containing more than 20 per cent of such materials, although in some cases concentrations between 10 and 20 per cent may be employed with advantage. In the ordinary practice of this invention, solutions of 7 to 10 per cent concentration give the best results with the ordinary processing procedures described ante.

Another marked advantage of the present invention is that cotton and other ordinary fabrics readily absorb the size-forming materials. It is not necessary to give the fabric pre-treatments, such as treatment with mercerizing agents or wetting out agents. In impregnating fabrics with solutions or colloidal dispersions of actual resins, pre-treatment of the fabric is a practical necessity, for otherwise resins do not attach themselves to the threads. In the present processes, no resin is present in the impregnating solutions and such opening up of the fabric by mercerization is not required. However, in the practice of the present invention, wetted out or mercerized fabric may be employed, as they may be processed with equal facility and in this way, a sized mercerized fabric may be readily obtained. If a mercerized fabric is not desired, then a cotton cloth may be directly employed, as the impregnating solutions here used are so thin and mobile that they penetrate the natural cotton fibers. In fact, it is advantageous to employ in these processes the thin, mobile solutions of simple urea-formaldehyde reaction products, such as are prepared by the processes given in the Howald Patent 2,056,455, such solutions being adjusted to the percentage concentrations given ante.

In the best embodiments of the present process as described, the impregnating liquid is thin and mobile and there is no production of gross material between the threads; granular matter analogous to ordinary sizing. However, if an inter-thread deposition is desired, the resinifiable solution, when used, may be so far advanced in process as to carry fine suspended particles.

What I claim is:

1. In the manufacture of sized textiles resistant to laundering and detergents and to crushing, creasing and wrinkling, said textiles carrying adsorbed urea-formaldehyde resin produced, in situ, in and on the fibers thereof, the improvement which comprises contacting the unsized fabric with a hot solution of an organic acid having the following formula



wherein X represents a substituent of the class consisting of H and COOH, said organic acid being difficultly soluble in cold water, until the fibers adsorb a catalytic amount of said acid, removing the excess solution and drying the so soured fabric, next contacting the dried sour fabric with a dilute, thinly liquid, practically neutral aqueous solution of formaldehyde-urea, and simple reaction products thereof, at room temperature to produce a further adsorption of said products by said fibers, said solution containing less than 20 per cent of dissolved solids and being practically free of insoluble products, removing the excess of the aqueous liquid, aging the damp impregnated fabric containing the co-adsorbed acid and formaldehyde-urea at room temperature until all the urea has reacted, drying the so-aged fabric to remove the residual water and formaldehyde without resinifying the adsorbed urea-formaldehyde condensation products by any fargoing catalytic action of the adsorbed acid, and then curing the dried impregnated fabric at a temperature sufficient to fully resinify the urea-formaldehyde products into permanent insoluble resins resistant to laundering detergents.

2. The process of claim 1 wherein the fabric is soured and impregnated with the acid catalyst by immersing the fabric in a boiling solution of benzoic acid, the so pre-impregnated cloth is squeezed between rolls to remove excess solution and then dried to obtain a dried, soured fabric containing a catalytic amount of absorbed benzoic acid.

3. The process of claim 1 wherein said diluted, neutral aqueous solution of formaldehyde and urea is prepared by dissolving urea in water to obtain a solution containing approximately 10 per cent of urea and this solution is mixed cold with a neutralized commercial aqueous formaldehyde solution containing sufficient formaldehyde to combine with the urea.

4. The process of claim 1 wherein the drying of the aged fabric to remove residual water and formaldehyde is effected at temperatures between 80 and 90° C. while the fabric is under tension.

5. The process of claim 1 wherein the curing is effected at temperatures between 125 and 135° C., the said resinification being completed in 3 to 5 minutes.

6. The process of claim 1 wherein the said curing is effected by passing the dried fabric between hot rolls.

7. The process of claim 1 wherein said acid catalyst is phthalic acid.

8. The process of claim 1 wherein said acid catalyst is a mixture of benzoic and phthalic acids.

LÁSZLÓ AUER.