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## TREATMENT OF FIBROUS MATERIALS

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No Drawing. Application June 23, 1953,  
Serial No. 363,689

6 Claims. (Cl. 117—141)

This invention relates to the treatment of fibrous materials and to the products of such treatment.

The application is a continuation in part of copending application Serial No. 277,292, filed by us on March 18, 1952, and entitled "Reaction Product of Dicyandiamide and Boric Acid." This copending application relates to the increase of stability of dicyandiamide and formaldehyde condensation products in aqueous solution by the action of boric acid.

Our issued Patent No. 2,567,238 describes the manufacture of dicyandiamide and formaldehyde resins by condensation of the dicyandiamide with formaldehyde in the proportion of 3.6–5 mols to 1 mol of the dicy.

The present invention comprises the treatment of organic fibrous or other porous material, in condition to neutralize or react with cationic material, with the resin resulting from the interaction and condensation of dicyandiamide, formaldehyde, and boric acid, the dicyandiamide being sometimes referred to as "dicy." The invention comprises also the herein described products made by treating various penetrable materials with the improved resin.

The invention is particularly useful in connection with the treatment of leather and will be first illustrated by description in connection with such use.

In general, the dicyandiamide, formaldehyde, and boric acid condensation product is introduced in leather and fixed in position by means to be described. The product containing the boric acid is not only more stable in shipment and storage than is the resin without the boric acid content, but also is less sensitive, when being introduced into the leather, to undesired precipitation on the surface by electrolytes such as salts or acids. The boric acid containing resin, when subjected finally to the desired precipitation or fixing in the leather, not only gives tanning and filling effects in the leather but also decreases the water extractibility of water soluble materials present, such as remaining uncombined vegetable tanning material.

Once the effect of the boric acid in preventing the premature gelling or precipitation by salts or acids has been observed, various theories may be advanced to explain the desirable results. We consider that the effect may be due in large part to the minimizing of continuing condensation as by the boric acid blocking of reactive groups of the dicy-formaldehyde condensation product. Thus, the boric acid may cause either esterification or dehydration of the methylol groups in the condensation product or react with previously unreacted amino groups in the same product. In fact, the effect may involve both these reactions.

We consider also that the action of the anionic condition of the material being treated, in fixing the cationic dicy, formaldehyde, and boric acid condensation product, is due to neutralizing the charge on the cationic condensation product. Unless material to be treated is not anionic or amphoteric initially, then an anionic agent is intro-

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duced, either before or after application of the condensation product.

The anionic agent used is one that contains a sulfo group ( $\text{SO}_3\text{H}$ ) and as used is soluble in water. The sulfo group may be in a free sulfonic acid, a water soluble salt thereof, or an ester, as in compounds of the type  $\text{RO}\cdot\text{SO}_3\text{H}$ , R being an alkyl or an arylalkyl group. We use to advantage an anionic agent that has a definite affinity for the leather or other material being treated, that is, must itself be substantive so that it is separated by the material being treated from the water solution in which the agent is applied.

Examples of anionic agents meeting these requirements that we use to advantage in fixing the resin are naphthalene sulfonic acid and formaldehyde condensation products, sulfonated phenolformaldehyde condensation products, the condensation product of sulfonated phenol and formaldehyde, sulfonated product of dihydroxydiphenyl sulfone or of dihydroxydiphenyl propane, preferably in the form of the omega sulfonation, sulfonated dihydroxydiphenyl methane, phenolic derivatives possessing a urea-formaldehyde-condensation bridge or other resin intermediates as a bridge formation, and sulfite lignin containing reactive sulfo groups which will react and form an insoluble compound with dicy and guanidine resin. Illustrative sulfonated oils that meet the requirements stated and that may be used are sulfonated castor, neat's-foot, teaseed, and the like. Other anionic agents that may be used are sulfonated alcohols such as sulfonated cetyl, lauryl, and stearyl; these are more stable in the form of their salts. We use them preferably in the form of the sodium salts. In general, we may use the acid sulfo compounds such as illustrated above or their more stable salts such as those of sodium or ammonium. All of these agents are precipitants for our resin in aqueous solution. They may be the original sulfo tanning agents.

As to proportions of materials in making the condensation product, we use 2–16 mols of formaldehyde to 1 mol of the dicyandiamide. An especially desirable and economical product is obtained when the proportion of formaldehyde is 3.6–5 mols. This proportion of formaldehyde is adequate, when warmed in aqueous solution with the dicy alone, to cause condensations first to a product that is water insoluble (precipitable by water on extreme dilution) and then, as the warming continues, a final resin that is water soluble (not precipitable on extreme dilution).

The boric acid is used in the proportion of 0.1 to 1 mol for 1 mol of the dicy. The use of more than 1 molecule of the boric acid is unnecessary and involves therefore, unjustified expense. Excess may also lower the pH objectionably. As to the lower limit of the boric acid, the 0.1 mol decreases the tendency to premature gelling of the solutions. As the proportion of formaldehyde within the range 2–16 mols stated is decreased, then the maximum effect of the boric acid in preventing gelling is obtained with selection of an amount of boric acid from the higher portion of the range of 0.1 to 1. Thus, when the proportion of formaldehyde used is 3.6–5 mols, we use not less than 0.3 mol of the boric acid.

When the leather or other material being treated is not anionic, that is, neither actually anionic nor amphoteric (neutralizing to the charge of either anionic or cationic agents), then we introduce into the said material an anionic agent such as one of those listed above. Suitable proportions are 1–10 parts of the anionic agent for 1–10 parts of the condensation product on the weight of the said material.

In making our improved condensation product, we heat to the final water soluble stage as stated in our copending application. If we effect the initial condensation of dicy

and formaldehyde in the absence of boric acid, we pass through the dicy and formaldehyde reaction, after which the boric acid is added. If the boric acid is added initially and the mixture of dicy, formaldehyde, and boric acid is then warmed, no insoluble product may appear at any stage but we continue the warming under such conditions and for such time as would, in the absence of the boric acid, give the final water soluble stage. A time for this reaction of 3 to 4 hours, at the temperature of reflux of the mixture, is usually satisfactory.

The invention will be illustrated in greater detail by description in connection with the following examples. In these examples and elsewhere herein proportions are expressed as parts by weight except when otherwise specifically stated to be molecular proportions. In these examples, the first three relate to the making of the condensation products including the boric acid component and the later examples to the treatment of various organic fibrous materials with the condensation products.

#### Example 1

168 pounds of dicyandiamide (2 mols) and 648 pounds of 37% formaldehyde solution (8 mols) were refluxed for 3½ hours at a temperature between 92° and 95° C. until the resin passed through an insoluble stage and again became soluble as described in our Patent No. 2,567,238. 124 pounds of boric acid powder (2 mols) was mixed with 350 pounds of water and heated to a boil until the boric acid dissolved. The solution of boric acid and the solution of the dicyandiamide resin were mixed and heated under refluxing conditions for two hours at a temperature of about 95° C.

The resulting resin was found to be substantially stable and to show very little tendency to gel or become water insoluble on long standing, though a slight precipitation was shown at low temperatures. However, even when this occurred a re-solution was had when the temperature was raised again to about 20° C.

#### Example 2

The procedure of Example 1 is followed except that the boric acid is mixed into the dicyandiamide and formaldehyde solution before the refluxing is begun, so that the reaction of the dicy and formaldehyde occurs in contact with the boric acid.

In general, the product of Example 1 is more readily impregnated into fine grain leathers, such as calf, than the product of Example 2.

#### Example 3

The procedure of Examples 1 or 2 is followed except that the amount of formaldehyde used is changed to any proportion within the range 2-16 mols for 1 mol of the dicy, the proportion of boric acid within the range 0.1-1 mol being higher for the lower proportions of formaldehyde used. When 2 mols of formaldehyde in commercial formalin solutions, 1 mol of dicy, and 1 mol of boric acid are mixed and refluxed, there results a product that is infinitely soluble in hot water.

#### Example 4

100 lbs. vegetable tanned leather, such leather being anionic, is split and shaved to the desired weight, washed with water for 10 minutes at 100° to 110° F., and then drained. Water in the proportion of 80% of the shaved weight is then put on the leather at 110° to 120° F. There is next applied a solution of the resins (condensation products made as described in Example 1) in the proportion of 8 parts of the resin solution (35% solids in the aqueous solution). After the solution of resin is added, the whole is tumbled in a rotating drum for 30 minutes, washed for 5 minutes at 120° F., and drained. Then the conventional fat liquoring is effected as follows:

Apply as the anionic agent 3 to 6 pounds of sulfated cod oil in water at 120° F. and drum or tumble for 30 minutes.

The leather made in this manner is very full, tight, smooth and tends to have an actual increase in tensile strength. Another characteristic imparted by this resin is a reduction in the water extractable or uncombined vegetable tanning materials previously introduced into the leather.

#### Example 5

In this example, the vegetable tanning material is replaced by our resin tanning.

100 lbs. of fleshed, unhaird, live stock hide is washed with water for 20 minutes at 85-90° F. and drained. This stock is then floated with 200% to 300% water at 85° F. and baited and completely delimed in conventional manner. The stock is then washed for 20 to 30 minutes with water at 80°-85° F. and drained. 10% to 15% of the resin solution of Example 1 (35% solids) is then applied and the stock is drummed or rotated in this solution until a shrinkage temperature in the range 80° to 85° C. is obtained. Then 5% sodium chloride is added and the whole drummed for 10 minutes. The normal amount of sulfuric acid is added and also the normal amount of the chromium containing salts. Normal or conventional methods of further processing are followed.

The hide stock as used is amphoteric and thus able to fix the cationic resin tanning material. There results an increase in thickness and weight of the finished leather as well as improved tightness and smoothness of grain.

#### Example 6

100 pounds of pickled sheep skins (amphoteric) are immersed in a drum containing 100% of a 2.5% sodium chloride solution. To this is added 12% to 20% of the resin solution described in Example 2, and the sheep skins are rotated in this solution for 4 hours. At the completion of this time, which is adequate for penetration of the resin throughout the skin, the pH is gradually adjusted to 6.0 by the addition of a suitable alkali such as borax or sodium bicarbonate. This leather as such is then fat liquored and processed in normal manner.

The leather so made is very white, soft, full, and strong, with good light resistance.

#### Example 7

The procedure of Example 4 is followed except that the vegetable tanned leather is substituted by chrome-tanned leather on an equal weight basis and any one of the anionic agents listed above is introduced into the leather (or skin) in amount equal to the weight of the resin (dicy-formaldehyde-boric acid condensation product), the selected agent being introduced either before or after impregnation by the resin.

#### Example 8

100 lbs. chrome tanned leather is split, shaved to desired weight, washed with water for ten minutes at 110°-120° F., drained and then placed in water in the proportion of 80% of the shaved weight of the leather at 110°-120° F.

There is then applied to the wet leather an aqueous solution of the sodium salt of dinaphthyl methane disulfonic acid of 3% concentration, this salt being the anionic agent.

The whole is then tumbled in a rotating drum for 30 minutes, washed with water for five minutes at 140° F., drained and the product again placed in 80% of water. There is then applied the dicyandiamide, formaldehyde, and boric acid condensation product made as described in any one of Examples 1, 2 and 3, the proportion of the condensation product being 3% of the shaved weight of the leather. The resulting mixture is tumbled in a drum for 45 minutes.

The inclusion of the boric acid in the condensation product decreases the tendency for the resin to precipitate on the surface of the leather and results in good penetration

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throughout. The material so impregnated is then precipitated by the action of the said anionic agent upon the resin, which is cationic.

The resulting material is then fat liquored by washing with water at 120° F., draining, applying 4% of white pigments, and 3%—4% of a sulfated fatty oil in 80% of water at 120° F., and tumbling in a drum for 30 minutes, all the proportions being on the shaved weight of the leather.

#### Example 9.

The procedure of Example 8 is followed except that the dicyandiamide, formaldehyde, and boric acid condensation product is applied to the leather in advance of the application of the anionic agent.

The additional examples given below relate to the use of our new resin composition in connection with cellulose textile materials. It may be applied to silk and wool and protein fibers, as, for example, to cotton, wood fiber, paper, rayon, and also to nylon, acrylic, and polyester fibers.

In the use of our resin with such products we have found that the resin acts as a dye mordant or dyeing assistant; dyes which alone do not have affinity for cellulose, wool or the like, are mordanted or fixed on the textile material by our resin. More specifically, we have found that anionic or acid dyes, normally with no or only poor affinity for fibrous materials such as cotton or rayon, when used in conjunction with our dicy-formaldehyde, and boric acid resin become fixed on such fibers. On nitrogen containing fibers, our resins increase affinity of the dyes, as on silk, wool, or nylon.

This improvement is particularly great in the case of anionic acidic dyes containing a sulfo, carboxylic, or other acid group. Examples of such dyes are Polar Brilliant Red 3B, Cloth Fast Yellow 260, and Acetate RLF 40.

With such dyes, our resin gives a greater effect to the dye, perhaps by increasing the bulk of the finished dyeing ingredient retained.

Our resin has direct affinity for cellulosic materials, is taken up from a water bath, and serves as a mordant for dyes of the anionic group applied to the cellulosic matter. This makes the fabric substantive to the dyes.

The resin, impregnated on fabrics and then cured, gives some shrink and crease-proofness and the insecticidal properties of boric acid.

#### Example 10

Cotton cloth was treated with a 5% solution of the dicy, formaldehyde, and boric acid resin and the bath brought to boiling. The fabric was afterwards washed, dyed with a direct dye, and the dye bath brought to boiling and maintained for one hour.

After this period, the fabric was washed and dried, the resin acting as a mordant and the dyed fabric having good wash fastness.

#### Example 11

A dye bath was prepared taking 3% of acid dye calculated on the wool material. Sodium bisulfate was added to exhaustion of the dye bath, the bath being brought to boiling. After being thus dyed, the goods were washed and, in a new bath, subsequently treated for ½ hour with 5% of the resin (dicy, formaldehyde, and boric acid condensation product) and dyeing continued for 1 hour. The dye was the Cloth Fast Yellow 260.

The material was washed with hot water. After such treatment the wool was strongly colored; the resin and the dye composition had much greater affinity for the fabric than the dye alone.

#### Example 12

The procedure of Examples 10 or 11 is followed except that the proportion of the dicy, formaldehyde, and boric acid resin is within the range 0.3–2 parts of the resin

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for 1 part of the fabric being treated, the resin and fabric weights being calculated on the dry basis.

#### Example 13

Two per cent of the resin (calculated on the dry basis and on the weight of a cotton yarn) was dyed with 2% of a direct dye. It was then washed. Then the yarn was immersed in 2% of dicy-formaldehyde resin, the resin being in aqueous solution and the 2% representing 2 parts dry weight for 100 of the dry yarn. After that the material was washed in hot water. The dyed goods showed excellent wash fastness.

#### Example 14

The procedure of Examples 10, 11, 12 or 13 is followed with the substitution for the textile material therein of silk, nylon, acrylic fiber, or glycol terephthalate, each being used separately.

The resin improves the intensity of color and wash-fastness of the dye.

#### Example 15

Paper stock in a beater is treated with the two materials (1) our resin and (2) any one of the anionic agents named herein, each of (1) and (2) in the proportion of 2% of the dry weight of the fibers in the stock, and the two materials being added separately, either (1) or (2) first, and the other after the one first added has penetrated the fibers.

The fibers so treated are then formed into paper in usual manner and dried.

To make a colored paper, an anionic dye is added.

#### Example 16

Resin made as described in any one of the Examples 1–3 is sprayed in aqueous solution upon wood fiber paper that has previously been sprayed with a solution of any one of the anionic agents listed above.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What we claim is:

1. The method of treating an organic fibrous material which comprises applying to the material, in cation fixing condition, an aqueous solution of a preformed water soluble dicyandiamide, formaldehyde, and boric acid condensation product, the proportion of formaldehyde being 2–16 mols to 1 mol of dicyandiamide, the condensation product being cationic, and the result being fixing of the condensation product within the said material.

2. In treating an organic fibrous material with the treating agents (1) dicyandiamide, formaldehyde, and boric acid condensation product in preformed water soluble condition, the proportion of formaldehyde being 2–16 mols to 1 mol of dicyandiamide, and (2) an anionic precipitating agent therefor, the method which comprises introducing into the said material a solution of one of the said treating agents and then a solution of the other of the said agents, the result being precipitation of the said condensation product within the said material.

3. The method of claim 1 in which the said fibrous material is leather.

4. The method of claim 2 in which the said fibrous material is leather and the result being the fixing of the said condensation product, as a tanning agent, within the leather.

5. In treating cotton, the method which comprises applying to the cotton an aqueous solution of dicyandiamide, formaldehyde, and boric acid condensation product, the proportion of formaldehyde being 2–16 mols to 1 mol of dicyandiamide, and then washing the treated cotton with water, the result being cotton retaining the said condensation product and being substantive to acidic dyes

of kind that are not water-fast in the absence of the condensation product.

6. In treating a protein textile material, the method which comprises applying to the material an aqueous solution of dicyandiamide, formaldehyde, and boric acid condensation product, the proportion of formaldehyde being 2-16 mols of 1 mol of dicyandiamide, and then washing the treated material with water, the result being material retaining the said condensation product and being substantive to acidic dyes of kind that are not water-fast in the absence of the condensation product.

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