

UNITED STATES PATENT OFFICE

2,072,408

METHOD OF TREATING POROUS MASSES

Elly Pollak, Vienna, Austria

No Drawing. Application November 30, 1934,
Serial No. 755,507. In Austria December 4,
1933

17 Claims. (Cl. 91--70)

This invention relates to the improvement of porous masses by the incorporation therewith of resinous matter in solution.

Carboxylic acid amides of hydrazine (diamide) or alternatively its substitution products or monothio-derivatives of these compounds yield with formaldehyde in the presence of acid or alkaline catalysts, condensates (hydrazo resins) which are soluble in water. These solutions are remarkable for their particularly thin liquid nature and low degree of viscosity, and also for their excellent adhesive resistance. If such solutions be hardened in a manner known per se, after filtration, highly elastic colorless masses result which are unusually acid proof and highly resistant to the action of caustic alkali. The described solutions are therefore particularly suitable for use in improving the quality of various porous masses such as paper, wood, felt, asbestos, and the like, and more particularly for use as a dressing medium in the treatment and finishing of textile fibers and fabrics.

In place of these solutions, it is also possible to use mixtures thereof with other artificial resin solutions which are capable of hardening. This feature is of significance, not only for the reason that the products derived from hydrazine are somewhat expensive, but also because they are capable of imparting their valuable properties in a surprisingly high degree to mixed products, even when they are present in these mixed products in relatively small quantities. For example, if resins obtained from urea or thiourea and formaldehyde be mixed with even slight proportions of solutions of the hydrazo resin, the particularly great adhesive resistance and elasticity as well as the resistance to the action of acid of the hydrazo resin will nevertheless be imparted in a high degree to the mixture.

Masses of comparatively great thickness or bulk are impregnated in a manner known per se, for example in vacuo, with the artificial resin solutions concerned, and then hardened, with or without the application of pressure, preferably at a temperature of 130 to 140° C. The masses thus obtained can be satisfactorily worked by mechanical methods, and possess high insulating value.

Paper can be successfully impregnated or coated with the solution, if a plurality of such layers are superposed upon each other, and the composite body thus converted, with the application of heat and pressure, into a shaped piece or body of laminated structure. A strip of paper coated on one side with the described solution can be

wound under tension, and with simultaneous heating, upon a mandrel in such a manner that a firm lapped tubing is obtained.

Porous, pulverulent, or finely fibrous materials, such as cork meal, asbestos, powdered wood, and the like, can be mixed with the solutions, after which the pasty mass thus obtained can be applied to a metallic or other substratum and there hardened by heat, with or without the application of pressure. Acid-proof coatings are obtained in this manner upon the substratum or other foundation surface. Small mica plates or flakes may also be held together with the aid of the described artificial resin solutions, and then converted into a solid composition by the application of pressure and heat. The material obtained in this manner has excellent electrical insulating properties.

Fabrics may be impregnated with a hot or cold solution of the resin, then pressed in the usual manner, dried, stretched and finished. The effect of the dressing can be varied within very wide limits, ranging from hard stiffening to elastic finish. The latter type of finish is particularly valuable for many purposes, since for example in this manner cellulose fibers can be improved so that they acquire the same resistance to creasing and crumpling as wool or natural silk.

If a fabric be impregnated with the described mixture of resins, the properties of the hydrazo resin, such as resistance to washing out, softness, and resistance to the action of acid and alkali are nevertheless realized in a high degree in the mixture of the resins, even when the hydrazo resin is added only in a proportion of 15-20%. Particularly favorable results are obtained with the use of hydrotropic wetting agents.

The two resin solutions can be produced separately, and applied to the fabric separately or conjointly. The textile fibres can however also be brought directly into contact with a solution into which the starting materials of the resin or resins have been introduced, before the resin frying reaction has started. In this case the resins or their intermediate products are produced in the textile bath or on the fibre itself, as for example when hydrazine and urea, which may serve as starting materials for the production of the hydrazo-dicarboxylamide, are caused to react directly with the formaldehyde in the textile bath. It is immaterial to know in this connection whether the formaldehyde reacts only with the hydrazo-dicarboxylamide evolved in the second stage of the reaction between the starting materials, or whether it reacts also with the semi-

carbazine evolved in the first stage of the reaction of urea and hydrazine. With this method of working particularly soft impregnations are obtained.

5 The production of these masses is effected, for example, as follows:

(1) 118 grams of hydrazo-dicarboxylamide are dissolved hot in 375 ccs. of formaldehyde of 40% strength (by volume), 50 ccs. of normal caustic soda solution, and 500 ccs. of water. The solution is then cooled, filtered, and HCl added until the solution shows a weak acid reaction on Congo. The solution is then diluted with water up to a total volume of 1200 ccs.

15 A fabric of cuprammonium silk is steeped in this solution, kneaded in the usual manner, spread out horizontally under tension, and finally hardened in a heated chamber at a temperature of 120° C. After soaping, a finished fabric is obtained which is resistant to creasing and crumpling and also resistant to the action of acids and alkalis.

Masses such as paper, wood, felt, asbestos, pressed compositions, and the like can also be treated with the same solution. The products thereby obtained are more elastic than they would otherwise be, have useful insulating properties, and are likewise resistant to the action of acid and alkali.

30 (2) Two solutions are made up as follows:

Solution A

	Grams
Urea.....	96
35 Neutralized 30% formaldehyde 30% strong (by volume).....	320
Boric acid.....	16

These ingredients are boiled under a reflux condenser until a sample does not become turbid on cooling.

Solution B

Hydrazo dicarboxyl amide.....	grams.....	32.6
Formaldehyde.....	do.....	65.3
Water.....	ccs.....	88
45 Normal caustic soda solution.....	do.....	10

These ingredients are dissolved under a reflux condenser, and then neutralized with hydrochloric acid, cooled and filtered. Solution A is then mixed with Solution B and incorporated as described with porous masses such as paper, wood, felt, asbestos, textile fibers, textile fabrics and the like.

(3) A viscose crêpe-de-chine is impregnated with a solution of 15 grams of hydrazo dicarboxyl amide, 85 grams of urea, 250 ccs. of 40% formaldehyde, and 1 cc. of formic acid in 650 ccs. of water, then wrung out, dried, and heated for a short time at 130° C. After boiling with soap, 60 the fabric has a soft elastic finish.

A strong cotton fabric is impregnated in the same manner after mercerizing, although it is preferable to add 2% of the sodium salt of a naphthalene sulfo acid condensated with formaldehyde referred to the weight of the fabric in the dry state.

(4) 15 grams of hydrazine hydrate, 85 grams of urea, 250 ccs. of 40% formaldehyde, and 2 ccs. of caustic soda solution (36° Baumé), are dissolved in 650 ccs. of water, and, after being left to stand for some time, acidulated with 3 ccs. of formic acid. A viscose crêpe-de-chine is impregnated with this solution and further treated as in Example 3. After boiling with soap, an elastic 75 firm finish is obtained.

(5) A viscose crêpe-de-chine is impregnated with a solution of 10 grams of hydrazine hydrate, 90 grams of thiourea, 250 ccs. of 40% formaldehyde, and 2 ccs. of formic acid in 650 ccs. of water, and further treated in the manner described in example 3. After boiling with soap, the material is soft and elastic to the touch.

I claim:—

1. The process which comprises incorporating with porous material a solution of at least one product obtained by condensing formaldehyde in the presence of catalysts with a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-thio derivatives of dicarboxylamides of hydrazine, and after the incorporation, hardening the condensation product by means of heat.

2. The process claimed in claim 1 using a porous material selected from the following: paper, wood, felt, asbestos, textile fibres, and textile fabrics.

3. The process which comprises incorporating with porous material a solution containing formaldehyde, a catalyst, the starting materials for producing a substance selected from the group: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-thio derivatives of dicarboxylamides of hydrazine, and subjecting the incorporated substances to the action of heat.

4. The process which comprises incorporating with porous material a solution containing formaldehyde, a catalyst, urea, the starting materials for producing a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-thio derivatives of dicarboxylamides of hydrazine, and subjecting the incorporated substances to the action of heat.

5. The process which comprises incorporating with porous material a solution containing formaldehyde, a catalyst, thiourea, the starting materials for producing a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-thio derivatives of dicarboxylamides of hydrazine, and subjecting the incorporated substances to the action of heat.

6. The process claimed in claim 3 using a porous material selected from the following: paper, wood, felt, asbestos, textile fabrics and textile fibres.

7. A product comprising a porous product and incorporated hardened condensation product of formaldehyde and a dicarboxylamide of hydrazine.

8. A process for improving textile fibres and fabrics, more particularly of cotton and artificial silk, consisting in treating the same with a solution of a product obtained by condensing formaldehyde in the presence of catalysts with a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-thio derivatives of dicarboxylamides of hydrazine, removing the surplus solution, drying the material, and hardening the condensation product by heating.

9. A product comprising a porous product and incorporated therewith at least one hardened condensation product of formaldehyde and a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and mono-

thio derivatives of dicarboxylamides of hydrazine.

10. A product comprising a porous product, incorporated therewith at least one hardened condensation product of formaldehyde and a substance selected from a group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and monothio derivatives of dicarboxylamides of hydrazine, and at least one other colorless hardened artificial resin admixed to the said condensation product.

11. In a product as claimed in claim 10, the said colorless artificial resin being a condensation product of formaldehyde and at least one substance selected from the group consisting of: urea and thiourea.

12. In a product as claimed in claim 9 the said porous product being a material selected from the following group consisting of: paper, wood, felt, asbestos.

13. A creaseproof material comprising a textile matter selected from the group consisting of: textile fibres and textile fabrics, and a thin film of at least one hardened condensation product of formaldehyde and a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and monothio derivatives of dicarboxylamides of hydrazine, covering each individual fibre of the said textile matter, the interior of said fibres being left free from the said condensation product.

14. A creaseproof material comprising a textile matter selected from the group consisting of: textile fibres and textile fabrics, and a thin film consisting of a mixture of at least one hardened condensation product of formaldehyde and a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and monothio derivatives of dicarboxylamides of hydrazine, and of at least one other colourless hardened

artificial resin, covering each individual fibre of the said textile matter, the interior of said fibres being left free from the said mixture.

15. In the process which comprises incorporating with porous material a solution containing at least one product obtained by condensing formaldehyde in the presence of catalysts with a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine, and monothio-derivatives of dicarboxylamides of hydrazine, and after the incorporation hardening the condensation product by means of heat, the step of incorporating at least one other colourless artificial resin to the said porous material at a time before hardening the said condensation product and hardening said other colourless artificial resin simultaneously with said condensation product.

16. In the process claimed in claim 15 the additional colourless artificial resin being of the type obtained from formaldehyde and at least one of the substances selected from the group consisting of: urea and thiourea.

17. In the process for improving textile fibres and fabrics, more particularly for rendering cotton and artificial silk less liable to creasing and crumpling, consisting in treating the unhurt fibres and fabrics with a solution of a product obtained by condensing formaldehyde in the presence of catalysts with a substance selected from the group consisting of: dicarboxylamides of hydrazine, substitution products of dicarboxylamides of hydrazine and monothio derivatives of dicarboxylamides of hydrazine, removing the surplus solution, drying the material, and hardening the condensation product by heating, the step of adding to the said solution at least one other colorless artificial resin and hardening the same simultaneously with the said condensation product.

ELLY POLLAK