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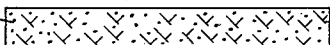
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2,027,973

STIFFENING MATERIAL

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*Highly Porous Deposit of Precipitated Colloidal  
Material e. g. Cellulose Ester*



*More Colloided and More Solvent Resistant Colloidal  
Material e. g. Cellulose Ester*

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## UNITED STATES PATENT OFFICE

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## STIFFENING MATERIAL

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This invention relates to methods of preparing stiffening material, and particularly to methods of preparing an improved stiffening material of the general type disclosed in U. S. Patent 1,256,240, Lovell, February 12, 1918. Although not restricted to such use, material of the present type finds advantageous application as stiffening material for boots and shoes, such as fabric, patent leather, cut-out, or perforated boots and shoes, and therefore is described with more particular reference to the boot and shoe industry.

Material of the Lovell type comprises a base fabric such as a woven material, for example cotton cloth, or a structureless material, for example felt or paper, with its interstices carrying precipitated colloidal material in a highly porous form termed "powdered" by Lovell, such as a cellulosic derivative, casein, albumin and various gum and resins. In use, the fabric is immersed in a solvent for the precipitated material, thereby to resolve the same into a coalescent flaccid condition, and when the material is in this condition the fabric is applied in the lasting operations, shaped, and allowed to harden, by evaporation of solvent, in its shaped condition. While material of the Lovell type is highly satisfactory in use, it sometimes gives rise to the difficulty that the colloidal matter becomes so soft and mushy when the stiffener is dipped into the solvent, that the colloidal matter can be forced through the upper of a shoe of fabric or similar material, during the lasting operations, thereby staining, disfiguring, and ruining the upper; and similarly, the coating on a patent leather shoe upper will be affected and softened during the lasting operations so that the coating will be peeled from the leather, thereby damaging the upper; and, again, in lasting shoes having cut-outs or perforations in the upper, the colloidal matter may be forced through the cut-outs or perforations.

I have now devised a method for the manufacture of stiffening material of the general Lovell type which method provides a material which, in itself, overcomes the difficulties mentioned.

In the accompanying drawing, the figure is a highly conventional exaggerated cross sectional view of stiffening material made in accordance with the present procedure.

One object of my invention is to provide a method for the production of an improved stiffening material of the mentioned and other desirable characteristics. To this end and also to improve generally on methods of the general

character indicated, my invention consists in the various matters hereinafter described and claimed.

These objects are accomplished by impregnating the fabric with a solution of colloid and introducing the undried, impregnated fabric into a precipitating bath, the colloid solution having present therein a restraining agent acting to prevent complete precipitation of the colloidal matter during treatment of the fabric in the precipitating bath. The result is that when the material is dried, e. g. air dried, although much of the colloidal material is in precipitated form there is also a certain amount that is in a harder or more colloided form. As the colloidal matter in the fabric is not entirely in a precipitated or highly porous condition, it does not absorb the solvent with which the stiffening material is ultimately treated for use in the lasting operation, as quickly or in such a large amount as would the ordinary stiffening material containing only precipitated colloidal material, and, therefore, does not become as mushy as would the ordinary material. Yet, on the other hand it will absorb enough solvent so that it will soften quicker than material prepared merely by subjecting a fabric impregnated with a cellulosic derivative dope to an air drying operation, e. g. that type of stiffener known as the "air dried colloided stiffener". Thus, the present method gives a material that overcomes the disadvantages of the ordinary stiffening material with precipitated colloidal matter, while retaining the fundamental advantages of such material.

Preferably, the fabric to be impregnated is impregnated in a bath containing a precipitation-restraining agent that is immiscible or but partially miscible in the following bath in which the material is immersed for the purpose of precipitating the colloidal material with which the fabric is impregnated in the first bath. The said agent may be either a solvent or a non-solvent for the colloidal material. Whether the agent be a solvent or a non-solvent, its primary characteristic is that it is immiscible or at most only partially miscible with the precipitating bath, as otherwise there would be complete precipitation in the precipitating bath. When the impregnating bath, so far as the liquid ingredients thereof are concerned, is composed of only a single ingredient, this ingredient must not only be a restraining agent but must also be a solvent for the colloidal material and be but partially miscible in the precipitating bath. When the impregnating

bath comprises, as regards the liquid ingredients, more than one ingredient, the restraining agent need not be a solvent, provided one of the other ingredients present is a solvent; and, furthermore, this ingredient that is a solvent may be entirely miscible in the precipitating bath since the agent furnishes the factor of immiscibility called for. The precipitating liquid in the precipitating bath tends to immediately and completely displace the impregnating liquid to the extent that that liquid is miscible in the impregnating bath; but to the extent that that liquid is immiscible in the impregnating bath it restrains its own immediate or complete displacement, and thereby to that extent prevents the precipitation of a part of the colloidal matter.

For the production of goods in accordance with the invention, when the precipitating bath is water, there may be added to the impregnating bath, of say cellulose nitrate with ethyl alcohol and acetone as the solvent, a quantity of toluol since this is nearly immiscible in water. A sheet of the fabric, that it is desired to treat is passed through the colloidal solution, to thoroughly impregnate the fabric and then, without drying, it is passed into the precipitating bath where the precipitating liquid tends to displace the solvent; the restraining agent prevents the immediate or complete displacement of the solvent and prevents the complete precipitation of the colloidal matter. When this operation is completed, and the material is removed from the bath and dried and as mentioned above, a portion of the colloidal matter will be found in a harder or more colloided form than the precipitated matter.

Without restricting the invention thereto, the following will serve as specific examples thereof:—

## I

This stiffener may be made by thoroughly impregnating a piece of cotton flannel with the following colloidal solution:

|                      |       |     |
|----------------------|-------|-----|
| Cellulose nitrate    | lbs.  | 300 |
| Ethyl alcohol        | gals. | 145 |
| Acetone              | do    | 15  |
| Carbon tetrachloride | do    | 30  |

The impregnated flannel is then, without drying, passed to a precipitating bath of water and immersed therein for 15 minutes, where the carbon tetrachloride, being nearly immiscible in water, will prevent the water from completely displacing the alcohol and acetone and precipitating completely the cellulose nitrate. The material is then air dried. For carbontetrachloride may be substituted an equal quantity of toluol, the treatment being otherwise the same.

## II

This stiffener may be made by thoroughly impregnating a sheet of fibrous material, such as felt, with the following colloidal solution:

|                   |       |     |
|-------------------|-------|-----|
| Cellulose acetate | lbs.  | 300 |
| Ethyl alcohol     | gals. | 80  |
| Acetone           | do    | 80  |
| Toluol            | do    | 30  |

The impregnated felt is then passed, without drying, to a precipitating bath of water and immersed therein for 15 minutes, where the toluol, being nearly immiscible in water, will prevent the water from completely displacing the alcohol and acetone, and precipitating completely the cellulose acetate. The material is then air dried.

## III

This stiffener may be made by thoroughly impregnating a sheet of absorbent paper with the following colloidal solution:

|                 |       |     |
|-----------------|-------|-----|
| Ethyl cellulose | lbs.  | 300 |
| Ethyl alcohol   | gals. | 80  |
| Acetone         | do    | 80  |
| Naphtha         | do    | 30  |

The impregnated paper is then, without drying, passed to a precipitating bath of water and immersed therein for 15 minutes, where the naphtha, being nearly immiscible in water, will prevent the water from completely displacing the alcohol and acetone and precipitating completely the ethyl cellulose. The material is then air dried.

The material as produced by each of the examples will be stiffer and less absorbent to solvent and so will not cause damage to fabric, patent leather or perforated shoes.

The particular colloidal matter and the stiffener to which the present invention is applicable may be, as above indicated, of many general types. When of cellulosic derivative, it may be of cellulose ester, e. g. cellulose nitrate or cellulose acetate or cellulose ether, e. g. ethyl cellulose or benzyl cellulose or any suitable combination thereof. Plastics made from these substances may be dissolved and used. The solvent for treatment in particular accordance with the present invention will, of course, be selected for compatibility with the particular colloid in question.

Other examples of mixtures of liquids that might be used as solvents are alcohol or acetone or methyl ethyl ketone, etc., together with one or more of the following, ethyl acetate, castor oil, toluol, gasoline, butyl alcohol, carbon tetrachloride, etc. to be used in connection with a precipitating bath of water. The solvent bath, the precipitating bath, the times of immersion therein, and such factors will, of course, be varied to meet the particular conditions as will be understood by those skilled in the art. The above examples are given merely as illustrations as the percentages of the restraining agent in the impregnating bath may be varied to meet the particular conditions.

In any case, in consideration of the result desired and as exemplified by the times stated in the above examples, the time of immersion in the precipitating bath is so correlated with the amount and efficacy of the particular restraining agent used that the restraining agent will, for the full length of the period of immersion in the precipitating bath, prevent the precipitation of more than a part only of the colloidal matter. As will be understood by those skilled in the art, these factors may be widely varied to meet the circumstances of particular cases.

In the use of the fabric, blanks of suitable shape may be cut therefrom and, when dipped into suitable solvent in general accordance with Lovell, the colloidal matter is resolved into a coalescent, flaccid body which may be placed and conformed into the desired shape and will dry in the desired shape, stiff, flexible, and resilient.

While boots and shoes have been more particularly referred to, it will be understood that stiffeners of the present type may be used in any article of footwear where their use recommends itself, and furthermore, may be used at any

particular location desired, as in the toe to form the box or in the heel to form the counter.

I claim:—

1. Method comprising impregnating a fabric throughout with a cellulose derivative solution, passing the fabric without drying into a precipitating bath, the solvent-liquid content of said solution and said precipitating bath being at least partially immiscible and the fabric being subjected to said precipitating bath for a period of time only sufficient to precipitate part of the cellulose derivative, drying said impregnated fabric, and thereafter treating said fabric with a cellulose derivative solvent to soften it, shaping it, and allowing it to dry in the desired final form.

2. Method comprising impregnating a fabric throughout with a cellulose derivative solution, said solution comprising a water-soluble solvent for the cellulose derivative and a water-immiscible liquid, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the cellulose derivative, drying said impregnated fabric, and thereafter treating said fabric with a cellulose derivative solvent to soften it, shaping it, and allowing it to dry in the desired final form.

3. Method comprising impregnating a fabric throughout with a cellulose nitrate solution, passing the fabric without drying into a precipitating bath, the solvent-liquid content of said solution and said precipitating bath being at least partially immiscible and the fabric being subjected to said precipitating bath for a period of time only sufficient to precipitate part of the cellulose nitrate, drying said impregnated fabric, and thereafter treating said fabric with a cellulose nitrate solvent to soften it, shaping it, and allowing it to dry in the desired final form.

4. Method comprising impregnating a fabric throughout with a cellulose nitrate solution, said solution comprising a water-soluble solvent for the cellulose nitrate and a water-immiscible liquid, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the cellulose nitrate, drying said impregnated fabric, and thereafter treating said fabric with a cellulose nitrate solvent to soften it, shaping it, and allowing it to dry in the desired final form.

5. Method comprising impregnating a fabric throughout with a cellulose nitrate solution, said solution comprising a water-soluble solvent for the cellulose nitrate and a water-immiscible liquid from the group consisting of carbon tetrachloride and toluol, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the cellulose nitrate, drying said impregnated fabric, and thereafter treating said fabric with a cellulose nitrate solvent to soften it, shaping it, and allowing it to dry in the desired final form.

6. Method comprising impregnating a fabric throughout with a cellulose acetate solution, said solution comprising a water-soluble solvent for the cellulose acetate and a water-immiscible liquid, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the cellulose acetate, drying said impregnated fabric, and thereafter treating said fabric with a cellulose acetate solvent to soften it, shaping it, and allowing it to dry in the desired final form.

7. Method comprising impregnating a fabric throughout with a cellulose ether solution, said solution comprising a water-soluble solvent for the cellulose ether and a water-immiscible liquid, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the cellulose ether, drying said impregnated fabric, and thereafter treating said fabric with a cellulose ether solvent to soften it, shaping it, and allowing it to dry in the desired final form.

8. Method comprising impregnating a fabric throughout with an ethyl cellulose solution, said solution comprising a water-soluble solvent for the ethyl cellulose and a water-immiscible liquid, passing the fabric without drying into a water bath, the fabric being subjected to said water bath for a period of time only sufficient to precipitate part of the ethyl cellulose, drying said impregnated fabric, and thereafter treating said fabric with an ethyl cellulose solvent to soften it, shaping it, and allowing it to dry in the desired final form.

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