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TREATMENT OF FIBROUS SHEETS

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This invention relates to the treatment of fibrous sheets and, more particularly, to a process of treating fibrous sheets with cellulose acetate compositions in the manufacture of stiffeners used in box toes and counters of shoes and similar articles.

Lovell U. S. Patent 1,256,240 discloses a method of precipitating colloidal substances such as cellulose esters throughout fibrous sheets by impregnating a fibrous sheet with a solution of the colloidal substance and then subjecting the sheet to a precipitating bath. The colloid treated sheet thus obtained is used as stiffening material in shoes, and the like, by treating same with a solvent to dissolve the colloidal material, shaping the stiffener and allowing it to dry in the desired shape. The fibrous sheets used for this purpose may vary widely and include woven material such as cotton cloth, either unnapped or napped, as in the case of flannel, or unwoven structureless material as felt, absorbent paper, matted wood pulp, and other fibers. The term "fibrous sheet" is used throughout the specification and claims to denote material of this general type characterized by the property of being absorbent.

Colloid treated sheets such as disclosed in U. S. Patent 1,256,240 have found a tremendous use in the shoe industry and the manufacture of these sheets has reached such proportions that even small economies in such manufacture are greatly to be desired.

An object of the present invention is to provide a simple and more economical process of preparing colloid treated sheets such as disclosed in United States Patent 1,256,240. A further object is to provide an economical process of preparing fibrous sheets having the cellulose acetate precipitated in discontinuous form throughout. A further object is to provide a process of preparing such fibrous sheets which process eliminates the use of the precipitating bath heretofore considered necessary in the preparation of such sheets. Other objects of the invention will be apparent from the description given hereinafter.

The above objects are accomplished according to the present invention by dissolving cellulose acetate having an acetyl number of 48 to 54½, and preferably a cellulose acetate of the "plastics" type, i. e., cellulose acetate having an acetyl number of 50–54, in a hot liquid capable of completely or substantially completely dissolving the cellulose acetate when hot but which will precipitate the cellulose acetate on a fibrous base in discontinuous form on cooling, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet. The expression "cellulose acetate having an acetyl number" is used throughout the specification and claims to mean a cellulose acetate of a certain acetyl value, calculated as acetic acid.

More specifically and in a preferred form, the invention is carried out by heating cellulose acetate having an acetyl number of 50–54 in a mixture of ethyl alcohol and water in which mixture the water content is 25–55%, to approximately the boiling point of the mixture but preferably not in excess thereof unless precautions are taken to prevent loss of the mixture through volatilization, the proportion of cellulose acetate in the mixture being such as to give a 10–20% cellulose acetate solution, impregnating a fibrous sheet with the hot solution formed, cooling said impregnated sheet to approximately room temperature to precipitate the cellulose acetate in discontinuous form throughout the sheet and removing any remaining alcohol-water mixture from the fabric.

All proportions and percentages given throughout the specification and the claims are by weight and not by volume. It is to be understood that, after the fibrous sheet has been impregnated with the hot cellulose acetate solution, it can either be exposed to artificial cooling means to cause precipitation of the cellulose acetate or merely be exposed to room temperature and thus gradually cooled down. Likewise, it is optional as to the manner of removing the alcohol-water mixture remaining in the fabric; it may be allowed to merely dry out under ordinary atmospheric conditions or, if desired, it may be removed by evaporation under reduced pressure, or similar means such as will occur to those skilled in the art.

In order to illustrate the invention, the following examples are given:

Example 1

A mixture of 118 parts of ethyl alcohol (92.4% strength) and 42 parts of water is heated in a steam jacketed kettle to a temperature just below the point at which boiling begins, namely 79° C. Twenty parts of cellulose acetate having an acetyl number of 52 are now introduced into the mixture with constant stirring until substantially complete solution takes place. This viscous solution is then pumped or dropped by

gravity through a jacketed pipe line to a steam heated impregnating tank and the web of fibrous material to be impregnated is run through this tank under and over rollers in the usual way employed in the impregnating art.

The impregnated material, after passing through the impregnating solution, is carried out of the solution into the air at room temperature to allow the cellulose acetate to precipitate in and on the material and to allow the material to dry. The alcohol volatilized may be recovered by any suitable means.

Example 2

A dope of cellulose acetate having an acetyl number of 52.2 is made up as in Example 1, using:

	Parts
Cellulose acetate	20
Ethyl alcohol (92.4% strength)	102
Water	63

and is used in the same manner as shown in Example 1.

Other compositions to be used in this manner are given in the following examples:

Example 3

	Parts
Cellulose acetate	20
Ethyl alcohol (92.4% strength)	92
Water	61

Example 4

	Parts
Cellulose acetate	20
Ethyl alcohol (92.4% strength)	46
Water	31.5

Example 5

	Parts
Cellulose acetate	20
Dimethyl phthalate	5
Eethyl alcohol (92.4% strength)	92
Water	61

In the above examples the cellulose acetate is of the type ordinarily used in the manufacture of plastics which type is ordinarily regarded as embracing acetates having acetyl numbers between 50 and 54, sometimes as high as 54½. Cellulose acetates having lower acetyl numbers in the range of 48 and 49 may also be used, however.

It is to be understood that the above examples are merely illustrative and it is not intended that the invention should be limited thereto. In place of the ethyl alcohol-water mixtures of the examples, other solvent liquids having the desired properties may be employed. The essential requirements of the solvent liquid, whether a single compound or a mixture of two or more, are: (1) that it shall dissolve the cellulose acetate completely, or nearly so, when hot, and (2) that, when cool, it will deposit the cellulose acetate from solution in and on the fibers of the sheet in the proper form, i. e., the precipitated cellulose acetate must not be in a continuous colloidal mass but in a discontinuous, finely comminuted or porous form.

Within the category of these liquids and mixtures which will function as required, the choice will be governed primarily by considerations of economy. For this reason and the further fact that it functions in such a highly satisfactory manner, the ethyl alcohol-water mixture possesses outstanding advantages. However, it is perfectly feasible to use other mixtures and, under specific conditions, other mixtures might be preferred.

When employing an ethyl alcohol-water mixture, the ratio of the water to the alcohol may be varied within wide limits but it has been found that to satisfactorily dissolve the cellulose acetate, the water content of the mixture should be between 25 and 55% and preferably should not exceed 45%. As a matter of expediency in carrying out the invention, it is desirable to heat the alcohol-water mixture, or other mixture employed, with the cellulose acetate to the boiling point of the mixture, in the case of the alcohol-water mixture in the neighborhood of 79° C. However, the mixture may be heated to any temperature as long as it is high enough to dissolve the cellulose acetate. Likewise, in cooling the sheet after impregnation, it is generally most convenient to cool it to room temperature, although any temperature sufficiently low to precipitate the cellulose acetate is operative. As a general rule, when using an ethyl alcohol-water mixture, the temperature of the mixture should be raised to at least about 55° C. in dissolving the cellulose acetate and the impregnated sheet should be cooled to at least about 35° C. It will be obvious that, during the impregnation, the cellulose acetate solution must be kept hot or otherwise premature precipitation of the cellulose acetate would occur.

The hot cellulose acetate solution to be used in impregnating the fibrous sheet must be of sufficiently low viscosity to impregnate the sheet fully and, at the same time, the solution must contain a sufficient amount of cellulose acetate so that the finished impregnated sheet will have a practical use. It has been found that the best results have been obtained by maintaining a concentration of cellulose acetate in the hot solution between 10 and 20%. A 10% cellulose acetate solution represents approximately the limit below which sufficient quantity of precipitated cellulose acetate will be lacking in the sheet for the uses desired. A 20% cellulose acetate solution represents the limit beyond which, with cellulose acetates of ordinary viscosities, the viscosity of the impregnating solution becomes too high for an efficient and satisfactory impregnation.

The present invention is applicable for the preparation of colloid treated fibrous sheets for all purposes and the use of such sheets as stiffeners for various parts of shoes has only been mentioned to illustrate an outstanding use for this material.

The invention provides a simple and economical process for the impregnation of fibrous sheets with cellulose acetate. In contradistinction to methods heretofore proposed and greatly to the advantage of the present invention, is its economy in the use of solvent and the fact that the particular solvent mixture most highly advantageous in the process, namely a mixture of ethyl alcohol and water, can be separated by a distillation in which the more valuable solvent component can easily be recovered. A substantial advantage of the process lies in the fact that the use of a precipitating bath may be eliminated, since the cellulose acetate will precipitate of itself when the impregnated fibrous sheets reach ordinary room temperature.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to

the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Process comprising dissolving cellulose acetate having an acetyl number of 48 to 54½ in a hot liquid capable of dissolving said cellulose acetate when hot but which will precipitate the cellulose acetate in discontinuous form on cooling, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

2. Process comprising heating cellulose acetate having an acetyl number of 48 to 54½ in a liquid capable of dissolving said cellulose acetate when hot but which will precipitate the cellulose acetate in discontinuous form on cooling, to approximately the boiling point of the liquid, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to approximately room temperature to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

3. Process comprising heating cellulose acetate having an acetyl number of 50–54 in a liquid capable of dissolving said cellulose acetate when hot but which will precipitate the cellulose acetate in discontinuous form on cooling, to approximately the boiling point of the liquid, the proportion of cellulose acetate to the liquid being such as to give a 10–20% cellulose acetate solution, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to approximately room temperature to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

4. Process comprising dissolving cellulose acetate having an acetyl number of 50–54 in a hot mixture of ethyl alcohol and water in which mixture the water content is 25–55%, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

5. Process comprising heating cellulose acetate having an acetyl number of 50–54 in a mixture of ethyl alcohol and water in which mixture the water content is 25–55%, to approximately the boiling point of the mixture, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to approximately room temperature to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

6. Process comprising dissolving cellulose acetate having an acetyl number of 50–54 in a hot mixture of ethyl alcohol and water in which mixture the water content is 25–55%, the proportion of cellulose acetate to the mixture of alcohol and water being such as to give a 10–20% cellulose acetate solution, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

7. Process comprising heating cellulose acetate having an acetyl number of 50–54 in a mixture of ethyl alcohol and water in which mixture the water content is 25–55%, to approximately the boiling point of the mixture, the proportion of cellulose acetate to the mixture of alcohol and water being such as to give a 10–20% cellulose acetate solution, impregnating a fibrous sheet with the hot solution formed, and cooling said impregnated fibrous sheet to approximately room temperature to precipitate the cellulose acetate in discontinuous form throughout said fibrous sheet.

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