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[54] **PROCESS FOR THE PRODUCTION OF A SHEET MATERIAL HAVING A SHAMMYING EFFECT, AND THE MATERIAL THUS PRODUCED**
7 Claims, No Drawings

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[51] **Int. Cl.** **B44d 1/44,** B32b 27/08

[50] **Field of Search** ..... 117/47, 63, 76 T, 102, 139.5 C, 140 R, 143 R, 135.5, 138.8 PV, 62.1; 161/151; 28/75

[56] **References Cited**

UNITED STATES PATENTS

2,673,825	3/1954	Biefeld et al.	117/135.5 X
2,969,791	1/1961	Ekenstam	117/63 X
3,000,757	9/1961	Johnston	117/63
3,067,483	12/1962	Hollowell	117/140
3,100,721	8/1963	Holden	117/135.5

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ABSTRACT: This invention relates to the production of a sheet material having a shammying effect by shrinking a web comprising retractable fibers in an aqueous medium and then providing it with a polymeric filler, wherein (a) a web which consists essentially of retractable polyvinyl alcohol fibers is caused to shrink and is treated with an aqueous solution of polyvinyl alcohol and a water-soluble resin composition; (b) the web is subsequently contacted with a liquid (e.g., an aqueous salt solution) which causes the polyvinyl alcohol to coagulate and in which the resin composition is practically insoluble; (c) the filled web is subsequently subjected to an acetalizing treatment (e.g., by means of an acidified aqueous solution of formaldehyde) in which the polyvinyl alcohol is rendered insoluble in hot water and the resin composition is at least partly removed from the web; and (d) the thus treated web is washed and dried. A suitable resin composition is a water-soluble composition of melamine and formaldehyde.

PROCESS FOR THE PRODUCTION OF A SHEET MATERIAL HAVING A SHAMMYING EFFECT, AND THE MATERIAL THUS PRODUCED

This invention relates to a process for the production of a sheet material having a shammying effect, in which process a web comprising retractable fibers is caused to shrink in an aqueous medium and is provided with a polymeric filler.

A process of the above type, broadly, is described in U.S. Pat. No. 3,067,483. In this known process a web comprising retractable fibers, after it has been caused to shrink in water, is impregnated with a polymer solution (in an organic solvent) or an aqueous polymer dispersion, followed by coagulation of the polymer. As polymer an elastomer is used which mainly acts as a binder for the fibers. The products obtained by this known process have only a limited shammying effect.

The present invention, on the other hand, relates to the manufacture of a sheet material which has properties, more particularly a shammying effect, which render the product excellently suitable to be used as wash-leather.

This invention is characterized in that a process of the type indicated above as broadly known is modified as follows:

a. a web which substantially consists of retractable polyvinyl alcohol fibers is caused to shrink and is treated with an aqueous solution of polyvinyl alcohol and a water-soluble resin composition;
b. the web is subsequently contacted with a liquid which causes the polyvinyl alcohol to coagulate and in which the resin composition is practically insoluble;
c. the filled web is subsequently subjected to an acetalizing treatment, by which the polyvinyl alcohol is rendered insoluble in hot water and the resin composition is at least partly removed from the web; and
d. the web thus treated is washed and dried.

It has been found that as hydrophilic synthetic substance polyvinyl alcohol (PVA) forms an excellent starting material for the manufacture of artificial wash-leather, which is due to the behavior of PVA relative to water, which behavior can with simple means be modified if desired.

PVA fibers retractable in an aqueous medium are known per se, and may be obtained inter alia as described in U.S. Pat. No. 2,962,762.

By a method known per se these fibers are made into a nonwoven web or mat by a dry process. The resulting fiber sheet may be rendered more coherent by subjecting it to a needle punch treatment. By contacting such a fiber sheet with water at a generally moderately elevated temperature, the fibers will shrink and will hardly stick together or show any loss of fiber structure. Owing to this shrinkage, which is generally attended with some crimping and/or spiralizing, an extremely coherent and yet very supple fiber web is obtained.

Here, too, as filler for the web use is made of PVA. To this end the web is impregnated with an aqueous solution of PVA, followed by treatment with a liquid coagulating agent for the PVA. As coagulating agent it is preferred to use an aqueous liquid such as an aqueous salt solution.

Impregnation of the web with the PVA solution may be effected in any convenient manner, for example by immersion or spraying. Impregnation with the aid of coating rollers or by padding may additionally (or alternatively) be employed for obtaining a denser filling at the surface of the web.

It has been found that the shrinking of the web and the impregnation with the PVA solution may very conveniently be carried out in one process step if the as-yet-not-shrunk dry web is directly treated with a moderately heated PVA solution.

The use of a 5 to 10 percent by weight PVA solution at 30° to 60° C. usually gives good results.

In general, it will be preferred to obtain a degree of filling of about 20 to 60 percent by weight of PVA, calculated on the dry unfilled web. To this end, the impregnated web is passed into the coagulation bath via squeeze rolls which, depending on the concentration of the PVA solution employed as well as the degree of filling required, are adjusted to the appropriate pressure.

In order that the web thus filled may be made suitable for use as wash-leather, the PVA, and more particularly the PVA filler, should subsequently be rendered insoluble in hot water of for example at least 80° C. For this purpose the web is subjected to a treatment with an acetalizing agent, part of the hydroxyl groups of the PVA being converted. The acetalizing agent may for instance be a monoaldehyde or a dialdehyde with which the filled web is treated in an acid aqueous medium at an elevated temperature.

Finally, the thus treated web is thoroughly washed, if necessary while using in the last washing stage a neutralizing agent and/or a softener, and then dried.

An artificial wash-leather prepared in the above-described manner is in many respects qualitatively equivalent or even superior to a natural wash-leather. In various tests, however, it has been found that, particularly with respect to such practical properties as squeeze-handle and surface-grip, the artificial wash-leather is not yet entirely satisfactory.

Surprisingly, it has been found according to the present invention, that these shortcomings can be removed if, prior to the coagulation of the PVA filler, the web is treated with a resin composition.

Resin compositions suitable for this purpose must be soluble in water or in a PVA solution, practically insoluble in the coagulation liquid used for coagulating the PVA, and at least partly extractable from the web when this is treated with the acetalizing agent.

It is preferred to use a resin composition having a basis of melamine and formaldehyde, in which the proportion of formaldehyde to melamine is such that the composition is soluble in water. Compositions of this kind are marketed inter alia by American Cyanamid Company under the trade name Accobond.

The resin composition may be introduced into the web in a separate process step or in combination with the PVA solution. In the latter case the best results are obtained if the web is first shrunk in a hot aqueous medium and subsequently immersed in an aqueous solution of PVA and the resin approximately at room temperature. However, it is preferred that the web, after a preceding shrinking treatment if desired, be successively treated with an aqueous solution of the resin at room temperature, dried, and immersed in a moderately heated PVA solution. As coagulating agent for the PVA, in which the resin is practically insoluble, there may be used aqueous salt solutions, such as an approximately 25 percent Na_2So_4 solution. The resin is generally used in such a concentration and amount that in this stage of the treatment the web contains about 10 to 20 percent by weight of the resin, calculated on the dry unfilled web.

In the succeeding acetalizing treatment a large proportion of the resin deposited in the web is extracted from the web. As a rule, the resulting web product will contain not more and usually less than 50 percent of the originally deposited amount of resin. As acetalizing agent it is preferred to use an acidified aqueous solution of formaldehyde at a temperature of at least 40° C.

The product obtained is subsequently finished in the usual manner. The use of a resin in accordance with the present invention, and more particularly a methylolmelamine resin composition, in the preparation of the present artificial wash-leather leads to a remarkable improvement of the shammying properties, more particularly with respect to the squeeze-handle and the surface-grip. Although there is as yet not certainty concerning the exact factors to which this favorable influence must be attributed, it is assumed that it is due to a combination of effects. Of influence may be the formalizing action of the resin, the formation of a resin deposit which may be chemically bonded or not, during which formation the fibers are probably slightly bonded locally, and the pore-forming action of the resin during the acetalizing treatment of the filled web.

It should be added that by the aforementioned PVA fibers are also meant continuous PVA filaments. Moreover, the starting web may contain a small amount of other natural and/or synthetic fibers. However, considering the specific pro-

perties of PVA, which are mainly responsible for the success of the method of the present invention and of the resulting wash-leather, the other fibers must as a rule be present in an amount not higher than about 5 percent by weight.

The process according to the present invention will be further described in the following examples.

EXAMPLE I

A PVA fiber web having a weight of about 120 g./m.² is needle-punched and subsequently immersed in water at 45° C. As a result, the surface area of the web shrinks by a factor of 1.4.

The shrunken web is squeezed and subsequently dried at 50° C., after which the web is immersed at room temperature in a solution of 1 part by weight Accobond 3900 (which is a product marketed by American Cyanamid Company) in two parts by weight of water. The web is squeezed to a liquid content of about 200 percent, and dried at 50° C. The dried web contains about 15 percent of the melamine-formaldehyde resin, calculated on the original web.

The web is then immersed in a 6.5 percent PVA solution in water at 20° C., squeezed to a liquid content of 650 percent, and subsequently introduced into a 20 percent sodium sulphate solution at 20° C. After an immersion time of 10 minutes, the filled web is slightly drained and subsequently immersed for 7 minutes at 50° C. in an acetalizing bath composed of a solution of formalin acidified with sulphuric acid and containing sodium sulphate. After this treatment the product is thoroughly washed and dried. The resulting web is then found still to contain about 2 to 2½ percent by weight of the melamine-formaldehyde resin, calculated on the product.

For the purpose of comparison, the above experiment is repeated but without employing the treatment with Accobond.

The two products thus obtained are found to display a good washing effect; but as regards the squeeze-handle and surface-grip the former, i.e., the "Accobond wash-leather," is distinctly superior. Moreover, the drying time of the latter product is shorter.

Expressed in relative merit ratings, the surface-grip (frictional resistance on glass under standard conditions) and the squeeze-handle (hand test) are, respectively, 28 and 6 for the Accobond wash-leather and 20 and 4.5 for the blank wash-leather.

EXAMPLE II

The needle-punched starting web of example I is immersed in the Accobond solution according to said example at room temperature, squeezed to a liquid content of 200 percent and dried at 50° C.

The web is subsequently immersed and shrunk in a 6.5 percent PVA solution at 27° C., and further processed as described in example I.

The Accobond treatment so influences the shrink behavior of the PVA fibers that even at 27° C. a surface shrink factor of 1.4 is obtained.

In order to obtain the same shrink factor for a blank wash-leather otherwise similarly prepared in accordance with this example (i.e., without the Accobond treatment) a PVA solution at 45° C. must be employed.

The surface-grip and squeeze-handle are, respectively, 26 and 6 for the Accobond wash-leather, and 17 and 4½ for the blank wash-leather.

EXAMPLE III

The needle-punched, shrunk, and dried PVA fiber web of example I is immersed at 20° C. in a 6.5 percent solution of PVA in water, in which also 10 percent by weight of Accobond 3900 is contained. The immersed web is subsequently squeezed and processed as described in example I.

As compared with the surface-grip and squeeze-handle of the blank wash-leather described in the latter part of example I, the values for the resulting wash-leather are 25 and 6, respectively.

What is claimed is:

1. In a process for the production of a sheet material having a shammying effect by shrinking a web comprising retractable fibers in an aqueous medium and then providing the sheet material with a polymeric filler, the improvement wherein
   a. a web which consists essentially of retractable polyvinyl alcohol fibers is caused to shrink and is treated with polyvinyl alcohol in an aqueous solution and a water-soluble resin composition of melamine and formaldehyde in an aqueous solution to provide from about 20 to about 60 percent by weight of polyvinyl alcohol and from about 10 to about 20 percent by weight of the water-soluble resin within the web, said weight percentages being based on the dry weight of the unfilled web;
   b. the web is subsequently contacted with a liquid which causes said polyvinyl alcohol to coagulate and in which the resin composition is practically insoluble;
   c. the filled web is subsequently subjected to an acetalizing treatment by which the coagulated polyvinyl alcohol is rendered insoluble in hot water and the water-soluble resin composition is at least partly removed from the web; and
   d. the thus treated web is washed and dried.

2. A process according to claim 1, wherein in the treatment under (a) the web is first treated with an aqueous solution of the resin composition at room temperature, subsequently dried, and finally impregnated with the polyvinyl alcohol solution.

3. A process according to claim 1, wherein the liquid referred to under (b) is an aqueous salt solution.

4. A process according to claim 1, wherein the acetalization referred to under (c) is carried out by treating the web with an acidified aqueous solution of formaldehyde at a temperature of at least 40° C.

5. A process according to claim 1, wherein the web is treated with an aqueous solution of the polyvinyl alcohol and the water-soluble resin at approximately room temperature.

6. A process of claim 1 wherein the water-soluble resin composition is removed during the acetalizing treatment to provide a filled web containing not more than about 50 percent by weight of the amount of resin initially deposited therein.

7. A sheet material having a shammying effect which comprises a fibrous mat consisting essentially of in situ retracted polyvinyl alcohol fibers, said mat containing a polymeric impregnant consisting essentially of from about 20 to 60 percent by weight of polyvinyl alcohol and not more than about 5 to 10 percent by weight of a water-soluble melamine formaldehyde resin, said weight percentages being based on the weight of the dry unfilled web, and said web having been subjected to an acetalizing treatment to render the polyvinyl alcohol impregnant insoluble in hot water.

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