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RESIN-IMPREGNATED LEATHER BOARD

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This invention relates to leather board of improved physical characteristics and to methods for its manufacture. A principal object is the provision of leather board of improved mechanical and tensile strength and wet-rub resistance, prepared by impregnating leather fibers with resinous materials followed by forming the impregnated leather fibers into a waterlaid product.

For many years it has been commercial practice to utilize scrap leather such as trimmings from shoe manufacture and also waste leather from worn-out leather products, etc. by shredding, grinding or otherwise converting it into leather fibers which are suspended in water and formed into a waterlaid or molded product, known as leather board. It has also been proposed to incorporate waxes such as paraffin wax, soaps, rosin and other organic materials into the leather fiber suspensions prior to the forming step in order to improve the water resistance of the leather board. The present invention provides an improved method of incorporating such organic materials into the leather fibers and also includes, among its more specific features, the incorporation of thermoplastic and thermosetting resins such as polystyrene, polyethylacrylate, phenol-formaldehyde resins and the like.

Our present invention is based on the discovery of an unusual type of flocculation and deposition that is brought about by the action of colloidal cationic melamine-aldehyde resins in an aqueous system containing leather fibers suspended therein together with an aqueous dispersion of water-insoluble coating or impregnating agents of the type referred to above. It has been found that in such a system the cationic melamine-aldehyde resin causes a controlled flocculation such that particles of the impregnating agent are uniformly coated upon or impregnated into the leather fibers. When dispersed or deflocculated water-insoluble impregnating or coating agents are applied in this manner the leather fibers retain their property of felting or forming into shaped or sheeted articles despite the presence of substantial quantities of the impregnating agent. Moreover, a high degree of retention of the flocculated material by the leather fibers is obtained, and losses of organic material in the white water system are largely avoided.

The process of our invention therefore comprises as an essential feature the flocculation of an aqueous dispersion of a water-insoluble organic impregnating agent in the presence of leather fibers suspended in an aqueous medium, this flocculation being brought about by the action of a cationic melamine-aldehyde condensation product such as cationic melamine-formaldehyde resin. The invention in its broader aspects includes any process wherein this flocculating action is used for the deposition or incorporation of an organic impregnating agent into leather fibers. One of its most important features is the discovery that the distinctive flocculating action of the cationic melamine-aldehyde resin continues, and is in many cases actually enhanced, after the cationic resin has been adsorbed on the leather fibers. The importance of this discovery resides in the fact that the cationic resin, being distributed uniformly over and through the leather fibers, causes a uniform deposition and retention of the impregnating agent on the leather fibers after it has been flocculated. The felting and sheet-forming properties of the fibers are therefore retained even though they may contain large quantities of the organic impregnating agent, and the aqueous fiber suspension, after the resin addition, can be formed into sheeted or molded products by conventional wet-molding or papermaking procedures.

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The flocculating agents which we employ in practicing our invention, and which are designated as "cationic melamine-aldehyde resins," are resinous materials containing melamine and carrying a positive electrical charge when in aqueous solution. These colloidal resin solutions may be prepared by dissolving ordinary melamine-aldehyde condensation products, such as methylol melamines, in acids such as hydrochloric acid to form acidified or "acid-type" resin solutions having a glass electrode pH valve within the range of about 0.5 to about 4 when measured at 15% solids, or pH values up to about 4.5 when measured in more dilute solutions, followed by aging to the colloidal condition, as described in U. S. Patent No. 2,345,543.

Any water-insoluble coating or impregnating agent may be applied by the process of our invention in amounts varying from a few per cent up to more than the weight of the leather fibers. By "coating or impregnating agent" we mean a material which will coat or impregnate the leather fibers and improve their value for their intended use in the production of leather board. Most of the coating or impregnating agents used in practicing the invention are organic amorphous or micro-crystalline materials of the type of waxes, gums, resins and the like such as micro-crystalline or amorphous petroleum waxes, bituminous materials such as tars and pitches, wood rosin or gum rosin, hydrogenated rosin, elastomers such as natural or synthetic latices, polymers, of butadiene, isoprene etc. and their copolymers with acrylonitrile; thermosetting resins such as alkylated or alcohol-reacted urea-formaldehyde resins, phenol-aldehyde resins, etc. and thermoplastic resins such as polyvinyl compounds, polystyrenes, polyacrylates, polymethacrylates, polyvinyl esters such as vinyl chloride and vinyl acetate polymers, coumarone and indene resins, esters of rosin with glycerine and other polyhydric alcohols and the like.

The leather fibers with which the above impregnating agents are incorporated may be obtained from any suitable source, and include leather tanned by any suitable procedure. Vegetable tanned leather, chrome tanned leather, alum tanned leather, as well as leather prepared by aldehyde tannages, aromatic sulfonic acid tannages, iron tannages and the like may be used, either singly or in admixture. The stock may consist entirely of leather fibers or may be a major proportion thereof, it may be admixed with other fibers such as various cellulosic fibers including kraft paper stock, rag stock, sulfate, ground wood or sulfite stock or other forms of fibrous cellulose such as hydrated cotton linters, jute, hemp, sisal, strings, chopped canvas, etc. Similarly, mineral fibers such as asbestos fibers or glass fibers may be incorporated if desired. This stock may be used as such, or it may be pretreated with rosin size, wax size or other common sizing agents and alum in the usual manner.

The organic impregnating agents such as those listed above, either singly or in admixture, are added to the aqueous stock suspension containing the leather fibers as a dispersion in water or aqueous liquid. Depending on the type of impregnating agent, the dispersions may require no added emulsifying or dispersing agents whatsoever, as in the case of natural latices. However, in many cases dispersions of finer particle size and better impregnating properties are obtained with the aid of dispersing agents, and many types of dispersing agents may be used. In general, any anionic or non-ionic dispersing agent may be employed in emulsifying or suspending the impregnating agents in water or other aqueous liquids, and in certain cases the cationic emulsifying agents may also be used. Typical anionic emulsifying agents that may be employed are the soaps of aliphatic and cycloaliphatic acids such as potassium oleate and potassium naphthenate, amine soaps such as triethylamine laurate, triethanolamine oleate and sulfated or sulfonated compounds such as sodium lauryl sulfate, sodium keryl benzene sulfonate, sodium isopropyl naphthalene sulfonate, esters of sulfocarboxylic acids such as sodium dioctylsulfosuccinate, sulfonated lignin and the like. Typical non-ionic emulsifying agents are polyhydric alcohol esters such as polyethylene glycol-substituted maleic acid esters, mannitan and sorbitan monoesters of palmitic, stearic or oleic acids or their ethylene oxide condensation products, and ethylene oxide condensation products of lauryl or tetradecyl or oleyl alcohols. Gums and proteins may also be used as emulsifying agents or as emulsion stabilizers such, for example, as gum arabic, soya bean protein, ammonium caseinate and the like.

The particular procedure whereby the impregnating agent is flocculated and coated on the leather fibers, or on mixed stock containing leather fibers, may vary somewhat with different impregnating agents but usually follows the same general plan. The leather is shredded or ground

or otherwise reduced to a finely divided, fibrous condition and may be washed and beaten in water if necessary to liberate undesired impurities and refine it to the condition necessary for treatment, and sizing agents may be added if desired. The stock is then suspended in sufficient water to dilute it to a consistency of about 0.5–6%, consistencies of 1–2% being preferred, after which the cationic melamine-aldehyde resin is added. This resin solution is preferably prepared from a melamine-formaldehyde resin containing about 2–4 mols of combined formaldehyde for each mol of melamine by dissolving it in about 0.8 mols of dilute hydrochloric acid for each mol of melamine and adding water at 60°–80° F. to make a resin solids content of 10–15%. This solution is allowed to age at ordinary temperatures for about 3–10 hours, preferably overnight, whereupon it is converted into a colloidal cationic melamine-formaldehyde resin solution. After adding the desired amount of this resin solution to the aqueous stock suspension the mixture is preferably allowed to stand for a period of time from about 15 minutes up to 3–4 hours or longer, after which an aqueous dispersion of the impregnating agent is added with agitation to insure a uniform mixture and the treated stock is run off on a papermaking machine or molded into the desired shape on a wet-molding machine. The amount of impregnating agent may vary from 1–2% up to 100% of the weight of the fibers, quantities of 15–40% being suitable for most purposes.

The amount of the colloidal cationic melamine-aldehyde resin solution to be used may also vary widely, since leather fibers will adsorb up to 50% of their weight of the cationic melamine resin. However, for most purposes it is unnecessary to use large amounts of this resin; experiments have shown that about 1–15%, based on the weight of the fibers to be impregnated (including the weight of the vegetable or mineral fibers if any) is sufficient for most practical purposes. These quantities of the cationic melamine resin will effect the flocculation and retention of much larger quantities of deflocculated organic impregnating agents, such as those outlined above, and will bring about a uniform deposition of these impregnating agents upon the fibers of the stock including particularly the leather fibers.

The reason for aging the stock suspension for 0.25–3 hours or longer after adding the colloidal melamine resin solution is to improve the drainage of the stock on the forming wire or screen. By allowing the suspension to stand for this period of time before adding the impregnating agent the drainage time of the treated stock is materially reduced, so that the forming or molding operation can be carried on at a higher rate. The drainage characteristics of the stock are also improved by the acid present in the colloidal melamine resin solution; experience has shown that when the stock is neutral or alkaline it is much slower in character than when it is acid, and for most purposes a pH of from slightly below 4.0 to about 5 will be found to give the best results.

Although a high degree of flocculation and retention of the added impregnating agent is obtained by the use of cationic melamine-aldehyde resins, as described above, it is sometimes advantageous to add an additional precipitating agent during the stock preparation. Thus, for example, small quantities of aluminum sulfate on the order of 0.5–3% may be added, as an assistant in controlling foam, sticking to the press rolls and other difficulties in sheet manufacture, or for purposes of pH control. The alum is almost always added after the other ingredients have been mixed, since it would tend to coagulate and precipitate the other materials if it were added first. The stock, after pretreatment with the cationic melamine resin and the impregnating agent, may also be given an after-treatment with sizes, pigments, coloring materials and the like if desired.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although these examples may describe in detail some of the more specific features of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

Leather fibers, obtained by shredding chrome tanned leather, were washed and suspended in water and diluted to a consistency of 1.5% and a colloidal cationic melamine-formaldehyde resin, prepared as previously described, was added in amounts equivalent to 5% of the melamine resin on the dry weight of the fiber. The pH of the suspension was adjusted to 3.6 and it was allowed to stand for 30 minutes after which a polystyrene emulsion was added with agitation in an amount sufficient to provide 40% of polystyrene resin, based on the dry weight of the leather fibers. This emulsion was prepared as follows:

A solution of 1.2 parts by weight of "Duponol C" in 58.8 parts of water was heated to 94° C. and 0.05 part of 40% hydrogen peroxide were added. To this solution 40 parts of styrene were introduced uniformly during 1.5 hours. The exothermic polymerization reaction proceeded smoothly and was complete after 3.5 hours. Steam was blown through the batch to remove unpolymerized material and the dispersion was adjusted to 25% solids. "Duponol C" is a higher alkyl sulfate (molecular weight 350) containing 10.8% Na_2SO_4 and 3.4% moisture.

The stock was made into board on a handsheet machine by diluting to 1% fiber consistency and drawing the suspension onto the papermaking wire with the aid of a vacuum. The sheets were pressed to remove excess water and then dried by heating in a laboratory oven at 100°–160° F. The white water from the sheetmaking wire was clear, showing that substantially all of the polystyrene had been flocculated and retained.

Example 2

A wax emulsion was prepared by adding 225 parts by weight of molten scale wax and 22 parts of oleic acid to 250 parts of hot water containing 2.6 parts of NaOH followed by heating for 15 minutes and homogenizing to a smooth emulsion of 1–2 microns particle size.

A portion of the leather fiber suspension of Example 1, having a consistency of 1%, was pretreated with 2% of the cationic melamine-formaldehyde resin, based on the dry weight of the leather fiber, allowed to stand 30 minutes, and sufficient of the above-described wax emulsion was added to incorporate 15% of wax, based on the weight of the leather fiber. The mixture was agitated until flocculation was complete and was then made into leather board by the procedure described in Example 1. The wax was impregnated uniformly throughout the leather board, which had a high degree of water resistance and improved flexibility and softness.

Example 3

A polyethylacrylate emulsion was prepared by heating a solution of 5 parts of sodium lauryl sulfate in 145 parts of water to 90° C., dissolving 25 parts of 30% hydrogen peroxide therein, and then adding 100 parts of ethylacrylate monomer slowly with continuous agitation. The mixture was maintained at 90° C. for one hour, after which time the polymerization was complete, and any small quantities of monomer that remained were removed by steam distillation. The emulsion was then adjusted to 25% resin solid.

Fibers of vegetable tanned scrap leather were suspended in water at 1.5% consistency and the suspension was divided into a number of portions. To three of these portions a colloidal cationic melamine-formaldehyde resin solution was added, the pH was adjusted to 4.0, and they were allowed to stand for 3 hours. To another portion 3% of alum was added. Amounts of the above polyethylacrylate emulsion were then added to two of the suspensions, one pretreated with melamine resin and the other with alum, and all the samples were made into leather board by the procedure described in Example 1 and dried at 130° F. The boards were tested for tensile strength, dimensional stability, water absorption, wet-rub resistance and tearing resistance, the results being given in the following table:

Sample No.	1	2	3	4	5
Melamine Resin, percent	0	0	3	3	10
Polyacrylate Resin, percent	0	30	30	0	0
Alum, percent	0	3	0	0	0
Basis Weight, lbs. (25×40–500)	159.8	204	215.5	186.7	201.5
Caliper (inches×1000)	19.4	18.1	19.1	20.4	20.0
Tensile Strength, lbs./inch:					
Dry	1.76	12.36	18.32	8.2	13.0
Wet	<0.4	4.6	8.2	1.6	3.4
Elongation, percent:					
Dry	2.1	19.6	17.6	1.8	2.0
Wet	5–8	31	33.5	3.0	3.2
Initial Tear, g	0	656	803	280	435
Elmendorf Tear, g	43.2	255.2	264	128	176
Wet Rub, Taber Cycles	2	79	130	6	88
Water Absorption, percent	126	72	54	108	90

A comparison of the tabulated results shows that the fiber pretreated with the cationic melamine-aldehyde resin and then with the polyacrylate emulsion produces leather board of greatly improved characteristics, as compared with the fiber pretreated with alum. The tensile strength of the melamine resin-pretreated board is greatly improved, as is also the wet-rub resistance and tearing resistance and the water absorption is considerably reduced.

Example 4

A 15% water suspension of the leather fiber described in Example 3 was treated with 3% of colloidal cationic melamine-formaldehyde resin and divided into several portions which were adjusted to varying degrees of acidity by the addition of hydrochloric acid or sodium hydroxide. The suspensions were then allowed to stand 3 hours, 30% of the polyethylacrylate emulsion of Example 3 was added, and the stock was made into leather board in a laboratory handsheet machine provided with a calibrated glass cylinder so that the rate of drainage through the wire could be measured. The drainage of stock adjusted to a pH of 3.2 was 13 seconds; that of stock having a pH of 4.0 was 45 seconds; when the pH was 4.9 the drainage time was 55 seconds, and at pH 6.1 it was 75 seconds. These figures emphasize the desirability of maintaining a low pH during the time when the stock suspension is allowed to stand before adding the impregnating agent.

What we claim is:

1. In a method of making leather board by the steps of preparing an aqueous suspension of fibrous sheet-forming material including a major proportion of leather fibers, impregnating the fibrous material with a water-insoluble hydrophobic organic impregnating agent and forming the impregnated fibrous material into a felted product, the improvement which consists in first adding to the aqueous fiber suspension 1–15% of melamine resin, based on the dry weight of said fibrous material, in the form of a colloidal solution of cationic hydrophilic melamine-formaldehyde resin, then aging the suspension for at least 30 minutes, then adding an aqueous dispersion of the water-insoluble hydrophobic organic impregnating agent in deflocculated condition and flocculating the impregnating agent in the presence of the suspended fibers by the action of the cationic melamine resin, and thereby depositing the impregnating agent uniformly on the fibers along with melamine-formaldehyde resin.

2. A method according to claim 1 in which the water-insoluble hydrophobic impregnating agent is a polyethylacrylate resin.

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