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MANUFACTURE OF ARTIFICIAL LEATHERS INTENDED FOR USE AS SHOE-SOLING, BELTING, AND ANALOGOUS PRODUCTS

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The subject of this invention is the manufacture of sheeted fibrous material in which the individual fibers are so arranged and bonded together as to simulate in many important respects, like body, pliancy, resilience, toughness, wear and water resistance, etc., the characteristics of tanned natural leathers of the type of tanned cowhide. An object of the present invention is the production of such leather-simulating sheet material from comparatively inexpensive, easily available raw materials, including short-fibered cellulose fibers of the character of chemical wood pulp and bonding materials of the nature of latex, glue, and the like.

One of the factors of great moment in the production of artificial leathers is the character of the fibrous base serving as the carrier for the bonding agents which impart thereto its leather-simulating qualities. In making comparatively thin artificial leathers designed for such uses as inner soles, shoe upper stock, automobile topping, furniture upholstery material, and the like, it is possible to start with a fibrous foundation prepared on machinery of the papermaking type. The fibers are supplied to the papermaking machine in the form of a dilute aqueous suspension, from which they are deposited in interfelted sheet form as a so-called waterlaid sheet. When short-fibered raw material like wood pulp is so formed into a waterlaid sheet, precaution must be taken to dewater and dry the sheet on the papermaking machine with the application of minimum pressure, in order to preserve sufficient porosity to permit imbibition of an adequate amount of the bonding agent, which imparts to the sheet its leather-like qualities. When a refined wood pulp is used in this connection, because of the inherent absorptivity of the fiber and its low shrinkage upon drying it is possible to arrive at a sufficiently porous and fluffy sheet satisfactory for use as an artificial leather base. The usual unrefined wood pulps of commerce, however, e. g., sulphite and kraft pulps, even when used in substantially unbeaten state and made into a web of interfelted fibers which undergoes little, if any, compacting during dewatering and drying, are incapable of producing a sheet of the desired low compactness and accompanying porosity for conversion into the best grades of artificial leather. This problem is aggravated when comparatively thick leathers suitable for such uses as shoe outer soles, belting, and the like, are desired. In such latter case, not only is one confronted by the preblem of securing a low compactness sheet, but also by that of making the sheet without laminations and sufficiently thick to meet the requirements of such usage. The fact is that, so far as I am aware, it has been impossible to make on machinery of papermaking type a sheet of the desired low compactness from unrefined wood pulps of the nature of sulphite and kraft, owing to the inherent tendency for such pulps to shrink markedly during dewatering and drying, even though practically no mechanical pressure be applied in the fabrication of the sheet. So, too, the fact is that machines of the papermaking type are not designed to produce economically low compactness sheets of the thickness required in leathers of the classification mentioned. If one were to endeavor to fabricate sheets by the wet or papermaking method of about 3/8 of an inch or so, the cost of drying such sheets would be prohibitively expensive if the water content were to be removed by the application of only suction and heat. Were one to press the sheet so as to extract all the easily removable water therefrom, the sheet would be altogether too dense for satisfactory leather manufacture and so, too, would tend to form separate laminae or layers. In my attempt to secure the product herein disclosed, I have resorted to all known expedients in the formation of a waterlaid web of the requisite thickness without the application of mechanical pressure, but I found that the shrinkage of the pulp and the surface tension of the water during drying inevitably gave rise to a structure altogether too dense and characterized by splitting tendencies on natural planes of cleavage.

In making artificial leather products in accordance with my invention, I can start with short, unrefined cellulose fibers, including sulphite and/or kraft pulps in dry condition, such as are available on the open market. The dry pulp, as in the form of so-called drier sheets, is then disintegrated into a loose, fluffy mass, as in a so-called hammer mill. The loose, fluffy mass is then placed in a hopper or feed device having a foraminous bottom or support, in which the mass is agitated so as to release individual fiber units which are sifted through the bottom while coarse aggregates or clumps of fiber and shives are retained. The fibers passing through the bottom as individual units are permitted to fall onto a traveling wire cloth carrier of sufficiently fine mesh, say, 60 to 80, to retain the fibers thereon. The rate of travel of the wire cloth is controlled so as to permit the building up of a uniform layer of fibers thereon of about three or more inches thickness. Because the fibers are deposited from suspension in air,

the layer is characterized by a random formation, by which I mean that there is no characteristic lay or direction of fibers in the layer of fibers. The layer proper is characterized by an exceedingly fluffy or spongy structure,—so much so that it has little strength and can be broken apart easily in any direction, without a clean fracture. The deposition of the fibers on the wire cloth may be promoted by the application of suction under that zone or stretch of cloth immediately below the bottom of the feed device. Starting with this fluffy layer of fibers, which has such poor tensile strength that it does not lend itself to impregnation on account of its tendency to fall apart in the presence of excess water into pulpous masses, I apply sufficient pressure to the sheet to reduce it to a compactness precisely in those regions which enable satisfactory handling of the sheet during impregnation with aqueous impregnants like rubber latex and aqueous glue solutions while arriving at a thickness value requisite in such ultimate products as shoe outer soles and belting. Assuming that wood pulp of the character of kraft is used as a raw material, a layer of fluffy fibers deposited from suspension in air to a height of about 3 inches is reduced by the application of heavy pressure to a thickness of about 5/8 inch, that is, to about one-fifth of the original height or thickness, at which reduced thickness not only does the sheet lend itself to handling and impregnation with aqueous impregnants while maintaining its integrity, but further has a compactness value about one-half, or even less, than that achieved when the best grade of refined wood pulp is deposited from aqueous suspension as a waterlaid sheet which has undergone no mechanical compacting whatever. Specifically, the compactness of a waterlaid sheet of this character will be in the region of about 28, whereas the condensed layer prepared in accordance with my invention has a compactness of only about 13. The compactness values herein given are obtained by dividing the basis weight by the thickness, and multiplying by the factor 10^{-2}. The expression "basis weight," as understood in papermaking circles, represents the weight in pounds of 480 sheets whose dimensions are 24 by 36 inches, this being equivalent to 2880 square feet of sheet material. In other words, the compactness value really represents the weight of fiber per unit volume of sheet material. It is to be observed that the compactness of the sheet produced in accordance with my invention is far less,—in fact, only about one-half that of the fluffiest sheet producible by a wet or papermaking method. Notwithstanding such low compactness, however, the sheet of my invention possesses sufficient strength to maintain its integrity during immersion in a bath of aqueous impregnating agent.

The condensed sheet prepared in accordance with my invention and having a thickness of about 5/8 of an inch, is impregnated with a bonding and reenforcing composition, preferably made up of rubber latex, glue, and formaldehyde or other tanning agent prepared in such a way as to avoid coagulation of the rubber and in such proportions as have been found to impart optimum leather-like qualities to the ultimate product. A specific example of procedure which may be adopted in preparing the impregnating composition in an instance where a sheet of kraft pulp serves as the foundation, may be substantially as follows. Twenty-six parts by weight of the usual ammonia-preserved latex of commerce having a solids content of about 33% is poured into a mixing vessel. To the batch of latex is then added 10 parts by weight of an aqueous solution of glue. The glue solution may be one which has been taken from a master batch prepared by soaking 2 parts by weight of so-called "broken glue" of commerce in 6 parts by weight of water for 24 hours, and then heating to ensure complete solution. The glue solution taken from a master batch so prepared is preferably cooled to about room temperature before being added to the latex in order to avoid local coagulation. The glue solution is thoroughly disseminated throughout the latex by slow stirring, whereupon about 1.4 parts by weight of 30% formaldehyde, diluted with 4 parts by weight of water, is commingled with the latex-glue mixture. The impregnating composition thus produced shows no sign of coagulation even after standing for considerable time. In this connection, it should be remarked that the sequence of mixing described is evidently of importance in maintaining the latex in substantially uncoagulated condition. For example, were the formaldehyde added to the latex directly, or added to the glue before its admixture with the latex, one would be apt to run into the trouble of coagulation. By initially adding the glue solution to the latex, coagulation is evidently circumvented, because the glue is a protective colloid and thus inhibits such coagulating effect as the formaldehyde might otherwise have upon the latex. One might avoid coagulation if the glue and formaldehyde were added as a mixture to the latex, but it is preferable initially to disseminate the glue as a protective colloid throughout the latex, so as to avoid local coagulation, which might otherwise ensue, especially were the glue initially set by the formaldehyde and thus rendered immiscible with the latex. In other words, upon long contact of the glue solution with the formaldehyde, there would be a decided tendency for the glue to become set or rendered insoluble in the latex by the action of the formaldehyde. Various ways of impregnating the condensed, air-laid web may be adopted, but a convenient procedure is merely to pour an excess of the impregnating composition uniformly over one face of the web until composition oozes from all surfaces. This procedure really corresponds to a dipping of the web in a bath of the impregnating solution and maintaining it immersed for a sufficient period of time to ensure complete permeation of the web. By the simple expedient of pouring the impregnating composition over one face of the web in excessive amount, however, such difficulties as a tendency to float the web on a bath of the impregnating composition are avoided. The permeated web can now be accurately adjusted in the ratio of absorbed solids to fiber to produce a product which, after drying, has the appropriate physical characteristics, including interstitial or void space, to permit "breathing" of the foot when the product is used as a shoe outer sole. This adjustment may be made by pressing the impregnated web to a thickness of about 1/2 inch, whereafter the pressed web may be dried. The pressed and dried web has an absorbed solids content approximately twice that of the weight of the dry fiber used as a raw material, approximately 72% of the absorbed solids being rubber and the rest being glue. The drying of the web may be effected as in a heated chamber, during which operation, as the water associated with the impregnant is removed therefrom, porosity is partially restored thereto, with little, if any, shrinkage. Immediate-

ly before complete drying of the impregnated web and setting of the impregnants to solid condition, the web may be subjected to a final pressing operation designed to reduce its thickness to that desired in shoe outer soles, say ⅜ of an inch, or less. The web is compressible at this stage substantially without recovery of original thickness and substantially without loss of absorbed solids, since they have already become fixed and bonded to the fibers. By carrying out a two-stage pressing operation, one immediately after soaking and one immediately before complete drying of the web, the absorbed solids in the web may be adjusted to the appropriate value and the web may be reduced to the desired thickness. It might be mentioned that the final pressing operation must be conducted under heavy pressures in the order of magnitude of about 30 tons per square foot, but there is no exudation of absorbed solids under these pressures. This demonstrates that there is sufficient void or interstitial space in the impregnated and previously pressed web, after substantially complete drying, to take up freely all the absorbed solids without any exudation whatever even under the heavy pressures necessary to effect the desired reduction in thickness. During the application of the impregnating composition and the initial pressing step, it is preferable to protect both faces of the web with an open-weave fabric, such as cheesecloth, as such fabric may be readily stripped from the web after these steps, without marring or otherwise injuring the facial portions on account of adhesion.

The finally pressed, impregnated web is then dried to completion and put through suitable finishing operations. Thus, it may be scoured on either or both faces, as by the use of emery wheels or sandpaper-covered rolls, until its faces are perfectly smooth, whereupon either or both faces may be coated with waxes, gums, varnishes, or other shoe sole finishes. The surface-finished product may then be cut into shoe sole blanks, which may be edge-finished with waxes, pigments, and the like. The finished product lends itself to machining like ordinary tanned cowhide, including skiving, splitting, stitching, pegging, cementing, etc. It can be used as an outer sole in the manufacture of so-called "turned" shoes. When used as an outer sole, its wear characteristics are like those of natural leather. Thus, upon prolonged wetting, it becomes more flexible, but still resists abrasion as does natural leather. It has excellent "breathing" qualities, as attested by the fact that it absorbs approximately the same quantity of water in the same period of time as tanned cowhide. Because there is no tendency to develop sliminess therein under the influence of water, it retains its gripping and frictional qualities when wet, as does high grade, tanned cowhide. It has phenomenally high resistance to abrasion, being equal to or even better than the best grade tanned natural leathers. This latter characteristic is traceable to the uniformity of its structure, as against the non-uniformity of structure of tanned natural leathers, which, as well known are characterized by a skin-side of greater density and toughness and resistance to abrasion than the flesh-side. All the characteristics hereinbefore noted may be attributed to the close approximation which my product has to natural leather. As is well known, natural leather, when observed under the microscope, shows up as a mass of tangled fibers having no observable formation. This mass of fibers is bound together by bonding agents of a colloidal, glutinous character. My product, too, is made up of a mass of fibers which, although of uniform texture throughout, has no definite fiber arrangement. The random fibers which make up my foundation are bonded together by materials possessing properties analogous to those present in natural leathers. In fact, the bonding composition which I employ includes tanned glue as one of its components; and this component is used together with rubber, which imparts to the ultimate product the desired pliancy, resiliency, and integrity which would be absent were tanned glue alone used as the impregnant. At a gage of about 10 irons or greater ($\frac{2}{10}$ inch thickness), my product has a resilience superior to that of ordinary sole leather, and is hence admirably adapted for making a shoe heel, which as regards wear is fully the equal of a leather heel, but as regards resilience is intermediate between a leather heel and one made from so-called live rubber. Preferably, one-ply heels are formed from my product, although one may build heels in accordance with standard practice from three or more plies of my product, each of approximately 10-irons gage, in which form, too, the heel is more resilient than one made of leather.

In making artificial leathers of the character hereinbefore described, it must be borne in mind that, aside from the necessity of depositing the wood pulp fibers as individual units from suspension in air or equivalent gaseous medium, the layer of fibers must be condensed to only a small fraction of its original depth before impregnation can be satisfactorily effected. In the specific example hereinbefore given, wherein kraft pulp was used as a raw material, the condensation of the layer was from about 3 inches to ¾ inch, as this yielded a foundation of the proper integrity and compactness to permit satisfactory impregnation and the ultimate securement of an artificial leather highly satisfactory for making shoe outer soles, belting, and analogous articles. This same ratio of reduction in thickness may be adopted in preparing foundations of a lower order of thickness, designed for use in making leathers of about 10-iron gage, and thus suitable for making multi-ply heels. Or the ratio may be somewhat departed from, depending upon the particular kind of wood pulp used as the starting material. In any event, however, the reduction of the original layer of pulp fibers is carried to a point where the web to be impregnated is only a small fraction of the depth of the freshly formed layer.

I claim:

1. A method which comprises depositing fibers of the nature of dry wood pulp as substantially individual fiber units from suspension in air into a layer of about 3 inches depth, condensing the layer into a web of a thickness of about ¾ inch, permeating the condensed web with an aqueous composition comprising latex, glue, and a tanning agent, squeezing the permeated web to a thickness of about ½ inch, drying the squeezed web almost to completion, pressing the almost dried web to a thickness of not greater than about ⅜ inch, and completing the drying operation.

2. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer, wherein the fibers exist in a loose, random, and unbonded state, condensing the layer to only a small fraction of its original thickness, permeating the condensed layer with

an aqueous composition comprising rubber latex and glue, squeezing the permeated layer to the desired absorbed solids content, and finally drying.

3. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer wherein the fibers exist in a loose, random, and unbonded state, condensing the layer to only a small fraction of its original thickness, permeating the condensed layer with an aqueous composition comprising latex, glue, and a tanning agent, squeezing the permeated layer to remove excess composition therefrom and further to reduce its thickness, drying the squeezed layer almost to completion, pressing the almost dried layer to the desired final thickness, and completing the drying operation.

4. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer, wherein the fibers exist in such a loose, random state that the layer is exceedingly fluffy and spongy and can be broken apart easily in any direction without a clean fracture, compacting the layer to only a small fraction of its original thickness, whereby it acquires sufficient tenacity to be impregnated in the presence of excess water without falling apart into pulpous masses, permeating the compacted layer with an aqueous composition comprising water-dispersed rubber, squeezing the permeated layer to the desired absorbed solids content, and finally drying.

5. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer, wherein the fibers exist in such a loose, random state that the layer is exceedingly fluffy and spongy and can be broken apart easily in any direction without a clean fracture, compacting the layer to only a small fraction of its original thickness, whereby it acquires sufficient tenacity to be impregnated in the presence of excess water without falling apart into pulpous masses, permeating the compacted layer with an aqueous composition comprising water-dispersed rubber, squeezing the permeated layer to remove excess composition therefrom and further to reduce its thickness, drying the squeezed layer almost to completion, pressing the almost-dried layer to the desired final thickness, and completing the drying operation.

6. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer, wherein the fibers exist in such a loose, random state that the layer is exceedingly fluffy and spongy and can be broken apart easily in any direction without a clean fracture, compacting the layer to downwards of about one-fifth of its original thickness, whereby it acquires sufficient tenacity to be impregnated in the presence of excess water without falling apart into pulpous masses, permeating the compacted layer with an aqueous composition comprising water-dispersed rubber, squeezing the permeated layer to the desired absorbed solids content, and finally drying.

7. A method which comprises depositing fibers of the nature of wood pulp as substantially individual, dry fiber units from suspension in air into a thick layer, wherein the fibers exist in such a loose, random state that the layer is exceedingly fluffy and spongy and can be broken apart easily in any direction without a clean fracture, compacting the layer to only about one-fifth of its original thickness, whereby it acquires sufficient tenacity to be impregnated in the presence of excess water without falling apart into pulpous masses, permeating the compacted layer with an aqueous composition comprising water-dispersed rubber, squeezing the permeated layer to remove excess composition therefrom and further to reduce its thickness, drying the squeezed layer almost to completion, pressing the almost-dried layer to the desired final thickness, and completing the drying operation.

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