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TREATMENT OF COLLAGEN FIBER SHEET

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8 Claims

ABSTRACT OF THE DISCLOSURE

Penetration of treating liquids into an intermeshed fiber sheet with swollen collagen fibers held in the interstitial spaces is improved by subjecting the sheet of intermeshed fibers to a light rolling pressure while still wet from penetration by an aqueous suspension of the collagen fibers and still at a pH outside the isoelectric range of the collagen fibers.

This invention relates to improvements in the manufacture of leather-like sheet material.

In the U.S. patent of Shu-Tung Tu No. 3,223,551 issued Dec. 14, 1965, there is described the manufacture of a strong leather-like material in which an aqueous suspension of swollen distinct collagen fibers of microscopic size is caused to penetrate a sheet of intermeshed fibers to carry the collagen fibers into the interstitial spaces of the intermeshed fiber sheet. Penetration is effected with a suspension having a pH outside the isoelectric range of the collagen fibers to maintain said fibers in swollen condition and thereafter the sheet is treated to remove the swelling water from the collagen fibers to reaggregate them into a larger collagen fiber structure within the interstitial spaces in the sheet of intermeshed fibers to reinforce the intermeshed fibers against displacement. Removal of the swelling water is effected by treating the intermeshed fiber mass with collagen fibers therein with a liquid agent which may be, for example, acetone or an aqueous solution effective to bring the pH of the sheet to a value within the isoelectric range of the collagen fibers, or by treatment with a collagen precipitating agent such as an aqueous ammonium sulfate solution, or finally by treatment of the sheet material with an aqueous solution of a tanning agent which has a collagen deswelling action and effects both reaggregation and tanning.

Excellent leather-like sheet materials have been obtained following the teachings of the patent; but undesirably long times of treatment have been involved in the treatment of the fiber sheet containing wet swollen collagen fibers with liquid treating agents to effect reaggregation and tanning. Efforts to speed up the process through using more active agents have introduced difficulties such as a condition comparable to case hardening (as the term is used in the leather industry) in which the surface might be excessively tanned while the interior was insufficiently or not at all tanned due to the blocking action of the tanned upper layers.

It is an object of the present invention to provide a process for making leather-like sheet material in which the time required for liquid treatment to effect reaggregation or tanning to form the reinforcing internal collagen fiber structure is reduced and a more uniform product is produced.

To these ends and in accordance with a feature of the present invention, swollen, distinct, fine collagen fibers are deposited from aqueous suspension in the interstitial spaces of an intermeshed fiber mass, the sheet is subjected to a controlled mechanical treatment effective to alter the character of the sheet to allow rapid penetration of liquid treating agents and is then treated with liquid agents such as reaggregating and tanning liquids.

In the present process an aqueous suspension of swollen collagen fibers of microscopic size is caused to penetrate a sheet of intermeshed fibers. The swollen collagen fibers are caught in the sheet and fill the spaces between the intermeshed fibers. At this stage the wet sheet is subjected to light rolling pressure and thereafter is treated with liquid agents to deswell the collagen fibers to reaggregate them into a larger collagen fiber structure and to tan the collagen and to introduce desired conditioning agents. Surprisingly, although the appearance of the sheet is substantially unaltered by the pressure treatment step, the liquid treating agents penetrate the sheet more uniformly and more easily and rapidly than without the step.

The microscopic collagen fiber suspension used in the present process may be any of the suspensions described in the Tu patent above referred to. As there described collagen material, for example, skin or hide is beaten in water under conditions which limit swelling of the collagen to reduce the collagen to distinct non-colloidal microscopic fibers and form an aqueous suspension in which these fibers are capable of relatively free movement in the aqueous medium in which they are formed. The skin material may be lightly tanned before separation into fibers, for example, the tanning may be carried to an extent comparable to 1/10% to preferably not over 3% of combined aldehyde such as formaldehyde, glutaraldehyde, or glyoxal based on the dried weight of the skin material. The fibers in the suspension thus formed may have a length of from about 0.01 mm. to not over about 4.0 mm. and preferably not over 1 mm. in length.

The suspension is adjusted to control the swelling of the suspended collagen fibers. The term "swelling" in the special sense here intended refers to the phenomenon that the surfaces of the fibers become slippery and the fibers increased in thickness and decrease in length but remain as distinct fibers. As in the above-referred-to patent the extent to which the collagen fibers in suspension are brought to a condition for effective penetration into an intermeshed fiber mat varies with the formaldehyde content and with the pH. With a given collagen fiber, penetration ability will increase from a minimum adjacent the isoelectric range along a curve which peaks about pH 2.0 on the acid side and at about pH 11.5 on the alkaline side of the isoelectric range and falls off on either side of the peaks.

The extent of tanning of the hide material as with formaldehyde is an important factor in the bringing of the collagen microscopic fiber suspension into the desired state for effective penetration and ability to carry the fiber into a mat and retention of the dispersed fibers within the mat. Penetration ability decreases and retention of the fiber increases with increase in the extent of tanning. It is generally desirable to use collagen fiber tanned to an extent corresponding to about 0.2% to about 1.1% formaldehyde by weight based on the weight of the collagen fiber. The preferred formaldehyde content range is from about 0.3 to about 0.6% by weight based on the weight of the hide material.

A wide variety of intermeshed fiber materials both woven and nonwoven may be used for association with the collagen fiber suspensions. Ordinarily nonwoven fiber materials are preferred because of the greater variety obtainable in thicknesses, densities and openness to penetration by the suspensions. The fibers of the mat are relatively long being of the order of one inch and larger and may be nylon, polyacrylic ester fibers (Orlon), polyester fibers (Dacron), polypropylene fibers, wool, extruded cellulosic fibers such as viscose or cellulose acetate and others. Also natural cotton fiber preferably treated to decrease its affinity for water is usable.

Since an important aspect of the present invention is the manufacture of leather-like products, the intermeshed

fiber materials are preferably in the form of relatively thin mats in which the fibers are in a relation providing relatively large interstitial spaces. The fiber mats preferably, although not necessarily, have been subjected to a treatment as with barbed needles to improve the intermeshing of the fibers.

A fiber density and relation which have been found satisfactory are those in nylon fiber mats having densities of the order of 4 oz. per sq. yd. at a thickness of 0.15 inch and 6 oz. per sq. yd. at a thickness of 0.175 inch. It is preferred that the fibers be relatively fine and fall in the range of from 1 to 5 denier with 3 denier being satisfactory. Other highly satisfactory materials are a 3 denier polypropylene fiber mat having a fiber density of 7 oz. per sq. yd. and a thickness of 0.2 inch and a 3 denier polypropylene fiber mat having a fiber density of 2.5 oz. per sq. yd. and a thickness of 0.125 inch.

Penetration of the suspension of textile fibers and swollen collagen microscopic fibers into an intermeshed fiber mass may be effected in a variety of ways. Thus the fiber mat may be disposed on a screen and the suspension forced in with the aid of pressure or suction. Suspensions having a collagen fiber solids content of, for example, from about 0.5% to about 5% by weight solids may be used in this procedure. Still other procedures are available including spreading the suspension on the surface of the mat and working it in. The quantity of suspension to be applied to a given area of mat is selected to provide a retained collagen fiber content in the mat of from about 5% to about 90% by weight and preferably from about 30% to about 50% by weight based on the combined weight of the fibers of the mat and the collagen fibers.

The wet mat with collagen fibers in the spaces between the intermeshed mat fibers is then given a light rolling pressure treatment while the collagen fibers are still in swollen condition. The desired result is not obtained if the mat has been dried before this step. Rolling pressure ordinarily is applied by passing the mat between driven rolls spaced apart only very slightly as, for example, from 5% to 15% less than the wet thickness of the mat containing the wet collagen fibers.

After this rolling pressure step the mat is impregnated with liquid agents to effect deswelling and reaggregation of the collagen fibers to form a reinforcing collagen fiber structure within the mat. Impregnation may be achieved by any convenient procedure such as simple immersion or vacuum- or pressure-assisted impregnation. It has been found that penetration of the mat is much more rapid and complete than is obtainable without the rolling pressure step.

It is believed that the greater ease and speed of penetration is due to the creation of very fine passageways in and through the mat by the action of the rolling pressure. That is, at the stage of the process where the intermeshed fiber mat has been filled with collagen fibers, the collagen fibers are swollen and packed together to fill substantially all spaces between the intermeshed fibers of the mat. This mass of swollen collagen fibers appears to constitute a complex continuous gel-like structure which interferes with movement of liquid through the mat. This complex gel-like structure is the result of the close association of the hydrated surfaces of the swollen collagen fibers which act with the surfaces of adjacent collagen fibers to lock in separate small bodies of water from the suspension which carried the collagen fibers into the intermeshed fiber mass. It is believed that the structure is comparable to a micellar structure such as exists in some hydro-gels. Additionally each of the collagen fibers making up the mass has taken up a substantial quantity of water to swell it and hydrate its surface.

The rolling pressure causes pressure changes within the sheet and produces localized and limited working or movement of the swollen collagen fibers laterally within the mat to accommodate the reduction in cross section produced by the advancing line of pressure.

It is believed that the slight and temporary increase in pressure and slight working produces a limited rupturing of the micelles which lock small bodies of water within the mat. Also the pressure may cause limited giving up of water by the swollen structure of the individual swollen collagen fibers with release of this swelling water at the surface of the fibers. The small proportion of water released is expressed from the mat at the nip of the roll. When the mat has passed the rolls, recovery of the mat to its original wet thickness leaves very fine passageways between the packed collagen fibers. These passageways may be due to rupture of the walls of micelles and resulting rearrangement of fibers or may be due to a reduction in size of the collagen fibers themselves due to loss of water or to a combination of these factors.

The above discussion of the manner in which rolling pressure improves the ease and completeness of penetration of the mat by treating liquids has been presented to aid in understanding the invention. It is to be understood that the process including this pressure step presents marked advantages and that patentability of the process is not dependent upon the accuracy or correctness of the explanation advanced.

The effectiveness of the pressure treatment can be increased still further by applying an astringent liquid to the surface of the intermeshed fiber mat filled with swollen collagen fibers. Ordinarily this involves supplying an aqueous solution of a salt such as sodium chloride or sodium sulfate to the surface of the filled fiber mat prior to pressure treatment. For example, the filled fiber mat may be immersed in a 5 to 25% solids aqueous solution of the salt for a period of at least about 30 seconds.

This brief treatment makes the surface of the filled mat less slippery so that it is easier to handle and so that presser rolls can feed the mat more rapidly and uniformly and with less slipping. In addition to the increased ease of handling, it appears also that the mat after passing through the rolls is penetrated by treating liquid still more evenly and rapidly than where pressure treatment alone without the preliminary astringent treatment is used.

It is believed that the astringent treatment causes a limited deswelling of the collagen fibers at the surface of the mat. Also the surface of the mat will retain some of the astringent agent, e.g. salt solution so that in subsequent treatment of the mat, the press rollers may distribute this astringent material into the mat to act on the internal structure. It should be understood, however, that the surface action and any internal action at this stage is not a substitute for the deswelling and reaggregation of the collagen fibers in the mat into a larger collagen fiber structure reinforcing the intermeshed fibers of the mat. Rather this astringent treatment is a preparatory step to improve still further the action of the pressure step to enable more rapid, more even and more complete penetration of the treating agents which will effect the re-aggregation, tanning and other action.

Reduction of the acid or alkali content of the collagen microscopic fiber material within a fiber mass and removal from the fibers of the water of swelling may be effected by subjecting the fibrous mass to extraction with distilled water or a water miscible volatile organic solvent such as acetone and other ketones, and lower alcohols such as methanol, ethanol and isopropanol to bring the pH to the isoelectric range. Treatment of the fiber mat with an aqueous solution of a buffer salt such as an acetate or phosphate buffer system is also effective to bring the pH to a value in the range of about 3.5 to about 6 at which reaggregation of the collagen microscopic fibers will occur with removal of the swelling water from the fibers. It is desirable in the use of buffer systems to use a solution having an ionic strength of about 0.2.

Reaggregation may also be effected by treating the fiber mat with a collagen precipitating agent in an aqueous vehicle. Thus, solutions of ammonium sulfate and other salts known to precipitate collagen may be applied

to the mat containing swollen collagen fibers to deswell the collagen fibers and form a collagen fiber structure reinforcing the intermeshed fibers of the mat. In a preferred form of the process, the collagen deswelling action of tanning agents is used to effect reaggregation of the swollen collagen fibers and operates to tan the collagen fibers in the same treatment. In this form of the process, the wet sheet material after having been subjected to rolling pressure as described above is treated with leather tanning agents including mineral tanning agents such as the chrome tanning liquors or vegetable tanning agents. Conventional leather tanning procedures may be used to effect the contact; but simple immersion of the wet sheet material in the tanning medium is effective because of the improved penetrability of the sheet material after the rolling pressure treatment.

The sheet material after deswelling of the collagen fibers by any of the procedures noted above is firm and has a high degree of porosity. At this stage the sheet may be impregnated with binders, softening agents, fat liquors, liquid solutions of dyes and pigments and the like. Aqueous suspensions or latices of synthetic polymers, i.e. rubbers or resins which after impregnation into the sheet and precipitation may provide both a binding and flexibilizing action. The improved penetration characteristics imparted by the rolling pressure treatment has been found to allow improved penetration of these materials. Moreover, a similar rolling pressure treatment after impregnation has been found to improve the uniformity of distribution of the liquid material.

Finally the sheet may be provided with any desired surface finish such as a conventional leather finish or a resin finish layer.

The following examples are given to aid in understanding of the invention and it is to be understood that the invention is not restricted to the particular materials, proportions or procedures set forth therein.

EXAMPLE I

A 2% solids aqueous suspension of collagen fibers was prepared by the procedure shown in the patent to Tu 3,223,551 above referred to. The procedure involved light formaldehyde tanning of limed hide and reduction of the hide material to a suspension of microscopic size fibers by beating in water. The fibers had a formaldehyde content of 0.2% by weight based on the weight of the collagen fibers and the suspension was adjusted to a pH of about 3.9.

A sheet of nonwoven intermeshed fiber mat of 1½ denier polypropylene having a weight of 4½ oz. per sq. yd. and a dry thickness of 0.055 inch was disposed on a filter bed with means for applying suction.

The suspension of collagen fibers was deposited on the fiber mat and suction to a value of about 6 inches of mercury was applied to the mat to fill the mat with collagen fibers from the suspension. On a dry basis, the ratio by weight of collagen fibers to mat fibers was 1:0.96. The mat with collagen fibers therein had a wet thickness of 0.060 inch.

The wet mat was then passed between 4 inch rolls spaced 0.055 inch at the nip of the rolls. The rolls were driven to provide a mat speed of 6 feet per minute.

A small amount of liquid collected before the nip of the rolls and was removed. Analysis of this liquid showed substantially no collagen content.

The wet sheet from the rolling step was then dipped in a chromium tanning solution in which it was allowed to stand for two minutes and then removed. The tanning solution was a standard buffered chromium tanning liquor containing 0.25% by weight chromium calculated as Cr₂O₃ and ½% by weight of sodium formate and having a pH of 4. It was observed that the tanning solution penetrated the sheet through and through directly upon immersion of the sheet into the tanning liquor. On removal from the tanning solution, the sheet was passed through rolls spaced as before, washed with water for 5

minutes then passed through the rolls, washed for a further 5 minutes in water and again passed through the rolls.

At this point the sheet was given a vegetable retan involving disposing the sheet on a filter bed provided with means for applying suction and supplying a vegetable tanning solution to the exposed surface while applying suction to the other surface. It was found that rapid penetration of the tanning solution was secured with use of only a 2 inch mercury vacuum.

The vegetable tanning solution was a 12.5% solids solution of equal parts of quebracho, wattle and a commercial synthetic tanning agent (Orotan TU) and had a pH of about 3.5.

After the vegetable tanning solution had been drawn through the sheet, weak aqueous ammonia solution was applied and drawn through the sheet to bring the pH of the sheet to a value between 7 and 9. A polymeric plasticizer and binder composition was then applied to the surface of the sheet and drawn through with the assistance of suction. The composition used was a 24.3% solids dispersion comprising butadiene acrylonitrile copolymer synthetic rubber latex (Hycar 1561) and a melamine aldehyde resin (Arotex M3) in the ratio by weight of 10:1. A heat sensitizing salt was included and after impregnation of the sheet, the sheet was subjected to heating in air for 7 minutes at 110° C. to set the latex in the sheet.

The sheet was then dried with circulation of air and after drying the sheet was subjected to a light buffing operation with fine sandpaper on both sides to form a dried sheet having properties similar to a chrome tan, vegetable retan leather. A cut section of this sheet had substantially uniform color through its thickness showing uniform penetration of the tanning and other agents. The sheet at this point was ready for application of a leather finish.

EXAMPLE II

The procedure for impregnation of an intermeshed fiber sheet with collagen fiber suspension was carried out as in Example I; but the sheet was not passed between the spaced rolls. The wet sheet was immersed in the same chrome tanning liquor for 2 minutes, withdrawn and washed and then disposed on a filter bed with means for applying suction and the vegetable tanning solution of Example I was applied to its surface. It was found that 12 inches of vacuum were required to draw the vegetable tanning solution into the sheet. After washing the sheet with weak ammonia as in Example I, the sheet was again disposed on the filter bed and the latex composition applied to its surface. It was found that the latex could not be drawn into the sheet.

After heating and drying of the sheet, it was found that the sheet was much stiffer and boardier than the sheet contained in Example I and the surface of the sheet was not as smooth nor as tightly knit as the product of Example I. The sheet was cut and it was found that there was a zone of lighter color in the center portion indicating that the chrome tanning had not successfully penetrated the central portions of the sheet.

EXAMPLE III

The procedure for impregnation of an intermeshed fiber sheet of collagen fiber suspension was carried out as in Example I but the wet sheet containing the collagen fibers was immersed in a 20% solids aqueous solution of sodium chloride and left in the solution for about one minute before the initial step of being passed to the spaced rolls. On removal from the salt solution, the surface of the mat was found to be less slippery than before dipping in this solution but the appearance of the mat was otherwise unchanged. The wet mat was then passed between spaced rolls as in Example I and treated with the chromium tanning solution, vegetable tanning solutions and polymeric plasticizer and binder compositions followed by heating and drying following the procedure of Example I.

The sheet obtained had properties similar to chrome tanned, vegetable retan leather and had a somewhat better hand than the product of Example I. A cut section of the sheet had substantially uniform color throughout its thickness indicating that uniform penetration of the tanning and other agents had been secured.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. In the process of forming a tough, flexible, porous sheet material including the steps of applying to an intermeshed fiber sheet in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct, fine collagen fibers of microscopic size to carry said collagen fibers into the interstitial spaces of said enmeshed fiber mass, said collagen fibers constituting from about 5% to about 90% by weight of the combined weight of said intermeshed fiber mass and collagen fibers, said suspension having a pH outside the isoelectric range of the collagen fibers, and while said fibers are still in wet condition with said fibers still swollen, impregnating said sheet with a liquid treating agent for removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure within the interstitial spaces in said sheet of intermeshed fibers to reinforce the intermeshed fibers against displacement, the improvement which comprises subjecting the wet sheet of intermeshed fibers after the swollen collagen fibers have been carried into the interstitial spaces to light rolling pressure to reduce, momentarily, the thickness of said sheet from about 5% to about 15% below the original wet thickness of said sheet before reaggregation and while still wet from penetration by the aqueous suspension and still at a pH outside the isoelectric range of the collagen fibers.

2. The process as defined in claim 1 for forming a leather-like sheet material in which said liquid treating agent is a leather tanning agent and both removes swelling water from said collagen fibers to reaggregate them into a large collagen fiber structure and tans said collagen fibers.

3. The process of forming a tough, flexible, porous sheet material as defined in claim 1 in which the surface of said wet sheet with swollen collagen fibers therein is contacted with an astringent aqueous solution of a salt for at least about 30 seconds prior to subjecting said sheet to said rolling pressure.

4. The process of forming a tough, flexible, porous sheet material as defined in claim 1 in which said sheet after reaggregation of said collagen fiber is impregnated with a further liquid material and subjected to light rolling pressure.

5. The process of forming a leather-like sheet material as defined in claim 2 in which said tanning agent is a mineral tanning agent.

6. The process as defined in claim 2 for forming a leather-like sheet material in which said sheet after re-aggregation and tanning of said collagen fiber is impregnated with an aqueous suspension of a synthetic polymer, subjected to light rolling pressure and treated to precipitate the polymer in binding relation to the fibers of said sheet.

7. The process of forming a tough, flexible, porous sheet material as defined in claim 3 in which said liquid treating agent is an agent for removing swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure.

8. The process as defined in claim 7 for forming a leather-like sheet material in which said liquid treating agent is a leather tanning agent and both removes swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure and tans said collagen fiber structure.

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