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3,362,849

MANUFACTURE OF STRONG FIBROUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

An aqueous collagen fiber dispersion is caused to penetrate rapidly and uniformly throughout the whole thickness of an intermeshed fiber mat by bonding the fibers of the mat at their points of contact either by a separately introduced binder or by a solvent or heat treatment which causes self-bonding of the fibers at their points of contact prior to treatment of the mat with the collagen fiber suspension. The collagen fiber is then caused to reaggregate into a larger collagen fiber structure reinforcing the intermeshed fibers of the mat against displacement.

This invention relates to an improvement in the manufacture of strong fibrous material.

In the application of Shu-Tung Tu Ser. No. 256,225, entitled, "Leather-Like Material and Method of Making the Same," now U.S. Patent 3,223,551 of Dec. 14, 1965, which was filed Feb. 5, 1963, as a continuation-in-part of an application with the same title Ser. No. 170,225 filed Jan. 31, 1962, now abandoned. There is disclosed a process for associating undissolved collagen with a mass of intermeshed fibers as a fiber structure extending through the mass in a relation in which the collagen fiber structure resists major displacement of the intermeshed fibers. In that process lightly tanned collagen is suspended in an aqueous medium as distinct slightly swollen fibers of microscopic size and this suspension is caused to penetrate and fill the open spaces in intermeshed fibrous masses, particularly nonwoven fiber masses. Thereafter by altering the conditions within the sheet the fibers are deswelled and associated with each other as a larger collagen fiber structure associated with the intermeshed fibers.

It has been found that, particularly where the intermeshed fiber mass or sheet has hydrophilic characteristics the content of collagen fiber in finished sheets may not be as uniform as is desired.

It is an object of the present invention to provide a method for making strong fibrous sheet materials of the type disclosed in which the collagen fiber content is distributed more uniformly.

To this end and in accordance with a feature of the present invention, the intermeshed fiber sheet material is treated before association with collagen fiber suspension to improve its ability to take up collagen fibers from the suspension evenly and effectively by controlled bonding of adjacent fibers in the intermeshed fiber sheet. The collagen fiber suspension is adjusted for cooperation with the treated fiber sheet to provide an improved system in which the swollen collagen fiber is taken up more rapidly and retained effectively to form a product with a high uniform collagen fiber content. The fiber sheet containing collagen fibers is then treated to deswell the collagen fibers to form a larger collagen fiber structure associated with the fiber sheet.

The method of the present invention is of particular advantage in the manufacture of leather-like sheet materials based on sheets of intermeshed fiber materials. Although woven sheets may be used, the advantages of the present invention are of more particular value with

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nonwoven fiber sheets. A wide variety of fibers in intermeshed sheet form may be used. Thus, sheets of fibers of nylon, polyacrylic esters (Orlon), polyesters (Dacron), polypropylene, wool, extruded cellulosic fibers such as viscose or cellulose acetate and others are useful. It has also been found possible to use a sheet of collagen fibrous material of greater fiber length than the fiber of the suspension where the fiber has been treated, for example by a chrome tanning or other treatment to decrease its affinity for water. Likewise, natural cotton fiber, preferably treated to decrease its affinity for water is also usable. These fiber materials are preferably used in the form of relatively thin mats in which the fibers are in a relation providing relatively large interstitial spaces. The nonwoven fiber mats may or may not have been subjected to a treatment as with barbed needles to improve the intermeshing of the fibers. The action of the present process is particularly important where the mats have not been needled. A fiber density of from about 1 to about 5 pounds per cubic foot may be used. Nylon fiber mats having densities of the order of 4 oz. per square yd. and a thickness of 0.15" and 6 oz. per sq. yd. at a thickness of 0.175" have been found useful. Another highly satisfactory material is a polypropylene fiber mat having a density of 7 oz. per sq. yd. and a thickness of 0.5". It is preferred that the fibers be relatively fine, suitably within the range of from 0.5–5 denier.

In these mats, as formed, the fibers are capable of movement relative to other fibers. Particularly, with fibers which are to some extent hydrophilic such as nylon fibers, extruded cellulosic fibers such as viscose or cellulose acetate, and wool fibers, the action of the water of the aqueous suspension of collagen fibers may have a softening effect which results in undesired and irregular compaction of the mats under the forces exerted in impregnating the mats with the collagen fiber suspension.

The mechanism of fiber entrapment in an intermeshed fiber sheet has many facets. The interfiber spaces in the sheet must be sufficiently large to permit entry of fibers and on the other hand there must be an ability in the fiber sheet to take up and to hold fibers from the suspension. It appears that there must be at least limited freedom of movement of the fibers of the sheet for effective penetration and effective cooperation between the fibers of the sheet and the fibers of the suspension. That is, with a sheet in which the intermeshed fibers are rigidly fixed it is possible to screen out almost all collagen fibers at the surface of the fiber sheet if the spacing of the intermeshed fibers is close or alternatively almost all of the collagen fibers of the suspension may pass through the sheet if the intermeshed fibers are fixed at a wide spacing. On the other hand with a completely free fiber sheet, small irregularities in fiber spacing tend to produce disproportionately large irregularities at the take up of collagen fibers by the sheet. That is, a portion of closer fiber spacing will entrap collagen fibers more rapidly to make it still less open so that pressure used to introduce the collagen fiber suspension into the sheet will exert a greater effect on that portion to compact it and reduce its openness still more.

Desired retention of openness of the intermeshed fiber sheets is maintained by treating the intermeshed fiber mat to bond fibers of the mat to the fibers of the mat at points of contact or adjacency leaving portions of the fibers intermediate the bonds free for fibrous movement. This may be done by chemical, solvent or thermal softening of the fiber to cause fusion or welding together of fibers at points of contact, or by treatment with a controlled amount of selected binder material. Fusion or welding may be effected by known procedures involving treatment of the mat with a solvent in limited amount, e.g., solvent

vapors or of limited solvent ability for the mat fibers to soften the fibers to bond contacting portions of fibers without destroying the fibrous character. Similar action may be obtained by controlled heating. In these procedures more readily softenable fibers may be included in the mat along with less readily softenable fiber or simplify temperature control.

Binder may be used to bond fibers of an intermeshed fiber mat at their points of adjacency; but it must be restricted in amount such that it does not interfere with the openings between the intermeshed fibers. Also the binder must be sufficiently small in amount and so disposed in the final sheet as not to interfere markedly with fibrous movement as distinguished from fibrous displacement of the intermeshed fibers in the final sheet. This is important for effective collagen fiber take up as discussed above and is also important in order to give the desired hand and conformability characteristics in the finished sheet and to allow such fiber movement as will enable distribution of stress. That is, if the fibers are not capable of limited movement in the final sheet the tear strength of the sheet material becomes undesirably low.

Intermeshed fiber sheet material may be treated to provide the desired small amount of binder localized at points of adjacency of fibers by treatment of the mats or sheets with solutions or suspensions of binder material under conditions of dilution or by special application procedures which will avoid filling up the openings or too rigidly holding the fibers.

The binders may be natural or synthetic resins or rubbers or mixtures of these, and may be thermoplastic, or thermosetting or curing type.

Binder compositions which have been found suitable include polyesters and copolyesters, resinous condensates of a phenol with an aldehyde, resinous condensates of an amine with an aldehyde, polyacrylic esters, polyamides, dienepolymers and copolymers such as polychloroprene, butadiene-acrylonitrile copolymer and butadiene-styrene copolymers, and polyurethanes or polyureas. Where these materials are compatible they may be used in admixture with each other. These materials may be applied as solutions or dispersions in liquid vehicles or as fine solid particles and are used in amount to provide from 1% to 15%, preferably from about 2% to 5% by weight of solids based on the weight of the fibers of the intermeshed fiber sheet. After impregnation of the fiber sheet with the solution or dispersion, the sheet is treated to remove the vehicle, for example by drying or volatile liquids or with a coagulating agent and physical separation of the liquid vehicle and to deposit the stabilizing agent or binder in the sheet in a relation holding the intermeshed fibers against major displacement but not in so rigid a relation as to prevent limited movement permitting distribution of stress applied to the sheet.

In addition to the strictly mechanical action of keeping open the interfiber spaces of an intermeshed fiber sheet and of giving improved dimensional stability, the binder material may be selected to have a precipitating or coagulating action on the collagen fiber suspension. For example, a binder containing a polyvalent metal such as chromium or iron tanning agent may be used, or there may be used a binder material such as a vegetable tanning agent or a synthetic tanning agent which will carry a charge opposite to that of the charge on the collagen fibers.

The desired uniform penetration and association of collagen fibers in the sheet according to the present invention involves the treatment of an intermeshed fiber sheet to give dimensional stability including resistance to loss of openness balanced against retention of at least limited freedom of movement of the fibers for collagen fiber take up and ultimate product quality reasons, in combination with adjustment of the properties of the collagen fiber dispersion to insure cooperation with the treated mat. That is, collagen fiber dispersions differ in their

ability to penetrate openings in an intermeshed fiber sheet so that, for example with a fiber sheet of a given openness, a highly penetrating suspension will penetrate readily while another suspension may deposit fibers in the intermeshed fiber sheet so readily as to "blind" the sheet, i.e., to block it against further penetration by the suspension. Again a highly penetrating suspension may pass through an intermeshed fiber sheet leaving only a low proportion of collagen fiber within the sheet while a less penetrating suspension may leave a high percentage collagen fiber within the intermeshed fiber sheet. A further factor is that the blinding of areas of a fiber sheet by deposit of collagen fibers on its surface due to mismatching of the penetrating ability of the collagen fiber suspension and the openness of the sheet is a self-accelerating action since the blinded area impedes passage of the suspension and results in an increased pressure drop through the sheet which has a compressive action and further reduces the size of the available openings.

Stabilizing the openness of a sheet of intermeshed fibers by a pretreatment of the intermeshed fiber sheet to effect a bonding together of fibers at their points of contact reduces the criticality of the relation between penetrating ability of the suspension and the openness of the intermeshed fiber sheet. Collagen fiber suspensions may be used in the present process which have a greater tendency to separate from suspension than is possible for use with unstabilized fiber sheets. Such suspensions give a high efficiency of fiber utilization and a high collagen fiber content in the finished sheet.

The suspension of microscopic lightly tanned collagen fibers used in the present process may be that described in greater detail in the applications of Tu referred to above. Briefly, the suspension is prepared by beating in water the collagen source, for example skin or hide, under conditions which limit swelling of the collagen to reduce it to fibers of microscopic size suspended in the water in a manner allowing the fibers relatively free movement in the suspension. The condition is markedly different from that referred to as "colloidal" in which collagen is reduced to a swollen viscous mass. In the preferred suspension, the collagen material will be lightly tanned, for example, to an extent comparable to 1/10% to preferably not over 3% of combined aldehyde such as formaldehyde or glyoxal based on the dried weight of the skin material, and the resulting suspension will be adjusted to a pH, suitably 0.5 of a pH unit outside the isoelectric range of the collagen fibers of the suspension. On the acid side of the isoelectric range the pH of the collagen fiber suspension may be from about 0.5 to about 3.5, and on the alkaline side, the pH may be from about 6 to about 12. For impregnation, the suspension will comprise distinct, noncolloidal fibers having a length of from about 0.001 mm. to not over about 4 mm. and preferably not over about 1 mm. in length.

Because of the wide variation in properties of collagen source material and the nature of the fibers in suspension resulting from the beating operation, the suspension after adjustment to a pH either above or below the isoelectric range is ordinarily calibrated by filtration through a mat of intermeshed fibers. With mats of the character employed for making a sheet and using a vacuum of 10" of mercury, the suspension of fibers is adjusted as to pH and concentration of fibers to provide a filtration time of from about one-quarter minute to about two minutes for passage of 600 ml. through a 6" diameter circular section of mat. Penetration ability increases as the pH departs from the isoelectric range so that a suspension having inadequate penetration characteristics, for example requiring over about two minutes for penetration into and through a given mat may be brought to a suitably high penetration value by adjusting its pH to a value farther removed from the isoelectric range. Conversely, a suspension having a high penetration ability and inadequate or undesirably low retention within the fiber sheet may be improved as

to these latter properties by adjusting the pH to a value closer to the isoelectric range. Also the rate of penetration is greater with lower concentrations of fibers in the suspension, and penetration may be improved by diluting the suspension.

After adjustment of the suspension to a pH value giving useful penetration characteristics for the selected intermeshed fiber sheet material, penetration of the stabilized mat with the collagen fiber suspension is effected. This penetration may be carried out in various ways as by impregnation of the intermeshed fiber mat with the suspension, using vacuum or positive pressure to create a pressure differential across the thickness of the mat for forcing the suspension into a fiber mat, or by spreading the suspension on the surface of a fibrous mat and working it in. In each of these various forms of procedure for penetration, the stabilizing action of the treatment of the fiber mat before penetration offers advantages both in effective retention of openness for entry of the suspension into the fiber mat and by maintaining the dimensions of the mat against change in the course of working or manipulating the mat.

Removal of the water of swelling of the collagen fibers may be effected by reducing the acid or alkali content of the collagen microscopic fiber material within the fiber mat to form a larger collagen fiber structure associated with the fibers of the mat and reinforcing them against displacement. This reduction 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 range of from about 3.5 to about 6. Treatment of the fiber sheet 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 within the range at which deswelling of the collagen fiber occurs. Deswelling and association of the collagen fibers into a larger collagen structure may also be effected by treating the fiber sheet with a 10% aqueous ammonium sulfate solution.

After deswelling, the sheet material is preferably subjected to tanning either with mineral tanning agents such as chrome tanning liquors or with vegetable tanning agents. It is to be noted that because of the collagen deswelling action of mineral tanning agents such as chrome tanning agents, these agents may be effective both to deswell the collagen fibers to form a collagen fiber structure and to tan the resulting collagen fiber structure. Conventional leather and tanning may be carried out either in an aqueous tanning medium or a solvent type tanning medium.

After tanning the sheet material may be treated by conventional procedures used in treating leather such as fat liquoring, coloring and the application of surface coatings to provide a desired finish. Included as one of the finishing treatments may be the step of needling comparable to the needling of the collagen fiber sheet material described in the copending application Ser. No. 805,032 entitled, "Collagen Fiber Sheet Material and Method of Making," filed Apr. 8, 1959, in the name of the present inventor and John H. Highbarger.

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

Example 1

2,2', 4,4'-tetrahydroxydiphenylmethane was dissolved in water to form a 1% solution. A needle-loomed nonwoven nylon fiber mat having a weight of 7 oz. per sq. yd. was dipped into the solution to impregnate it, removed, pressed to remove excess solution and air dried. A section of the mat having an initial weight of 45.5 grams weighed 47.3 grams after impregnation and drying indicating a 1.8 gram pick up of the impregnant. This was a concentration

of 2.56% based on the weight of the initial mat. The impregnated mat was flexible and resilient.

An aqueous dispersion of collagen fibers of microscopic size was prepared by tanning hide material with formaldehyde to give a formaldehyde content of about 0.4% and beating the hide material in a paper beater at a pH of about 5. The collagen fibers thus produced had a length of from about 0.2 to about 1 mm. The suspension was diluted to bring the solids content to about 1% and the pH adjusted to 8.77.

A section of the impregnated and dried nylon fiber mat was disposed on a filter bed provided with means for applying suction. A quantity of the above-prepared fiber suspension was deposited on the fiber mat in a layer of uniform thickness and suction was applied to pull the suspension into the mat. Vacuum applied was 26 inches and after five minutes the mat was uniformly filled with the suspension, the filtrate indicating substantial removal of collagen fiber by the mat. Two portions of acetone were applied successively to the sheet on the filter bed and sucked through to effect reaggregation of the collagen fiber in the mat.

The resulting sheet material after removal from the filter bed had a collagen content of about 46% based on the total weight of mat fibers, impregnating material and collagen. By observation about 88% of the collagen fiber slurry applied was held in the mat.

The sheet was thereafter tanned by immersion for 24 hours in a vegetable tanning bath comprising 30% solids comprised of 80% Quebracho extract and 20% of resorcinol formaldehyde resin. The sheet was removed from the tanning liquor and washed in running tap water for 8 hours. It was then squeezed of excess water and immersed in a standard fat liquor bath after which it was removed and dried. The dried sheet was similar to a vegetable tanned leather and its physical properties were in the range of leather.

Example 2

A needle-loomed nonwoven nylon fiber mat having a weight of 7 oz. per sq. yd., a thickness of 0.175" and a fiber denier of 3 was dipped in a 1% aqueous solution of a thermosetting melamine aldehyde resin to impregnate it. The mat was then removed, squeezed to remove excess solution and air dried. A portion of the mat having an initial weight of 43.4 grams weighed 44.4 grams after impregnation and drying indicating a net gain of 1 gram or 2.3% by weight based on the weight of the initial mat.

An aqueous suspension of collagen fibers was prepared as in Example 1, diluted to a 1% solids content and acidified with sulfuric acid to a pH of about 2.

A section of the resin impregnated and dried fiber mat was disposed on a filter bed and impregnated with the collagen suspension as in Example 1. Filtering time was two minutes to secure full impregnation. The filtrate was somewhat milky. The collagen fiber slurry impregnated sheet was dried as in Example 1 by treatment with acetone. Thereafter the impregnated sheet material was subjected to a tanning and fat liquor treatment as in Example 1. The dried sheet resembled a vegetable tanned leather.

Example 3

Collagen fiber slurry prepared as in Example 1 was adjusted to a solids content of 6.28% and a pH of 3 by addition of phosphoric acid. A portion of nylon fiber mat impregnated and dried as set forth in Example 2 was immersed in the slurry and subjected to mild working involving successive compression and release of pressure to effect impregnation of the mat by the slurry. After solvent drying it was found that the mat had picked up a collagen fiber content of about 25% based on the combined weight of the fiber mat and collagen fibers. The material was tanned and fat liquored as described in Example 2 to form a product resembling a vegetable tanned leather.

Example 4

A needle-loomed nonwoven nylon fiber mat having a weight of 6 oz. per sq. yd., a fiber denier of 3 and a thickness of about 0.175" was immersed in a 0.5% aqueous solution of a synthetic tanning agent (Orotan TV) to impregnate the mat. The mat was removed from the solution, squeezed to remove excess solution and air dried. It was found that the mat had picked up about 1% by weight solids based on the initial weight of the mat.

A collagen fiber slurry prepared as in Example 1 was adjusted to a 1% solids content and to a pH of about 2 (acidified with sulfuric acid).

A section of the impregnated and dried fiber mat was disposed on a filter bed as in Example 1 and a quantity of the fiber suspension was deposited on the mat in a layer of uniform thickness. A vacuum of 26 inches was applied to pull the suspension into the mat. The mat was thoroughly impregnated in 10 minutes. Precipitation of the collagen fiber from the dispersion was indicated by an opaque appearance which developed as the collagen fiber suspension came in contact with the mat. The resulting sheet material after drying with acetone and removal from the filter bed, had a collagen fiber content of about 46% based on the combined weight of the collagen fiber, impregnating material and fiber mat. The sheet was subjected to a vegetable tanning fat liquoring and drying as in Example 1. The dried sheet was similar to a vegetable tanned leather.

Example 5

A section of needle-loomed nonwoven nylon fiber mat as in Example 1 was immersed in an aqueous solution containing 2% by weight of solids of a thermosetting melamine formaldehyde resin and 2% by weight of solids of a styrene-alkyl acrylate copolymer latex resin ("Lytron" manufactured by Monsanto) and 1% by weight, based on the weight of the melamine aldehyde, of a catalyst for the melamine aldehyde resin. The copolymer resin was incorporated to provide a plasticizing action on the melamine-aldehyde resin. The mat was removed from the solution after impregnation and allowed to air dry. The mat picked up about 14.7% by weight of the impregnating composition. After drying the mat was cured at 300° F. to form a resilient sheet resistant to compression.

The impregnated dried and cured sheet was impregnated with a 1% collagen fiber slurry at a pH of 2 using a vacuum of only 2 inches. The impregnated mat was dried by sucking acetone through the impregnated sheet and evaporating the acetone. Thereafter, a further quantity of collagen fiber slurry was applied to the surface and caused to impregnate it by applying suction.

It was found that the collagen content of the fiber mat was 39.1% by weight after the first impregnation and 44% by weight after the second impregnation, the percent being based on the weight of the fiber mat, the resinous impregnant and collagen fiber. After the second impregnation, the impregnated mat was removed from the filter bed and while still wet with water was placed in a chrome tanning bath containing 1% by weight of chromium calculated as Cr_2O_3 and 2% by weight of sodium formate. After standing overnight in this tanning bath, the sheet was removed, washed in warm tap water for 6 hours, pressed between filter papers to remove further water and disposed in a fat liquor bath. After fat liquoring the sheet was removed and air dried. The dried sheet resembled a chrome tanned leather.

Example 6

A needle-loomed nonwoven polypropylene fiber mat having a weight of 7.5 oz. per sq. yd., a thickness of 0.10" and a fiber denier of 3 was immersed in a 10% solids by weight emulsion of a butadiene-acrylonitrile copolymer synthetic rubber. The mat was then removed from the emulsion, blotted to remove excess solution and

air dried. The mat picked up about 15% by weight of the copolymer and showed resilient recovery when pressed.

An aqueous dispersion of collagen fibers of microscopic size was prepared as in Example 1 with the modification that the hide material was tanned to give a formaldehyde content of about 0.29% and that the pH of the diluted solution was adjusted by addition of sulfuric acid to a value of pH 2.48.

A section of the impregnated and dried fiber mat was disposed on a filter bed and impregnated with the collagen fiber suspension as in Example 1. After completion of filtration, the sheet was treated with acetone to remove water and effect reaggregation of the collagen fiber in the mat.

The resulting sheet material after removal from the filter bed had a collagen content of about 20% based on the total weight of mat fibers, impregnated material and collagen.

After tanning and fat liquoring, a sheet similar to leather was obtained.

Example 7

The procedure of Example 6 was repeated with the modification that the pH of the collagen fiber suspension was 3.46. The collagen content of this sheet material was about 28% by weight based on the total weight of the mat fibers, impregnating material and collagen. A somewhat "fuller" sheet having superior feel and hand than the product of Example 6 is obtained when this material is tanned and fat liquored.

Example 8

A mat of nonwoven intermeshed cotton fibers having a weight of about 2 oz. per sq. yd. and a thickness of 0.05 inch was immersed in a 10% by weight solids emulsion of a rubbery butadiene acrylonitrile copolymer. The mat was then removed, blotted to remove excess solution and air dried in a glass plate. The mat picked up about 15% by weight of the copolymer based on the weight of the initial mat.

A leather-like sheet material is obtainable by impregnating a sheet with a collagen fiber suspension as in Example 6 followed by drying, tanning and fat liquoring.

Example 9

A nonwoven cotton fiber mat having a weight of about 2 oz. per sq. yd. and a thickness of about 0.05" was sprayed with a 1% aqueous solution of 2,2',4,4'-tetrahydroxydiphenylmethane, the spraying being in amount sufficient that after drying the mat contains about 5% by weight of the 2,2',4,4'-tetrahydroxydiphenylmethane after drying the percent being based on the weight of the initial mat.

The mat was impregnated with an aqueous collagen fiber dispersion having a solids content of 1% and a pH of 1.5 using the procedure of Example 6. Water was removed and the collagen fibers reaggregated by treatment with acetone.

The resulting sheet material after removal from the filter bed had a collagen content of about 30% by weight based on the total weight of mat fibers, impregnating material and collagen.

On tanning with a vegetable tanning bath as in Example 1 fat liquoring, and drying a sheet similar to vegetable tanned leather is obtainable.

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

1. The process of forming a strong fibrous material which comprises providing a mat of intermeshed fibers having an apparent density of from about 1 to about 5 pounds per cubic foot, the fibers of said mat being from about 0.5 to about 5 denier, bonding fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of ad-

jacency free for fibrous movement, thereafter penetrating the thickness of said mat with a liquid aqueous suspension containing from about 1% to about 5% based on the weight of the suspension of swollen, distinct, the collagen fibers of microscopic size and in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the weight of said intermeshed fibers and the collagen fibers and removing the swelling water from said collagen to reaggregate the collagen fibers into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

2. The process of forming a leather-like material which comprises providing a mat of intermeshed fibers having an apparent density of from about 1 to about 5 pounds per cubic foot, the fibers of said mat being from about 0.5 to about 5 denier, distributing a binder throughout said intermeshed fiber mat to bond fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of adjacency free for fibrous movement, said binder being incorporated to the extent of from about 1% to about 15% by weight based on the weight of said intermeshed fibers, thereafter supplying to a surface of said mat an aqueous suspension containing from about 1% to about 5% based on the weight of the suspension of swollen, distinct, fine collagen fibers of microscopic size and in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and the collagen fibers, applying differential pressure across the thickness of said mat to force said suspension into penetrating relation in said mat, removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

3. The process of forming a leather-like material as defined in claim 2 in which the binder is a synthetic elastomer.

4. The process of forming a leather-like material as defined in claim 2 in which the binder includes a material effective to precipitate said swollen collagen fibers from suspension.

5. The process of forming a leather-like material as defined in claim 4 in which said material effective to precipitate said collagen fibers is a tanning agent.

6. The process of forming a leather-like material which comprises providing a mat of the intermeshed fibers having an apparent density of from about 1 to about 5 pounds per cubic foot, the fibers of said mat being from about 1 to about 5 denier, softening surface portions of fibers of said mat to bond fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of adjacency free for fibrous movement, thereafter supplying to a surface of said mat an aqueous suspension containing from about 1% to about 5% based on the weight of the suspension of swollen, distinct, fine collagen fibers of microscopic size and in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and the collagen fibers, applying differential pressure across the thickness of said mat to force said suspension into penetrating relation in said mat, removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

7. The process of forming a leather-like material as defined in claim 6 in which fibers of said mat are softened by a solvent.

8. The process of forming a leather-like material as defined in claim 6 in which fibers of said mat are softened by heat.

9. The process of forming a leather-like material which comprises providing a mat of intermeshed fibers having an apparent density of from about 1 to about 5 pounds

per cubic foot, the fibers of said mat being from about 0.5 to 5 denier, distributing a binder throughout an intermeshed fiber mat to bond fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of adjacency free for fibrous movement, said binder being incorporated to the extent of from about 1% to about 15% by weight based on the weight of said intermeshed fibers, thereafter supplying to a surface of said mat 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, said suspension having a pH at least about 0.5 of a pH unit outside the isoelectric range of said collagen fiber, and being supplied in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and the collagen fibers, applying differential pressure across the thickness of said mat to force said suspension into penetrating relation in said mat, adjusting the pH of the suspension of collagen fibers in said intermeshed fiber mat to the isoelectric range of said collagen fibers and removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

10. The process of forming a leather-like material which comprises providing a mat of intermeshed fibers having an apparent density of from about 1 to about 5 pounds per cubic foot, the fibers of said mat being from about 0.5 to about 5 denier, distributing a binder throughout an intermeshed fiber mat to bond fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of adjacency free for fibrous movement, said binder being incorporated to the extent of from about 1% to about 15% by weight based on the weight of said intermeshed fibers, thereafter supplying to a surface of said mat 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, said suspension having a pH of from about 0.5 to about 3.5 and a content of aldehyde combined with said collagen fibers of from about 0.1% to about 3% based on the dry weight of said collagen fibers and being supplied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and the collagen fibers, applying differential pressure across the thickness of said mat to force said suspension into penetrating relation in said mat, reducing the acid content of the suspension in said fiber mass to bring the pH to and maintain the pH at from about 3.5 to about 6.0 and removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

11. The process of forming a leather-like material as defined in claim 10 in which the binder is a synthetic elastomer.

12. The process of forming a leather-like material as defined in claim 10 in which the binder includes a material effective to precipitate said swollen collagen fibers from suspension.

13. The process of forming a leather-like material as defined in claim 12 in which said material effective to precipitate said collagen fibers is a tanning agent.

14. The process of forming a leather-like material which comprises providing a mat of intermeshed fibers having an apparent density of from about 1 to about 5 pounds per cubic foot, the fibers of said mat being from about 0.5 to about 5 denier, distributing a binder throughout an intermeshed fiber mat to bond fibers of said mat to other fibers of said mat at points of adjacency leaving portions of said fibers intermediate said points of adjacency free for fibrous movement, said binder being incorporated to the extent of from about 1% to about

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15% by weight based on the weight of said intermeshed fibers, thereafter supplying to a surface of said mat 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, said suspension having a pH of from about 6 to about 12 and a content of aldehyde combined with said collagen fibers of from about 0.1% to about 3% based on the dry weight of said collagen fibers and being supplied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and the collagen fibers, applying differential pressure across the thickness of said mat to force said suspension into penetrating relation in said mat, reducing the alkali content of the suspension in said fiber mass to bring the pH to and maintain the pH at from about 3.5 to about 6.0 and removing the swelling water from said collagen fibers to reaggregate them into a larger collagen fiber structure reinforcing the intermeshed fibers of said mat against displacement.

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