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LEATHER-LIKE MATERIAL AND METHOD OF MAKING THE SAME

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This application is a continuation-in-part of my copending application Serial No. 170,225, entitled "Leather-Like Material and Method of Making the Same," which was filed January 31, 1962, and is now abandoned.

This invention relates to a strong leather-like material and to a method of making the same.

In my earlier application Serial No. 94,999, filed August 24, 1961, entitled "Processes of Making Leather-Like Materials," and now abandoned, there is disclosed the manufacture of a leather-like material in which an aqueous slurry of collagen fibers is formed into a wet web by straining the water from the slurry through a foraminous surface, introducing a gelatin or collagen solution into the web and treating the web for example, with a chromium tanning agent to convert the gelatin or collagen material to insoluble state in which it holds the collagen fibers in open-fibered leather-like relation after removal of the remaining water. The resulting sheets possess many of the characteristics of leather including excellent water vapor transmission, warmth, feel and so on.

It is an object of the present invention to form a sheet having comparable properties but having superior strength and to provide a simple method for making this sheet material.

To this end, and in accordance with a feature of the present invention, I have devised 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 holds the intermeshed fibers against major displacement to give a novel product having high strength coupled with the moisture vapor transmission and absorption characteristics of collagen fibers and a warmth and hand comparable to leather.

I have found that lightly tanned collagen suspended under special conditions in an aqueous medium as distinct, slightly swollen fibers of microscopic size will remain in suspension for penetration of intermeshed fibrous masses. Thereafter by altering the conditions the fibers are deswelled and associated with each other as a larger collagen fiber structure extending through the fiber masses and associated with the fibers of the masses to reinforce them against displacement. The novel reinforced fiber masses are strong and possess many of the characteristics of leather.

The microscopic fiber suspension used in the present process is a special material from the special treatment of the collagen material. The collagen source, for example, skin or hide, is beaten under conditions which limit swelling of the collagen into fibers of microscopic size to form a suspension in which the fibers are capable of relatively free movement in the aqueous medium in which formed. The condition is markedly different from that referred to as "colloidal" in which collagen is reduced to a swollen viscous mass.

A suspension of collagen microscopic fibers useful in the present process may be formed by beating skin material in an aqueous medium. In this procedure, skin material preferably is lightly tanned for example, to an extent comparable to $\frac{1}{40}\%$ to preferably not over 3% of combined aldehyde such as formaldehyde, glutaraldehyde, or glyoxal based on the dried weight of the skin material to bring the skin material to a condition in which

it can best be reduced by beating in water under controlled pH conditions to its separate fibers. From about 1% to about 8% by weight of small skin pieces is placed in water in a beater similar to a paper beater and beating is carried out at a pH of from 2 to 8. Beating at pH 5 to 8 is preferred since the fibers obtained in this range show a special change to a shortened condition favorable to penetration into fiber batts when brought to penetration pH values. Also there are marked advantages in ease of beating and avoidance of degradation of the collagen.

The tendency to swelling of skin material in an aqueous medium increases as the departure of the pH of the medium from the isoelectric range of the skin material increases. The tendency to swelling is reduced as the extent of tanning, e.g., the aldehyde content increases. The swelling is also dependent on the collagen swelling property of the pH control agent used. For example, sulfuric acid is a lightly swelling acid while formic acid, phosphoric acid, acetic acid and citric acid are strong swelling acids. Best results for purposes of the present invention are secured by balancing these factors to bring the skin or hide to the condition of incipient swelling so that the bonds between fibers are weakened but the fibers are separable as distinct elements.

For purposes of the present invention, a suspension of microscopic distinct fibers may be prepared from skin material, preferably lightly tanned by controlling the pH in the beater relative to extent of tanning and the collagen swelling character of the pH control agent to give incipient swelling. The beating of the skin material is carried to an extent to form distinct non-colloidal fibers which have a length of from about .001 mm. to not over about 4 mm. in length and preferably not over 1 mm. in length. If desired the beating may be carried out in stages to form first coarse fibers which optionally may be separated from the beater water, introduced into further water and then subjected to further beating to form fine fibers. The suspension obtained by beating in the preferred range of from pH 5 to pH 8 is white and opaque. If spread on the surface of a batt of fibers, it remains substantially on the surface allowing the water content to drain through the fiber batt leaving a crusty deposit of the fibers on the surface.

I have found, however, that by subjecting the collagen fibers in suspension to controlled swelling conditions, the fibers of the suspension will penetrate into the interstitial spaces of a fiber batt and will be retained by the fibers of the batt so that the batt is filled through and through with the dispersion. The term "swelling" in the special sense here intended refers to the phenomenon that the surfaces of the fibers become slippery and the fibers increase in thickness and decrease in length but remain as distinct fibers. The suspension loses its whitish opacity, becomes translucent and increases in viscosity.

The extent to which 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 at 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.

A useful degree of swelling is obtainable at pH values about 0.5 of a pH unit outside the isoelectric range of the collagen fiber. Where the collagen fiber is obtained from hides which have been limed, the isoelectric range may be from about 4 to 5.5 while with hides which have not been limed the isoelectric range may be from about 7 to about 8. Ordinarily limed hides which are more readily available will be used and the following description sets forth conditions particularly useful with

fibers from limed hides. Adjustment of pH values for use with fibers from other hides can be made readily by chemists. On the acid side of the range the pH of the suspension of collagen fiber from limed hide will ordinarily be kept in the range of from about pH 0.5 to about pH 3.5 and most desirably from about pH 2 to about pH 3.0. The higher portions of this range are used with the more highly swelling acids such as formic acid, acetic acid, citric acid, phosphoric acid and others.

Effective swelling above the isoelectric range has been obtained in a suspension of collagen fiber from limed hide at a pH in the range of from about pH 6.0 to about pH 12 and more desirably from about pH 8 to about pH 10. The fiber suspension may be brought to this range by addition of alkaline reagents such as sodium hydroxide, tri-sodium phosphate, potassium hydroxide and various other alkaline hydroxides and salts which do not form insoluble compounds with the collagen.

The collagen fiber dispersions having pH values above the isoelectric range offer certain advantages over the acidic collagen fiber suspensions. An important factor is that on the alkaline side, the properties of the collagen fiber slurry remain fairly constant on storage, while on the acid side there may be a progressive loss of tanning agent particularly where formaldehyde is the tanning agent so that the properties of a fiber suspension on the acid side change on storage, apparently due, at least partially, to loss of formaldehyde from the fiber. Additionally, many synthetic resin and synthetic rubber polymer and copolymer emulsions or latices are at least mildly alkaline and may be admixed to the alkaline collagen fiber suspension without difficulty, while addition of such alkaline materials to an acid collagen fiber suspension would result in coagulation of the synthetic resin or synthetic rubber emulsion and/or precipitation of the collagen fibers from suspension. With the alkaline collagen fiber suspensions thus, it is possible to include synthetic rubber or synthetic resin additionally to modify the properties of the final product. Also other alkaline emulsions, for example, fat liquor emulsions and liquid solutions or suspensions of various dyes or pigments may be included.

The extent of tanning of the hide material as with formaldehyde has been found to be an important factor in the bringing of the collagen microscopic fiber suspension into the desired state for effective penetration and retention of the dispersed fibers within the batt. Penetration ability decreases and retention of the fiber increases with increase in the extent of tanning. It has been found 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. Thus, it has been found that with a formaldehyde content of 0.2% by weight based on the weight of the hide material, the fiber suspension at the important pH range penetrates well into a given fiber batt but that retention of the fibrous material in the batt is barely acceptable. Where the formaldehyde content is 1.1% by weight based on the weight of the hide material, a proportion of the fibers may be retained on the surface of the same fiber batt to which the suspension is applied and the penetration properties are poor. Within this range and preferably at a formaldehyde content of from about 0.4 to about 0.6% by weight based on the weight of the hide material the suspension penetrates well and the fibers are retained effectively within the fiber batt. It is important that the fibers have been swollen to a controlled degree for effective use and it is believed that one effect of this swelling is a plasticizing of the fibrous collagen material enabling the fibers to move effectively through the interstices in the fiber batt. Higher tanning agent contents restrain the extent of swelling to reduce the ability of the fibrous material to enter the batt and if no tanning agent is used, there is not only an undesirable increase in viscosity which makes it difficult to use

it to penetrate a fiber batt but the fibrous material is not retained well by the fibers of the batt.

There is some indication that, at least with the more highly tanned collagen fibers, for example, fibers containing from about 0.6% to about 0.8% by weight formaldehyde based on the weight of the fibers, the "swelling" may occur primarily at the surfaces of the fibers. This offers the advantage that the fibers develop a surface character allowing the fibers to slip relative to one another and to the fibers of the mat to be impregnated so that the fibers will penetrate a fiber mat, while the volume of individual fibers is not greatly increased so that the ultimate quantity of collagen fiber solids on a dry fiber basis which can be introduced into a mat to fill the interstitial spaces in the mat may be greater with the more highly tanned fibers than with the less tanned fibers.

Where a collagen fiber suspension in which the collagen has a high tanning agent content for example, 1.1% of formaldehyde which ordinarily would penetrate poorly with a substantial portion retained on the surface of a given fiber batt, is blended for example, in the range of ratios of from 2:1 to 1:2 parts by weight with a low aldehyde content collagen fiber suspension for example, one having a 0.1% to 0.4% formaldehyde content, the resulting mixtures, which will have respectively .8 and .65% formaldehyde by weight, penetrate the fiber batt effectively and are retained effectively within the fiber batt. Although applicant does not wish to be bound by the theory, it appears that the low formaldehyde content fibers serve as a carrier for the high formaldehyde content fibers to aid in penetration. On the other hand, the high formaldehyde content fibers impart to the mixture the desired retention characteristics. Because of the importance of maintaining the formaldehyde content within the range useful at the selected pH, the ability to adjust the formaldehyde content by addition of high formaldehyde or low formaldehyde content fiber suspension is of considerable practical value. The carrier action of the low formaldehyde content fibers may also be used to enable penetration of a suspension of chrome tanned collagen microscopic fibers or other fine fibers such as nylon, polyester, rayon and others into a fiber batt. Thus, a suspension of microscopic fibers of collagen having a chromium content of from 0.5% to 4% by weight calculated as Cr_2O_3 based on the weight of the collagen may be combined with a suspension of microscopic collagen fibers having an aldehyde content of from 0.17% to 0.4% based on the weight of the collagen in the range of ratios of from 2:1 to 1:2 to form a mixed suspension with useful penetration and retention properties.

Suspensions in which the collagen fiber has a relatively high formaldehyde content and relatively poor penetration into a fiber may be improved in this respect by adding a solution of gelatin to this suspension. Noticeable improvement has been obtained with addition of as little as one part of gelatin to 10 parts of the microscopic collagen fibers, and as much as one part of gelatin to one part of microscopic collagen fibers may be used.

An addition of a cationic or anionic surface active agent, depending on whether the slurry is acidic or basic, to a suspension of microscopic collagen fibers having poor penetration characteristics is also effective to improve the penetration of the suspension into a fiber. This effect is obtainable with as little as 1% based on the weight of the collagen fiber in suspension.

The ability of fibers to penetrate a mat depends also on the retained openness of a mat during application of the collagen fiber slurry or suspension. Fiber mats which retain a high degree of openness may be penetrated with collagen fiber suspensions with a degree of tanning and under pH conditions giving a relatively low penetrating ability which would not effectively enter less open fiber mats. It is possible to form fiber mats filled with collagen fibers by adjusting the penetrating ability of the collagen fiber suspension through control of extent of tanning and

pH conditions relative to the retained openness of the fiber mat.

In addition to the factors of extent of tanning and pH control which exert a primary effect on the penetration ability, it has been found that a limited control over penetrating ability can be obtained by adjusting the collagen fiber solids content of a suspension. That is, suspensions of collagen fibers with relatively low penetrating ability may penetrate more effectively where the collagen fiber solids content is reduced to a relatively low percentage. Suspensions having collagen fiber solids contents of at least 0.5% preferably from about 1% to about 5% are preferred from the standpoint of securing a good penetration and the introduction of a desired high collagen fiber solids content into a fiber mat with desirable efficiency in time and amount of suspension handled. It will be understood that it is possible to operate somewhat outside these ranges; but, for example, the use of a lower solids content suspension entails the separation of collagen fiber from a large volume of liquid; and use of a higher solids content suspension may require an undesirably open mat or result in uneven penetration.

When the pH of a collagen fiber suspension in which controlled swelling has been produced as above described, approaches or reaches the isoelectric range, there is an observable association of the fibers into substantially aligned relationship. It appears that as association of the individual fibers proceeds, a larger collagen fiber structure is reaggregated from a multitude of the microscopic fibers and is comparable to native larger collagen fibers. This association which is believed to be of a physical-chemical nature is what is referred to herein as "reaggregation" and is a phenomenon different from the reconstitution of collagen from solution on the one hand and from the cementing together of colloidal collagenous material on the other hand. It is to be noted with particular respect to the heretofore known processes for extruding swollen or colloidal material that there it has been found necessary to induce an orientation of the collagenous material by stretching for example, an extruded filament. In the present case, on the other hand, it appears that the collagen microscopic fibers are able to align and orient themselves under the influence of the electrical charges in the microscopic fibers by reason of the relative freeness of the fibers in the liquid phase so that the advantages of an oriented fibrous material are obtainable under conditions existing in a fibrous batt where stretching to induce orientation is not possible.

The above discussion is advanced as of assistance in understanding the invention but it is to be understood that patentability is not dependent on the correctness of the explanation advanced on the observed phenomena.

A wide variety of intermeshed fiber materials both woven and nonwoven may be used for association with collagen microscopic fiber suspensions. Ordinarily nonwoven fiber materials are preferred because of their greater variety of thicknesses, densities and openness to penetration by the suspensions. Thus, the fibers may be nylon, polyacrylic ester fibers (Orlon), polyester fibers (Dacron), polypropylene fibers, wool, extruded cellulosic fibers such as viscose or cellulose acetate and others. It has been found that best results are secured when the fibers are hydrophobic. In this connection a batt of longer collagen fibrous material which has been treated for example, by chrome tanning or other treatment to decrease its affinity for water may be used. Also natural cotton fiber preferably treated to decrease its affinity for water is also 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 batts in which the fibers are in a relation providing relatively large interstitial spaces. The fiber batts 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 very satisfactory are those in nylon fiber batts having densities of the order of 4 oz. per sq. yd. at a thickness of 0.15" and 6 oz. per sq. yd. at a thickness of 0.175". 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. Another highly satisfactory material is a polypropylene fiber batt having a density of 7 oz. per sq. yd. and a thickness of 0.2".

Penetration of the suspension of swollen collagen microscopic fibers into an intermeshed fiber mass may be effected in a variety of ways. Thus, a fiber batt may be immersed in a suspension, suitably a relatively low solids suspension of the order of 1% to 3% by weight solids. The rate of impregnation may be increased by use of a vibrator. Another procedure involves disposing the fiber batt on a screen and forcing the suspension in with the aid of pressure or suction. Suspensions having a solids content of for example, from about 1% 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 batt and working it in.

Products having a higher collagen content at the surface may be formed by first treating the fiber batt with a collagen suspension having good penetrating ability and thereafter treating the batt with a suspension having a lower penetration ability. If desired suspension may be applied from alternate sides.

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 batt 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 batt with a 10% aqueous ammonium sulfate solution which effects a deswelling of the fibers.

The fiber batt is compacted and reduced in thickness in the course of penetration by the suspension and reaggregation of the collagen material so that, for example, starting with a 4 oz. per sq. yd. nylon fiber batt with an initial thickness of 0.15", after penetration by suspension and reaggregation of the collagen material, the thickness will have reduced to from about .015 to about .03". Correspondingly a sheet prepared from a 6 oz. per sq. yd. nylon batt having an initial thickness of 0.175 will form a sheet about 0.04 inch in thickness. This reduction in thickness is due in considerable measure to the action of the suspension in being forced into the batt. A further action which influences the reduction in thickness is the pulling together of the collagen material by water bonding; and this factor may range from very slight where water is extracted from the sheet by solvent to relatively large where a substantial portion of the water is removed by evaporation.

The sheet material is preferably subjected to tanning with mineral tanning agents such as chrome tanning liquors or with vegetable tanning agents. Because of the collagen deswelling action of mineral tanning agents such as chrome tanning agents it is possible to effect both reaggregation and tanning with such agents. Conventional leather tanning procedures may be used and the tanning may be carried out either in an aqueous tanning medium or a solvent type tanning medium.

After tanning the sheet material will be washed and pressed to remove excess water. Ordinarily the sheet is subjected to a treatment to introduce a "plasticizing" or

softening agent into it as by fat liquoring or preferably by immersing it in an acetone solution containing for example, 4% by weight of oleic acid. After this treatment, the sheet is dried in air and may be subjected to various finishing treatments including the step of needling comparable to the needling of the collagen fiber sheet material described in an application Serial No. 805,032, now U.S. Patent 3,073,714, issued January 15, 1963, and entitled "Improved Collagen Fiber Sheet Material," filed April 8, 1959, in the names of the present inventor and John H. Highberger.

For use, the surface of the sheet may be coated with leather finishes or resinous and/or waxy material. A preferred finish for the sheet material involves the application of a solution of a suitable nylon in a 70% isopropanol solution, this solution suitably containing pigment to give the desired color. After the solution is applied the sheet is dried, subjected to a needling treatment, and thereafter embossed or plated. The surface so obtained is a soft, strong and flexible film closely resembling the grain surface of leather and firmly adherent to the sheet.

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 particular materials, proportions or procedures set forth therein:

Example I

Pickled belly split was washed and 35 lbs. of the washed material was introduced into a drum along with a buffer made of: 1200 ml. of glacial acetic acid, 1000 gms. of sodium hydroxide and 1000 ml. of a 37% solution of formaldehyde and 80 lbs. of water. The drum was rotated for 21 hours and the splits were then drained, washed for one hour, hosed and drained for ½ hour and then cut into approximately one inch pieces. The formaldehyde content of the material at this time was about 0.85% by weight based on the weight of the dry collagen. The chopped material was introduced into a Hollander type paper beater and made up to a 200 lb. batch by addition of water. The pH of the material in the beater at this time was about 5.4. The beater was operated until 4 kw. hours of energy had been supplied to the beating operation. At this time 250 cc. of an emulsifying agent were added and beating continued for three minutes. This beating emulsified the fat content of the split material and the resulting emulsion was drained off. Half of the split material was put back in the beater along with 80 lbs. of water and the beating continued. The pH of the material was adjusted to approximately pH 7 by additions of a 4 N solution of sodium hydroxide. After 4½ hours of beating, the material was reduced to a suspension of collagen fibers having a length of from about 0.2 to about 1 mm. The suspension was diluted by addition of water to bring the solids content to about 2%, and had a viscosity at 20° C. of 1250 centipoises. The suspension was acidified in the beater by addition of phosphoric acid to bring the pH to about 2.3 and its viscosity increased to about 5000 centipoises.

A rectangular sheet 18 inches by 12 inches of nylon fiber batt having a weight of 6 oz. per sq. yd., a thickness of 0.175 inch and a fiber denier of 3 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 batt, leveled with a rubber squeegee. Suction was applied which pulled the suspension into the batt, the liquid leaving the batt being a relatively fiber-free material. The resulting sheet had a collagen fiber content of about 50% based on the dry weight of the sheet. Six liters of dry acetone were then

drawn through the batt to remove water and to effect a reaggregation of the microscopic fibers of the suspension. This acetone is added in two portions of which the first portion consisting of 4 liters is drawn through immediately and the last two are allowed to stand on the surface of the treated batt for 10 minutes and then drawn through.

The resulting sheet material after removal from the filter resembled a solvent dried skin material and was subjected to tanning by immersion for ½ hour in a standard buffered chromium tanning liquor containing 0.5% chromium calculated as Cr₂O₃ and 1% of sodium formate and having a pH of 4. The sheets were then removed from the tanning liquor and allowed to stand overnight in a covered receptacle; the sheets were then washed in water for three successive periods of 15 minutes.

After washing the sheets were dried by immersion in successive acetone baths and the dried sheets were then immersed in a 4% by weight solution of oleic acid in acetone for 1½ hours. Thereafter the sheets were removed and allowed to dry at room temperature. The dried sheets were similar to a chromium tanned skin and its physical properties were in the range of leather.

A coating solution was prepared by combining the following ingredients and beating in a Waring Blendor at 40 to 45° C. for from 20 to 25 minutes.

Component:	Parts
Isopropanol	315
Water	135
Ammonium citrate	2.5
Type 800 nylon (BCI No. 807 manufactured by Belding-Corticelli Industries)	50
Tri-n-butylamine	15
2% aqueous solution of cellulose acetate butyrate (Carbopol 934)	85
White pigments	30

The above solution was cooled and sprayed in several pieces on the dried sheets and the sprayed sheets were then dried in an oven at 150° F. for three hours.

The dried sheets were subjected to a needling operation to provide about 1500 perforations per sq. inch. Thereafter the sheet was plated at 250° F. and 500 pounds per sq. inch pressure for about 15 seconds.

The finished sheet resembled a good grade of leather suitable for shoe manufacture.

Example II

Limed hide was delimed and washed to remove salts. Fifty pounds of the wet hide (15% dry hide solids) was put in a tanning bath comprising 80 pounds of water, 1.6 liters of glacial acetic acid, 1000 grams of sodium hydroxide and 1000 ml. of 37% formaldehyde. The pH of the bath was about 5. After 16 hours the hide was removed, washed and drained. The formaldehyde content was about 0.4% by weight. The hide was then chopped into ¾ inch pieces and introduced into a Hollander along with water in amount to make the hide solids content about 6%. After 15 minutes beating in the Hollander a small amount of a wetting agent was added and beating continued for about 5 minutes. The resulting suspension of fiber was drained and then squeezed between rollers to remove further water. The fiber was returned to the Hollander together with water to make the solids content about 6%. The pH was adjusted to about 7 and the Hollander operated for four hours. At the end of the time the hide material had been teased into microscopic fibers uniformly suspended in the water. The suspension was diluted by addition of water to bring its solids content to about 1.5% and the suspension was made alkaline in the beater by addition of sodium hydroxide to bring its pH to 8.59.

A rectangular sheet 18" x 12" of nylon fiber batt having a weight of 7 ounces per square yard, a thickness of

0.175" and a fiber denier of 3 was disposed on a filter bed provided with means for applying suction.

Four liters of the fiber suspension was deposited on the fiber batt and leveled with a rubber squeegee and pulled into the batt by application of suction. Five minutes were required to pull the suspension into the batt. The resulting sheet had a collagen fiber content of about 42.7% based on the dry weight of the sheet. The sheet was treated with acetone, tanned and dried as in Example I. On examination it was found that the fiber had penetrated uniformly through the sheet and that the physical properties of the sheet were in the range of leather.

Example III

A suspension of collagen fiber was prepared by procedures similar to that set forth in Exchange II, but using only 700 ml. of the formaldehyde solution to provide a formaldehyde content combined with fiber of 0.18% by weight based on the weight of the dry collagen. After the beating step, the suspension was diluted by addition of water to bring its solids content to about 1.5% and the suspension was made alkaline in the beater by addition of sodium hydroxide to bring its pH to 9.4.

A rectangular sheet 18" x 12" of nylon fiber batt having a weight of 7 ounces per square yard, a thickness of 0.175" and a fiber denier of 3 was disposed on a filter bed provided with means for applying suction.

Three liters of the fiber suspension was deposited on the fiber batt on a level with a rubber squeegee and pulled into the batt by application of suction over a period of about five and one-half minutes. The resulting sheet had a collagen fiber content of about 38.1% based on the dry weight of the sheet. The sheet was treated with acetone, tanned and dried as in Example I. On examination it was found that the fiber had penetrated uniformly through the sheet and that the physical properties of the sheet were in the range of leather.

Example IV

A collagen fiber suspension was prepared as in Example II to have a formaldehyde content combined with fiber of 0.41% by weight based on the weight of the dry collagen. The suspension was diluted with water to bring the solids content to about 1.0% and adjusted by addition of sodium hydroxide to bring its pH to 11.0.

A rectangular sheet 18" x 12" of polypropylene fiber batt having a weight of 7 ounces per square yard, a thickness of 0.190 and a fiber denier of 3 was disposed on the filter bed and 4 liters of the suspension was deposited on the fiber batt and leveled with a rubber squeegee. Suction was applied to pull the suspension into the batt. After 1¼ minutes, all of the suspension had been pulled into the batt. The resulting sheet had a collagen fiber content of about 34.6% based on the dry weight of the sheet. The sheet was treated with acetone and dried as in Example I. On examination of the sheet it was found that the collagen fibers were distributed through the batt with a fair degree of uniformity.

Example V

Using the same fiber suspension as in Example IV and following the procedure of Example IV but after a day's storage of the suspension, it was found that the suspension was pulled into the batt in ¾ minute and that the resulting sheet had a collagen fiber content of 37.2% based on the dry weight of the sheet. Also, the collagen fiber was distributed more uniformly through the sheet.

Example VI

A further portion of the collagen fiber suspension prepared in Example IV was adjusted to a pH of 7.3 and four liters of this suspension was disposed on a nylon fibers batt having a weight of 7 ounces per square yard and a fiber denier of 3 on a filter bed. Suction was applied to pull the suspension into the batt. Three and

one-half minutes were required to pull the liquid into the batt. The resulting sheet was treated with acetone and tanned in accordance with the procedure of Example I. On examination it was found that the resulting sheet had a collagen fiber content of about 43.1% based on the dry weight of the sheet and the collagen material was distributed uniformly throughout the sheet.

Example VII

The procedure of Example VI was repeated with the fiber suspension at a pH of 6.55. The suspension had been pulled into the fiber batt in 1¾ minutes and the resulting sheet had a collagen fiber content of 50.2% based on the dry weight of the sheet. On examination of the tanned sheet it was found that the fiber distribution was not as uniform as in Example VI and that there was a markedly higher concentration of fiber adjacent the surface of the sheet on which the suspension had initially been disposed.

Example VIII

The collagen fiber slurry of Example IV was diluted to 0.5% solids. When deposited on a 7 ounce per square yard nylon fiber batt (fiber denier of 3) it was found that the slurry would penetrate the fiber batt at pH of 2.7 and below, that it would not penetrate at values in the range of 2.75 to 6.80 and that it would penetrate effectively at pH 7.35 and above.

Using a polypropylene fiber batt having a weight of 7 ounces per square yard and a fiber denier of 3 it was found that the suspension would penetrate the fiber batt at pH of 3.09 and below, that it would not penetrate at pH values of from 3.10 to 6.08 and that it would penetrate effectively at pH of 6.55 and above.

Using a polypropylene fiber batt having a weight of 2½ ounces per square yard and a fiber denier of 3, it was found that the suspension would penetrate the fiber batt at pH of 3.0 and lower, that it would not penetrate the batt at pH values in the range of 3.3 to 5.8 and that it would penetrate effectively at pH values of 6.10 and above.

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 leather-like material which comprises the steps of applying to an intermeshed fiber mass 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 intermeshed fiber mass, said suspension having a pH outside the isoelectric range of said collagen fiber, removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

2. The process of forming a leather-like material which comprises the steps of applying to an intermeshed fiber mass 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 short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH outside the isoelectric range of said collagen fiber and a content of aldehyde chemically combined with said collagen fibers of from about 0.1% to about 3.0% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers

and the collagen fibers, adjusting the pH of the suspension of said collagen fibers in said intermeshed fiber mass to the isoelectric range of said collagen fiber and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

3. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass 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 short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about 0.5 to about 3.5 and a content of aldehyde chemically combined with said collagen fibers of from about 0.1% to about 3.0% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, 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 7.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

4. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass in penetrating relation a mixture of a synthetic polymeric latex and an aqueous suspension containing about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about 0.001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said mixture having a pH at least about 0.5 of a pH unit outside the isoelectric range of said collagen fiber and said collagen fiber having a content of chemically combined aldehyde of from about 0.1 to about 3.0% based on the dry weight of said collagen fibers, said mixture containing from about 5% to about 20% by weight of synthetic polymer solids based on the weight of said collagen fibers, said suspension being applied to said intermeshed fiber mass in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, adjusting the pH of the mixture in said intermeshed fiber mass to the isoelectric range of said collagen fiber and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

5. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass in penetrating relation an aqueous alkaline suspension containing from about 1% to about 5% based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about pH 6 to about pH 12 and a content of aldehyde chemically combined with said collagen fibers of from about 0.1% to about 3% based on the dry weight of said collagen fibers, said sus-

pension being applied in quantity sufficient to provide about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the alkali content of the suspension in said fiber mass to bring the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

6. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass in penetrating relation a mixture of a synthetic polymeric latex and an aqueous alkaline suspension containing about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about 0.001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said mixture having a pH of from about pH 8 to about pH 10, and said collagen fiber having a content of chemically combined aldehyde of from about 0.1 to about 3.0% based on the dry weight of said collagen fibers, said mixture containing from about 5% to about 20% by weight of synthetic polymer solids based on the weight of said collagen fibers, said suspension being applied to said intermeshed fiber mass in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the alkali content of the mixture in said intermeshed fiber mass to bring the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

7. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass in penetrating relation an aqueous acidic suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about 2 to 3 and comprising a mixture of collagen fibers tanned to so high an extent that the suspension has poor penetration ability and collagen fibers having a chemically combined aldehyde content of from about 0.4% to about 0.6% by weight based on the dry weight of the fibers, the collagen fibers of said mixture being combined in the ratio of from about 1:2 to about 2:1 based on the dry weight of the collagen fibers in said suspension, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the acid content of the suspension in said fiber mass to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

8. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed fiber mass in penetrating relation an aqueous acidic suspension containing from about 1% to about 5%

by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about 2 to 3 and comprising collagen fibers tanned to so high an extent that a suspension of such fibers has poor penetration ability and a cationic surface active agent to improve the penetration ability of the suspension, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the acid content of the suspension in said fiber mass to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

9. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed nylon fiber mass in penetrating relation an aqueous acidic suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about 0.5 to about 3.5 and a content of formaldehyde chemically combined with said collagen fibers of from about 0.1% to about 3.0% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the acid content of the suspension in said fiber mass to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement, said reduction of acid content and removal of water being effected by treating said fiber mass with a volatile water-miscible organic solvent.

10. The process of forming a leather-like material which comprises the steps of applying to a nonwoven open-intermeshed nylon fiber sheet an aqueous acidic suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 1 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber sheet, the fibers of said sheet having a denier of from 1 to 5, said suspension having a pH of from about 2 to 3 and a content of formaldehyde chemically combined with said collagen fibers of from about 0.4% to about 0.6% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 30% to about 50% by weight of collagen fibers within the spaces in said intermeshed fiber sheet based on the combined weight of the nylon fibers of the sheet and the collagen fibers, reducing the acid content of the suspension in said sheet to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber sheet to reaggregate them into a larger collagen fiber structure within the interstitial spaces between the nylon fibers throughout said sheet to reinforce the fibers of said sheet

against displacement, said reduction of acid content and removal of water being effected by treating said sheet with a volatile water-miscible organic solvent.

11. The process of forming a leather-like material which comprises the steps of applying to a nonwoven intermeshed nylon fiber mass in penetrating relation an aqueous acidic suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH of from about 2 to about 3 and a content of formaldehyde chemically combined with said collagen fibers of from about 0.1% to about 3.0% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 5% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber mass based on the combined weight of said intermeshed fibers and the collagen fibers, reducing the acid content of the suspension in said fiber mass to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement, said reduction of acid content and removal of water being effected by treating said fiber mass with a volatile water-miscible organic solvent, and thereafter tanning the collagen fibrous material with a mineral tanning agent.

12. The process of forming a leather-like material which comprises the steps of applying to a nonwoven open-intermeshed nylon fiber sheet in penetrating relation an aqueous acidic suspension of swollen distinct fine short collagen fibers from about .001 mm. to about 1 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber sheet, the fibers of said sheet having a denier of from 1 to 5, said suspension having a pH of from about 2 to 3 and a content of formaldehyde chemically combined with said collagen fibers of from about 0.4% to about 0.6% based on the dry weight of said collagen fibers, said suspension being applied in quantity sufficient to provide from about 30% to about 90% by weight of collagen fibers within the spaces in said intermeshed fiber sheet based on the combined weight of the nylon fibers of the sheet and the collagen fibers, reducing the acid content of the suspension in said sheet to bring and maintain the pH to from about 3.5 to about 6.0 and removing the swelling water from said fine short collagen fibers in the interstitial spaces of said intermeshed fiber sheet to reaggregate them into a larger collagen fiber structure within the interstitial spaces between the nylon fibers throughout said sheet to reinforce the fibers of said sheet against displacement, said reduction of acid content and removal of water being effected by treating said sheet with a volatile water-miscible organic solvent, and thereafter tanning the collagen fibrous material with a chromium tanning agent.

13. An open-fibered leather-like material comprising a mass of intermeshed nonwoven fibers and associated collagen fiber structure extending through the interstices in said mass of fibers to reinforce the fibers of said mass against displacement, said collagen fiber structure possessing the special association with the fibers of said mass secured by formation in situ in the interstitial spaces of said mass of intermeshed fibers from an aqueous suspension of short distinct swollen collagen fibers of microscopic size by removing the swelling water from the collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure in reinforcing relation to the fibers of said mass.

14. An open-fibered leather-like sheet material comprising a mass of intermeshed nonwoven fibers and asso-

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ciated collagen fiber structure extending through the interstices in said mass of fibers to reinforce the fibers of said mass against displacement, said collagen fiber structure constituting from about 5% to about 90% by weight based on the combined weight of the mass of fibers and the collagen fiber structure and said structure possessing the special association with the fibers of said mass secured by formation in situ in the interstitial spaces of said mass of intermeshed fibers from an aqueous suspension of fine distinct and swollen collagen fibers of microscopic size by removing the swelling water from the collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure in reinforcing relation to the fibers of said mass, said collagen fiber structure having a content of chromium combined in tanning relation of from about 1% to about 3% by weight calculated as CR_2O_3 based on the weight of the collagen fiber.

15. An open-fibered leather-like sheet material comprising a mass of intermeshed nonwoven nylon fibers having a denier from 1 to 5 and associated collagen fiber structure extending through the interstices in said mass of fibers to reinforce the fibers of said mass against displacement, said collagen fiber structure constituting from about 30% to about 50% by weight based on the combined weight of the mass of fibers and the collagen fiber structure and said structure possessing the special association with the fibers of said mass secured by forma-

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tion in situ in the interstitial spaces of said mass of intermeshed fibers from an aqueous suspension of short distinct and swollen collagen fibers of microscopic size by removing swelling water and acid from the collagen fibers in the interstitial spaces of said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure in reinforcing relation to the fibers of said mass, said collagen fiber structure having a content of chromium combined in tanning relation of from about 1% to about 3% by weight calculated as CR_2O_3 based on the weight of the collagen fiber.

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