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FIBROUS MATERIALS AND PROCESSES OF MAKING SAME

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This invention relates to the manufacture of fibrous sponge, chamois-like and leather-like products, and to processes for forming such products from nylon fibers.

Both natural and man-made or synthetic fibers have been formed into non-woven structures by addition of adhesive materials. Thermoplastic fibers and mixtures of thermoplastic fibers and non-thermoplastic fibers may be formed into non-woven sheets at temperatures and pressures high enough to soften and fuse the thermoplastic fibers which serve as a binder for the non-thermoplastic fibers. If either of these treatments is extended sufficiently to give the high degree of interfiber bonding required in materials of high tensile and tear strength, the products become undesirably stiff and boardy for many uses. Efforts to manufacture materials having the admirable qualities of leather (e. g. high vapor permeability, tensile and tear strengths, flexibility and scuff resistance) have been noteworthy for their failure to produce a product excelling in all these qualities.

The present invention provides an answer to the problem of devising leather-like structures and also teaches the production of two novel intermediates having the characteristics of sponge and chamois. The utility of the products described below is readily apparent from the existing demand for a wide range of durable leathers and sponges for a multitude of uses, as from window wipers to shoe leathers and from cushions to surgical sponges.

The objects of this invention include the formation of sponges, chamois-like and leather-like products. Further objects are the provision of processes for the formation of the sponge, chamois-like and leather-like materials from nylon fibers. These and other objects will be readily apparent from the following description of the invention.

According to the present invention the fibrous materials are prepared by gathering together a loose assemblage of nylon fibers in the form of a batt, treating the batt with an aqueous solution of a mixture of a metal chloride, such as zinc chloride or ferric chloride, and nitric acid to produce a softening or gelation of the surface of the nylon fibers. Pressure is applied to the batt during or immediately following the metal chloride/nitric acid treatment to render the contiguous fibers in the batt coherent. Depending upon the temperature, the concentration of the metal chloride and nitric acid in the aqueous solution, pressure and heat applied to the batt during or immediately after immersion in the metal chloride/nitric acid bath; the products range from sponges to chamois-like and leather-like products. Lower temperatures and concentrations of the metal chloride/nitric acid bath produce sponge-like products which are converted to chamois-like products by the application of heat and pressure to the dry sponge. Higher temperatures and concentrations of the metal chloride/nitric acid bath produce leather-like products. The resultant structures have a pronounced fibrous form, but are sufficiently coherent that the fibers cannot be separated without the

performance of considerable work. Additional optional treatments involve treating the fibrous sheet, formed as described above, with softening agents and/or treating the surface with aqueous phenol to form a smooth surface on the sheet.

Fibers treatable according to this invention may be designated broadly as nylon, such as, e. g., the diamine-dibasic acid condensation products described in U. S. Patents 2,130,948; 2,071,250 and 2,071,253. For use according to this invention, a mass of nylon fibers is gathered together in a loose assemblage or batt, such as, e. g., carding. In some of the preferred embodiments of this invention some of the fibers are oriented perpendicular to both the length and width of the batt, which is customarily appreciably smaller in thickness than in length or width. The original batt may be a single ply or a plurality of plies formed by conventional lapping or cross-lapping processes. The partial perpendicular orientation required for laminar strength may be effected by passing a single ply or multiply batt one or more times through a conventional needle loom. These steps in batt formation are described at some length in patent application S. N. 312,067 filed September 29, 1952, by H. G. Lauterbach, but the manner of preforming them is not critical, and many ways of forming a satisfactory batt will come to mind. Instead of subjecting the batt immediately to the retraction step employed to produce the felt-like structures claimed in the Lauterbach application, a practitioner of the present invention may form quite different kinds of products by different treatments of the batt so formed.

The following specific examples are given by way of illustration and not limitation. Unless otherwise specified the percentage figures in the specification and claims for the aqueous bath are based on the total weight of the aqueous bath.

Example I

A fibrous sponge was prepared in accordance with the following procedure:

A batt of 6 denier, 3 inch nylon staple fibers weighing about 8 ounces per square yard and about 2.3 inches thick was immersed in an aqueous bath of the following composition at 30° C.

	Parts by weight
Zinc chloride	60.0
Nitric acid	1.0
Water	39.0
	100.0

for one minute. Slight pressure was applied while the batt was wet to consolidate or condense it. The batt was washed with water to remove residual zinc chloride and nitric acid and then dried.

The dried product was about .1 to .2 inch thick and had substantially the same width and length as the original batt. It was fibrous and had the characteristics of a sponge in that it was capable of absorbing water weighing about eight times its own dry weight.

Example II

A chamois-like product was produced by subjecting the dry sponge of Example I to a pressure of about 500 p. s. i. at 110° C. for about 2 minutes.

The chamois-like product was about .04 inch thick and had the appearance and feel of chamois skin. It was capable of absorbing water weighing about 1.5 times its own weight.

Example III

A batt of nylon (polyhexamethylene adipamide) 6 denier staple fibers, 3 inches in length and weighing about

8 ounces per square yard was formed to a thickness of 1.5 inches and needled to an extent of about 50 punches per square inch from each side, which reduced the average batt thickness to about .25 inch. The needled batt was immersed for 15 seconds in a bath of 35% zinc chloride, 4.5% nitric acid and 60.5% water at 38° C. and then passed through wringer rolls at about 20 p. s. i. pressure. The compacted batt was again placed in the same solution for one minute, during which time it shrunk about 10% of the original area. It was passed through the wringer again at about 20 p. s. i. pressure. The partially fused and retracted sheet so formed was rinsed in water, and dyed in an aqueous brown dye bath. The resulting brown sheet was padded with 3:1 sulfonated castor-oil glycerine mixture and pressed two minutes at 110° C. and 500 p. s. i. pressure. The leather-like product exhibited a tear strength of 3 pounds per ounce per square yard, measured by ASTM Method D–39–49.

The permeability of the product to water vapor was 4000 g./100 m.²/hr. when measured by a modification of a test for water vapor permeability developed by the Bureau of Standards—Kanogy & Vickers, J. Res. Nat. Bur. Stds., 44, 347–62, 1950 (Apr.).

The water vapor permeability test is carried out as follows: A 3 inch diameter crystallizing dish, filled with 12 mesh calcium chloride, is covered with a membrane of the substance under test, and suspended inverted in an atmosphere of high humidity (23° C. and 90% relative humidity). The assemblage is weighed at intervals and the equilibrium rate of sorption recorded in grams of water/100 square meters of surface/hour.

A water vapor permeability value of 4000 g./100 m.²/hr. compares favorably with heavy shoe uppers which have a water vapor permeability of 2000–10,000 g./100 m.²/hr. under the above test conditions.

Additional properties of this new product are :

Thickness	.043 inch.
Tensile strength	2.5 lbs./inch/oz./sq. yd.
Scrub	9000 cycles.
Schiltknecht flex	7,500,000 cycles.
Elongation to break	82%.

The scrub test was carried out on a flexing machine, such as described in Automotive Industries 49, 1262–6. The Schiltknecht flex test was carried out on the Schiltknecht flex apparatus described in Bulletin #105, published by Alfred Suter, 200 Fifth Avenue, New York, N. Y.

The product of this example compared favorably with that of a medium grade of cowhide.

Example IV

A needle loomed nylon batt prepared as in Example III was immersed in a bath of 58.5% ferric chloride ($FeCl_3 \cdot 6H_2O$), 4.5% nitric acid and 37.0% water at 46° C. for one minute and then passed through wringer rolls at about 5 p. s. i. The batt was washed with water to remove residual ferric chloride and nitric acid after which it was dyed and dried. The dried batt was pressed at 500 p. s. i. for about two minutes at 110° C. The product was a chamois-like material capable of absorbing water weighing about 1.5 times its own weight.

Example V

A needle loomed nylon batt prepared as in Example III except that only one-third the weight of fibers were used was immersed in a bath of 35% zinc chloride, 4.5% nitric acid and 60.5% water at 25° C. for 10 seconds and then passed through wringer rolls at about 20 p. s. i. There was no appreciable change in width and length of the nylon batt. The partially compacted batt while wet was pressed at 25° C. at 500 p. s. i. for 2 minutes in contact with a previously untreated woven fabric composed of nylon (polyhexamethylene adipamide) fibers, then rinsed thoroughly in water, dyed and dried. Good adhesion was obtained between the compacted batt and the woven fabric. This product also compares very favorably with cowhide used for shoe uppers.

The woven fabric used in this example may be prepared from fibers other than nylon fibers such as cotton fibers, polyacrylonitrile fibers, etc., or from mixtures of other fibers with nylon fibers. Adhesion between the nylon batt and a fabric containing little or no nylon fibers may be improved by needle looming the composite structure before the chemical treatment.

Structures, other than woven fabrics, such as felts, may be used in place of the woven fabric in Example V.

The final pressing treatment in Example V may be modified with engraved plates to produce embossed effects on the surface of the laminated assembly.

Example VI

A needle loomed two layer batt was prepared as in Example III using one-third nylon staple fibers and two-thirds cotton fibers in each layer. This batt was immersed in a bath of 35% zinc chloride, 4.5% nitric acid and 60.5% water at 25° C. for 10 seconds and then passed through wringer rolls at about 20 p. s. i. The partially compacted batt was then pressed at 25° C. and 500 p. s. i. for 2 minutes and then rinsed thoroughly in water. The compacted batt which changed very little in area was dyed and dried. This product also compared very favorably with cowhide used for shoe uppers in water vapor permeability, tear strength and appearance.

Fibers, other than cotton, may be used in Example VI as components of a multi-layer batt for formation into a leather-like product. Also, the fibers may be randomly mixed in a single layer or ply instead of being prepared into multi-layer construction. The use of nylon fibers of 6 denier and 3 inches in staple length in the surface layer of a batt and 15 denier and 3 inches in staple length in the backing layer in the procedure of Example VI, produced a flexible leather-like product with a highly scuff-resistant surface.

The following table illustrates the range of concentration of the metal chloride (zinc chloride or ferric chloride), nitric acid and the temperature range for the aqueous bath for treating (1 minute immersion) nylon batts to produce products ranging from fluffy sponges to dense leather-like product.

Aqueous Bath			Temperature of Bath, ° C.	Approximate Area Loss (Percent Orig. Loss)	Product
Percent Metal Chloride	Percent Nitric Acid	Percent Water			
60.0	1.0	39.0	30	None	Sponge.
40.0	2.0	58.0	50	None	Do.
40.0	2.0	58.0	70	55	Leather-like.
30.0	4.0	66.0	85	70	Do.
20.0	10.0	70.0	67	60	Do.
10.0	15.0	75.0	65	65	Do.

It will be noted that the lower percentages of metal chloride in the above table require the higher percentages of nitric acid, i. e. the sum of the percentages of metal chloride and nitric acid in the aqueous bath should be at least 25%.

Chamois-like products can be made by pressing the sponge products at about 500 p. s. i. at about 110° C. for about 2 minutes.

Essentially equal results are obtained with either zinc chloride or ferric chloride ($FeCl_3 \cdot 6H_2O$) as the metal chloride within the ranges set forth above. Throughout the specification and claims, the percentage figures given for the ferric chloride are expressed as the hydrate, i. e.: $FeCl_3 \cdot 6H_2O$.

Generally reduced concentrations, temperature or time of immersion in the aqueous bath will result in a lessening of the change brought about in the batt. A treatment that is too weak will result in little or no change in the starting material; excessive conditions often will

cause the starting material to dissolve. However, judicious adjustment of the conditions to obtain the desired effect is not difficult. The pressure applied to the batt during immersion in the aqueous bath or immediately after emerging from the aqueous bath need not be particularly high; usually a pressure of about 20–100 p. s. i. will prove satisfactory. The high pressure treatment to further compact the dry product is optional except in the production of the chamois-like materials and where the treated batts are laminated to other sheet materials.

Thorough and complete washing of the batts after the metal chloride/nitric acid treatment is necessary since any free metal chloride left in the batt causes loss of fiber character, while free nitric acid causes embrittlement and discoloration during subsequent drying operations and/or aging.

In place of the sulfonated castor oil/glycerine mixture used as the softening agent in Example III, sulfonated castor oil alone, methyl-10-phenylol stearate or sulfonamides may be used as the softening agent. To further enhance the appearance and surface characteristics of the leather-like products the surface of the leather-like products may be treated by spraying with a 10%–15% aqueous solution of phenol at about 65° C.

When the fibers in the original batt are oriented more in one direction than in another, as by the effect of carding, tensile and tear strengths and flex-life of the resultant leathers show pronounced differences in the longitudinal (strong) and lateral (weak) directions.

In the preparation of leather-like products of this invention it is possible to dye the fibers before chemical treatment, so as to obtain a uniformly colored structure. This structure will not readily reveal cuts in its surface. Natural leather is dyed only on the surface; therefore a cut in the surface of the leather will stand out, objectionably, as a light spot. This is particularly in evidence in leathers used for shoe uppers.

In addition to the methods of preparation given above, another additional treatment of the fused and retracted product may be used to weaken the surface fibers and render them less likely to retain a scuff, permitting them instead to break off when subjected to sufficient abrasion. For this step, immersion in 60% aqueous zinc chloride for five seconds at 110° C. is quite satisfactory. Other strong chemical treatments may be chosen by analogy with the normal treatments given above. This kind of treatment may be desirable to harden the softer side of products showing dissimilar characteristics from one surface to another, which may be caused by unequal access to the usual reagent during processing. Sanding the after-treated product may be useful in preparing a buck-like surface. An additional method for finishing the leather-like product is by heating one surface near the melting point for a short time in a press. A thin, flexible, durable and shiny surface may be imparted to the synthetic leather in this way. The well-known abrasion resistance of nylon is a primary factor in assuring the utility of either the normal or after-treated leather-like products.

The high degree of quality control possible in preparation of sponge, chamois, and leather-like materials according to this invention is a clear advantage over the formation of natural products. No particular limit exists on the external dimensions of the products of this invention. The well-known chemical stability of nylon is a further recommendation for these products. Many other advantages of their manufacture and use will be readily apparent. The leather-like materials alone are useful in

a wide range of household and industrial applications, including shoe uppers, upholstery, suitcases, game balls, harnesses, many forms of apparel, machine belting, and coverings for working surfaces, to name but a few. As illustrated in Example V the materials can be embossed to provide simulated grain or novel effects. Many uses for the intermediate products in the formation of finished articles also are obvious.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. The process of forming a fibrous structure which comprises forming a batt of nylon fibers, treating said batt with an aqueous solution comprising 10% to 60% a metal chloride and 1% to 15% nitric acid, said metal chloride being a member of the group consisting of zinc chloride and ferric chloride, said aqueous solution being at a temperature of 30° C. to 85° C., the sum of the percentages of metal chloride and nitric acid being at least 25%, pressing said batt while wet with said solution, washing the batt substantially free of unreacted metal chloride and nitric acid and drying.

2. The process of forming a fibrous chamois-like structure which comprises forming a batt of nylon fibers, treating said batt with an aqueous solution comprising 10% to 60% a metal chloride and 1% to 15% of nitric acid, said metal chloride being a member of the group consisting of zinc chloride and ferric chloride, said aqueous solution being at a temperature of 30° C. to 85° C., the sum of the percentages of metal chloride and nitric acid being at least 25%, pressing said batt while wet with said solution, washing said batt free of unreacted metal chloride and nitric acid, drying said batt, and pressing and heating said dry batt to reduce its thickness.

3. The process of claim 2 in which the aqueous solution contains about 35% zinc chloride, about 4.5% nitric acid and which has a temperature of about 38° C.

4. The process of claim 2 in which the dry pressed product is treated with a softening agent.

5. The process of claim 2 in which the aqueous solution contains about 35% ferric chloride and about 4.5% nitric acid and which has a temperature of about 38° C.

6. The process of forming a fibrous structure which comprises forming a batt of nylon fibres, treating said batt with an aqueous solution comprising 10–60% metal chloride and 1% to 15% nitric acid, said metal chloride being a member of the group consisting of zinc chloride and ferric chloride, said aqueous solution being at a temperature of 30° C. to 85° C., pressing said treated batt while wet with said solution against an untreated fabric comprising nylon fibers whereby the treated batt and untreated fabric are bonded together, washing said assembly free of metal chloride and nitric acid, and drying, the sum of the percentages of metal chloride and nitric acid being at least 25%.

7. The product of the process of claim 6.

References Cited in the file of this patent

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OTHER REFERENCES

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