

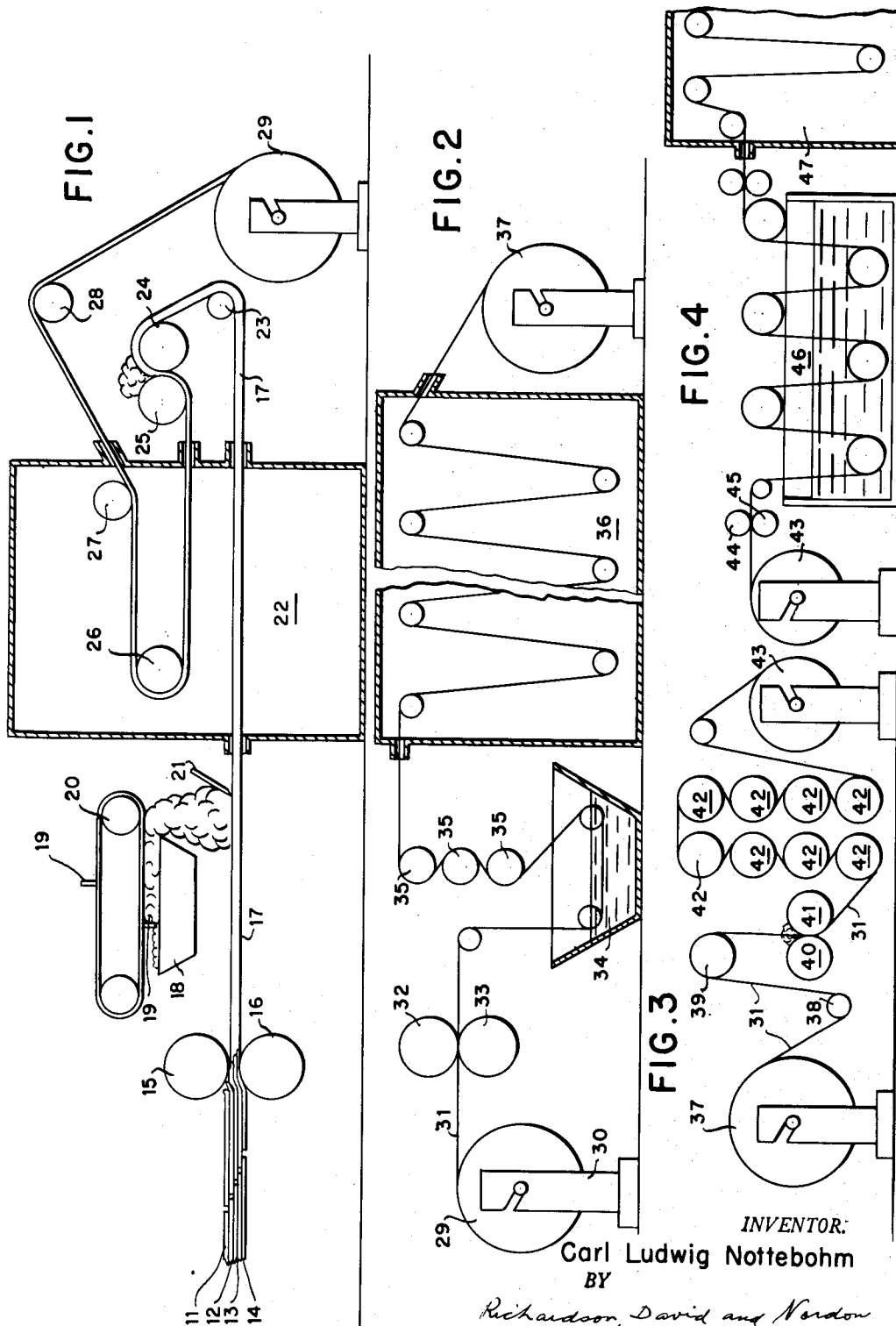
Oct. 4, 1955

C. L. NOTTEBOHM
ABSORBENT FIBROUS SHEET MATERIAL AND
PROCESS OF MANUFACTURING THE SAME

2,719,795

Filed Dec. 22, 1951

4 Sheets-Sheet 1



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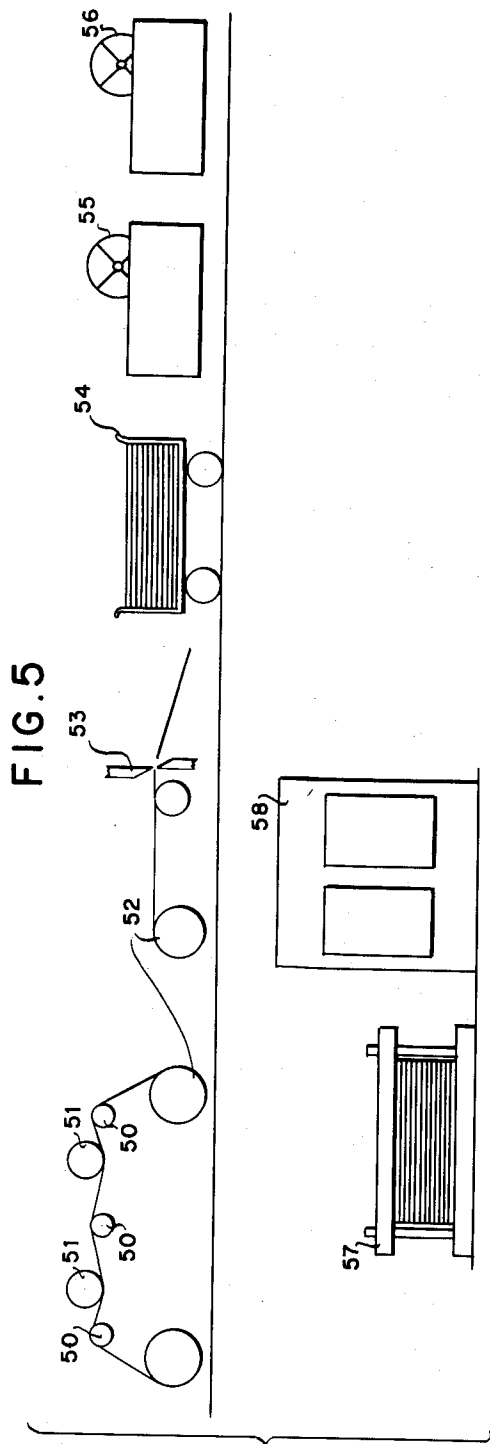
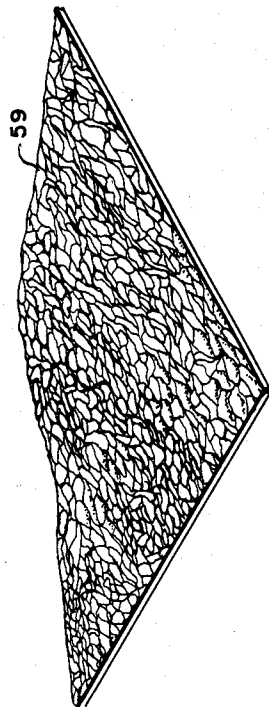


FIG. 11



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FIG. 6

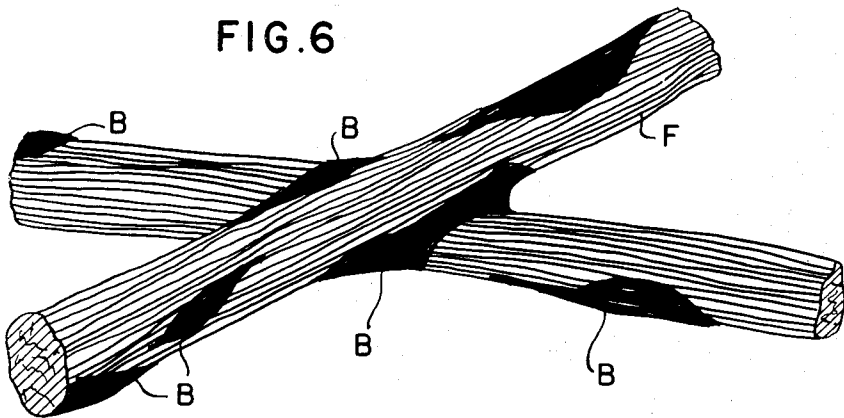


FIG. 7

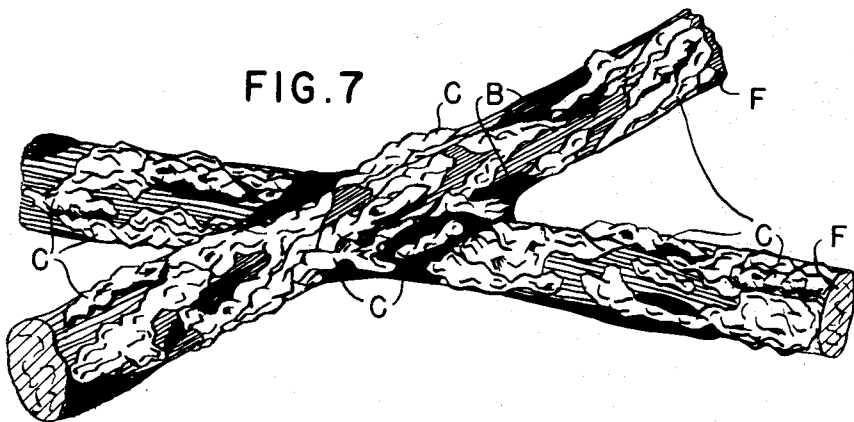
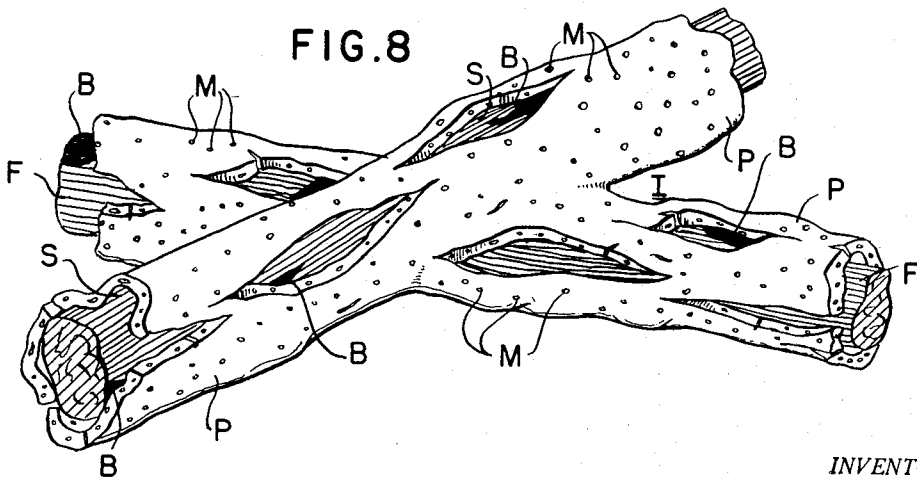


FIG. 8



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4 Sheets-Sheet 4

FIG. 10

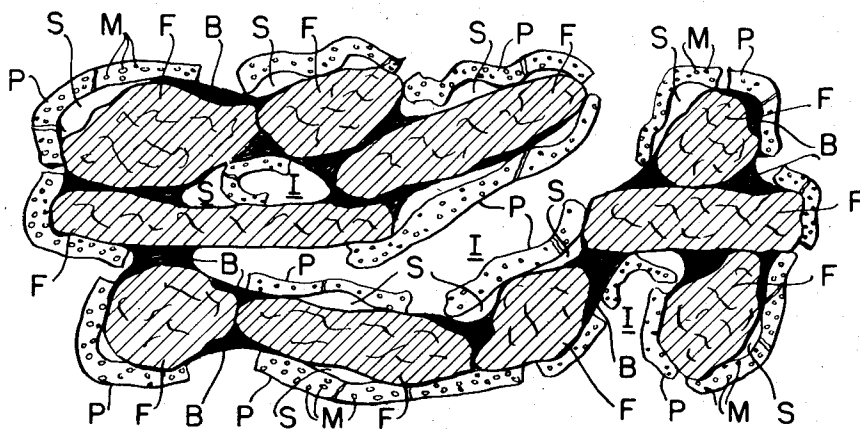
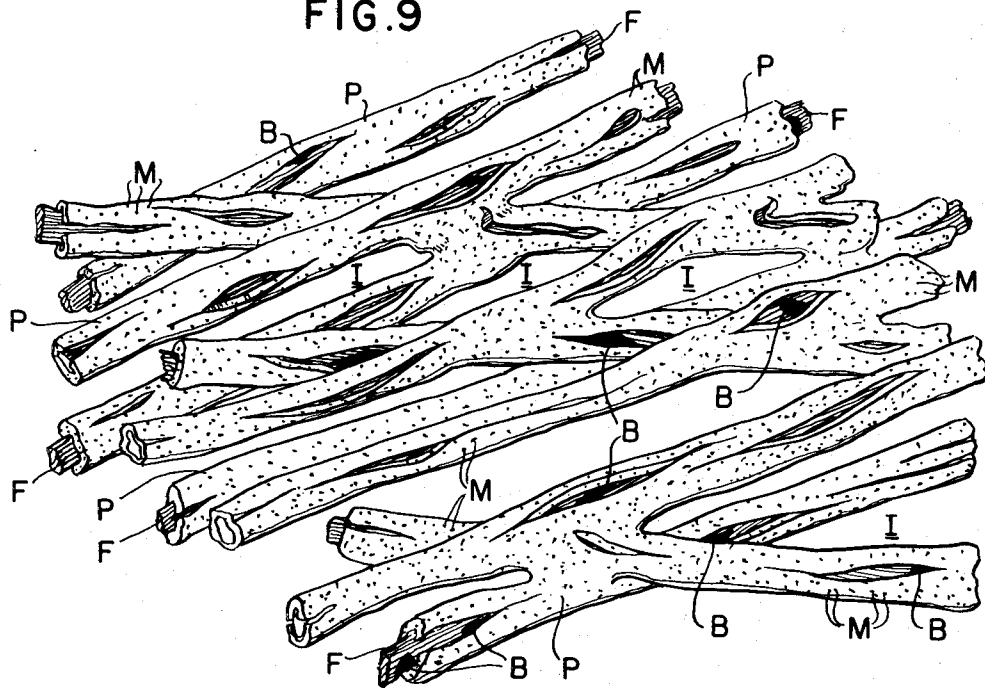


FIG. 9



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2,719,795

ABSORBENT FIBROUS SHEET MATERIAL AND PROCESS OF MANUFACTURING THE SAME

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Application December 22, 1951, Serial No. 262,943

Claims priority, application Germany October 1, 1948

20 Claims. (Cl. 117—11)

My invention relates to porous, fabric or leather-like fibrous sheet material of high absorptivity and to a process for manufacturing such material. The present application is a continuation-in-part of my co-pending U. S. patent application Ser. No. 102,424, filed on June 30, 1949.

One object of my invention is to produce a porous, fabric or leather-like, fibrous sheet material of high water absorptivity.

Another object of my invention is to produce an absorbent, fabric or leather-like fibrous sheet material which consists of an open skeleton of intermingled, fine, cardable, water swellable fibers arranged in random or polyposed directions, said skeleton having adhering to the fibers vulcanized, flexible, water insoluble binder particles uniformly distributed throughout the fiber skeleton and cementing the fibers together at their crossing points without preventing the access of water to the interstices between the fibers or to the swellable fibers themselves, and additional microporous binder particles reinforcing the sheet formed.

Still another object of the invention is to produce a porous, fabric or leather-like sheet material of the type described which combines with a high absorptivity for good water abrasion resistance, tensile strength and tear resistance.

A still further object of the invention is the production of a porous, water absorbent sheet material which is substantially uniform throughout its length with respect to its thickness, its weight per square m., its surface, its water-absorbent properties and its fiber and binder content, and which is free from irregularities and weak or defective spots.

Still another object of the invention is to provide a process whereby a variety of highly water absorbent, porous sheet materials can be produced which may have a thickness from about 0.3 to about 2.5 mm. and a weight from about 85 g. to 350 g. per square m., and which may be adapted to a variety of purposes, e. g. as hand towels, dish towels, window leather, car washing cloth, polishing cloth, etc.

One of the specific objects of the invention is to produce a fibrous sheet material which has substantially the same absorptivity, the same appearance and the same feel as natural chamois leather, while exhibiting a better heat resistance, greater durability and less sensitivity to organic solvents.

These and other objects, which will appear more clearly as the specification proceeds, are accomplished according to the present invention by a process which uses as starting material a loose fleece of intermingled, polyposed, fine, cardable fibers containing at least a major proportion of fibers capable of swelling in water.

Suitable cardable fibers are fibers which upon passage through a carding machine will form a web wherein the fibers are held together, as opposed to non-cardable fibers such as horse hair, coconut fibers, and the like.

Suitable swellable fibers are, for instance, cotton, jute,

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rayon and wool. Fibers, such as ramie, which are not swellable in water, and particularly the non-swellable synthetic fibers such as superpolyamide fibers, glass fibers, etc., should not be present in major proportions.

Preferably, the starting material for my process is a fiber fleece which has a weight of about 45 g. to about 300 g. per square m.

Best results are obtained with fleeces containing a plurality, e. g., 6 to 18 or more thin webs of fibers laid upon one another, each web having a thickness of about 0.12 to about 1.0 mm. and weighing from about 10 g. to about 50 g. per square m. Preferably, adjacent webs are arranged at an angle with respect to each other.

According to the present invention, a fiber fleece of the type described is first prestabilized by a treatment including the step of applying to the fleece a dilute vulcanizable latex and drying without pressure to cause deposition of about 26 to 133 parts by weight of solid binder particles per 100 parts by weight of fibers throughout the fleece, and mainly at the crossing points between the fibers, in such a manner that the fibers are cemented together at their crossing points probably without being completely encased by the binder and with retention of numerous relatively large interstices between the fibers and a sufficient stabilization of the resulting material to prevent it from being deformed or destroyed by stretching during the subsequent stages of my process. A lengthwise stretching of the fleece up to about twice its original length and a corresponding reduction in fiber weight per square m. by about 20% to 50% may occur during the prestabilization of the fleece.

The term "vulcanizable latex," as used in the present specification and claims includes generally the natural and synthetic rubber latices yielding, on drying, filmy, water-insoluble precipitates which can be elastically stabilized by vulcanization. Latices or dispersions of natural or synthetic vulcanizable rubber may be used which contain, in addition to the vulcanizable binder solids, suitable quantities of wetting agents, vulcanizing agents, vulcanization accelerators, antioxidants and the like. Dispersions of synthetic rubbers which have a negligible tendency toward ageing, such as butadieneacrylonitrile polymers, butadienestyrene polymers and chloroprene, have given excellent results. Mixed chloroprene dispersions containing per 100 parts b. w. of elastically vulcanizable binder solids up to about 25 parts b. w. of thermo-plastic binder solids such as polystyrene, polyvinylchloride, polyvinylacetate or mixtures thereof and the like may also be employed.

According to a preferred embodiment of the invention, the prestabilization of the fiber fleece is accomplished by pressing into the fleece through at least one surface thereof a stable, flowable latex foam. Such latex foam may comprise from about 2 to about 8 volume parts of air per volume part of binder liquid, and the latter may contain from about 14% to about 35% by weight of vulcanizable binder solids.

It has been found that the latices to be used for the prestabilization of the fleeces should be substantially free of fillers, such as starches or water soluble salts, which can subsequently be washed out to form micropores, because the presence of such fillers, on the one hand, increases the viscosity of the latices to such an extent that it becomes practically impossible to produce a stable foam or to obtain in any other manner a satisfactory impregnation of unstabilized fleeces, while, on the other hand, binder particles deposited from binder liquids containing such fillers exhibit, after washing out of the pore formers, insufficient mechanical strength to effect by themselves a reliable and uniform stabilization of the fleeces.

It has, however, been found most advantageous to

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add to the latices, particularly if the prestabilization is effected by means of latex foams, a very substantial amount of wetting agents. Up to about 60 parts by weight of wetting agents per 100 parts by weight of binder solids have given excellent results. The wetting agents not only facilitate the conversion of the latices to foams, the penetration of the binder into the fleeces and the subsequent washing of the sheet material formed but, moreover, when the finished sheet is washed, the previously deposited wetting agent solids are eliminated with the result that the internal structure of the vulcanized binder particles seems to be softened without any appreciable reduction in their mechanical strength, and the sheet material obtained is pliable and soft.

Optimum results are obtained if the initial impregnation of the fleece is effected by the method described in my copending U. S. patent application Ser. No. 262,941, filed December 22, 1951, which is a continuation-in-part of my U. S. patent applications Ser. Nos. 102,423 and 102,425, filed on June 30, 1949. In this method a loose fleece of fibers is first treated superficially on one side to produce a light surface cohesion and is then through impregnated by pressing a latex foam into the opposite untreated surface of the fleece and drying without pressure.

The intermediate products, obtained from the prestabilization treatment in the form of fibrous sheet materials, display considerable stability and high water absorptivity. It is believed that the binder solids are largely concentrated at the crossing points between adjacent fibers and, thus, relatively large interstices are maintained between the fibers and substantial portions of the fiber surfaces are not covered by binder material so that water brought into contact with the sheet material has substantially free access to the swellable fibers and is readily absorbed by the latter. However, the prestabilized sheet material has a comparatively low resistance to abrasion and a tensile strength which is not more than sufficient to prevent deformation of the sheet material by stretching during the subsequent steps of my process.

According to the present invention, it has been found that it is possible to obtain a radical improvement in the abrasion resistance and tensile strength of the sheet material resulting from the prestabilization without decrease and even with a considerable increase in the water absorptivity of the material, if the prestabilized material, either before or after partial or complete vulcanization of the binder particles incorporated therein, is reinforced by pressing into it through at least one surface thereof, a vulcanizable latex in the form of a heavy, flowable aqueous suspension, preferably in the form of a paste containing, in addition to the vulcanizable binder material, a filler which, after drying and vulcanization, can be washed out to produce micropores throughout the binder solids deposited from the latex paste. It is an essential feature of the present invention that the latex paste containing the filler is embodied into the fibrous material only after the latter has been prestabilized because it is impossible to incorporate sufficient binder material containing fillers of the type desired into a loose, unstabilized fiber fleece without either destroying the fleece or eliminating all the interstices between the fibers.

The latices which may be used for the reinforcing paste impregnation are vulcanizable latices of the same type as those used for the prestabilization, but they contain, in addition to about 8% to about 20% by weight of vulcanizable binder solids per 100 parts by weight of binder solids, between about 100 parts and 275 parts by weight of a filler or pore-forming agent, which in the final impregnation is preferably selected from the group consisting of the water soluble and water solubilizable high molecular organic substances and mixtures of such organic substances with not more than about twice their weight

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of water soluble alkali metal salts. The term "water solubilizable" is used in the present specification and claims to designate such high molecular organic substances which can be easily converted from a less water soluble form to a more water soluble form, for instance, by an after-treatment with enzymes.

Starches, sugars, cellulose derivatives and similar materials are suitable organic fillers.

Sodium sulfate (Glauber's salt) and sodium chloride are preferred examples of suitable alkali metal salts, but other water soluble alkali metal salts capable of forming large crystals may be used.

A preferred mixture contains, for instance, per 100 parts by weight of vulcanizable binder solids, 90 parts by weight of a water soluble starch and 100 parts by weight of a water soluble salt.

In carrying out the reinforcing paste impregnation, it is preferable to press the latex paste into the prestabilized fleece through at least one surface thereof with a pressure sufficient to introduce into the fleece about 40 to about 160 parts by weight of solid vulcanizable binder particles per 100 parts by weight of fibers. Thereafter, the sheet material is dried again without pressure, to cause deposition, on the fibers and on the previously deposited binder material, of the solid binder particles which contain distributed therethrough the water soluble or water solubilizable fillers, numerous, relatively large interstices still being preserved in the material.

Finally, the sheet material is subjected to an elevated temperature without pressure to effect substantially complete vulcanization of all the vulcanizable binder material. During or after this vulcanization, the sheet material is treated with water to wash out the water soluble fillers, thus causing the formation of numerous micropores in the binder particles deposited from the paste.

It can thus be seen the filler or pore-forming agent is a material which is normally solid and which is heat stable under the conditions of vulcanization. As previously described this material must also be water-soluble or water-solubilizable so that in its solid form it can be washed out from the sheet material after vulcanization.

According to one embodiment of the invention, vulcanization is effected by means of hot air, and the water soluble fillers are washed out with hot water after vulcanization.

According to another embodiment of the invention, vulcanization and washing out of the fillers are accomplished substantially simultaneously by passing the impregnated sheet material through a hot water bath having a temperature of about 80 to 100° C.

According to still a further modification, final vulcanization is effected in a salt solution which may have a temperature as high as about 105° C. to 110° C. In this case, a separate washing out step is preferably employed after completion of the vulcanization.

According to a preferred modification of the invention, the sheet material resulting from the paste impregnation is cut into short pieces. It is vulcanized in a paddle bath in which the short pieces of sheet material are continuously beaten by the paddle during the vulcanization. It has been found that this treatment produces on the sheet material obtained according to the present invention a surface grain which is very similar to the surface grain of natural chamois leather.

If, on the other hand, smooth surfaces are desired, the material is vulcanized and washed or washed after vulcanization in a continuous full width washing machine.

The resulting smooth-surfaced material may be cut into pieces and treated in a hot paddle bath to produce a leather-like surface grain.

The final product of my process is a porous sheet structure reinforced by microporous vulcanized binder particles which also act as a protective coating on the fibers. By comparison with the prestabilized material, its tensile

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strength and abrasion resistance are greatly increased, and its absorbent properties are not only maintained, but even improved, because, due to the prestabilization of the material, numerous relatively large interstices are retained between the fibers, and the micropores in the outer coating act as capillary suction tubes to transport any water contacting the sheet rapidly into the interstices between the fibers and to the swellable fibers themselves.

The water absorbent properties of the sheet material obtainable according to the process described heretofore may be further improved, according to a preferred embodiment of my invention, by subjecting the prestabilized sheet material, prior to the paste impregnation thereof, to an intermediate treatment which comprises applying to the prestabilized material an aqueous solution of a pore-forming agent capable of forming, on drying, relatively large water soluble deposits, and then drying the material. Solutions of alkali metal salts, such as Glauber's salt or sodium chloride, and of organic water soluble substances, such as polyvinyl alcohol or sugar solutions, have been found to be useful for this purpose.

When a sheet treated in this manner is thereafter subjected to a paste impregnation as described above and washed after complete vulcanization, the salt crystals or other precipitated water soluble particles are washed out together with the water soluble fillers present in the coating deposited from the paste impregnation. This leaves between the outer surfaces of the fibers and of the first binder particles on the one hand, and the inner surfaces of the microporous coatings on the other hand, hollow spaces which are in direct communication with the interstices between the fibers and with the micropores.

A desired dye may be incorporated in my material at any stage of its production. According to one embodiment of the invention, a suitable dye is added, for instance, to the salt bath through which the sheet material is passed prior to the paste impregnation, but it is also possible to include a dye in the vulcanizing bath or to effect dyeing as a separate step after completion of the impregnation.

Particularly in the case where an intermediate salt impregnation is carried out between the foam impregnating step and the paste impregnating step, it has been found practical to subject the sheet material, before vulcanization and prior to the washing out of the fillers and salt crystals, to a surface grinding in order to loosen up the smooth bonded surfaces of the sheets in such a manner that some fiber particles are caused to project from the bonded surfaces. This gives to the product a soft hand similar to that of chamois leather and increases the absorptivity of the material due to the wick action of the loose fiber ends.

The finished sheet material according to my invention may weigh about 85 g. to about 350 g. per sq. m., have a thickness of about 0.3 to 2.5 mm. and contain from about 45% to 75% by weight of vulcanized binder material. It is highly water absorbent, tough, flexible and abrasion resistant.

Several modifications of the process according to my invention and some of the products obtainable by such process are illustrated by way of example in the accompanying drawings in which:

Figs. 1 to 4 are flow diagrams illustrating a process of producing an absorbent, fibrous sheet material according to one embodiment of the invention,

Fig. 1 showing the prestabilization stage;

Fig. 2 the salt impregnation stage;

Fig. 3 the paste impregnation stage; and

Fig. 4 the final vulcanization and washing stages of the process.

Fig. 5 is a flow diagram illustrating a modification of the final vulcanization and washing stages of the process according to the invention.

Figs. 6 to 8 are greatly enlarged, somewhat diagram-

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matic, perspective views of two crossing fibers of a fiber fleece at the end of three successive stages, respectively, of the process according to my invention,

Fig. 6 showing the fibers at the end of the prestabilization stage;

Fig. 7 showing the fibers after completion of the salt impregnation; and

Fig. 8 showing the fibers after completion of the paste impregnation.

Fig. 9 is a perspective view on an enlarged scale showing diagrammatically the mutual relationship of a number of fibers in the completed sheet material;

Fig. 10 is a greatly enlarged cross section through an absorbent fibrous sheet according to the present invention, and

Fig. 11 is a perspective view of a piece of synthetic chamois leather produced according to the invention and showing the peculiar surface grain imparted to the material by my process.

Referring now to the drawings and first to Figs. 1 to 4, a preferred modification of the process according to the present invention comprises the following stages:

In the prestabilization stage shown in Fig. 1, a fiber fleece is built up by laying upon one another, for instance, four thin webs 11, 12, 13 and 14 of fine, cardable, water swellable fibers arranged in random, i. e., in a plurality of intersecting or polyposed directions. Preferably, adjacent webs are disposed at an angle to each other. The resulting multi-layer material is passed between heated rollers 15 and 16, where it is compressed to form a light, loosely coherent fleece 17. Simultaneously, the fleece is slightly stretched in lengthwise direction.

A foam of a liquid binder material, such as rubber latex, is produced in a foam trough 18, and successive quantities of foam are pushed by blades 19, mounted on an endless conveyor belt 20, over the edge of the foam trough 18 whence they drop on the upper surface of the fleece 17. As the fleece 17 travels on, the foam is spread uniformly on the surface of the fleece 17 by means of a stationary doctor blade 21. The fleece, now carrying on its upper surface a very light surface coating of foamy binder material, is next passed through a drier chamber 22 where the foam is caused to collapse and to solidify in very thin, filmy particles, thus producing a light surface cohesion on one side of the travelling fleece without any appreciable loss of porosity. The pretreated fleece 17 is next passed over a guide roller 23 and hence over one of a pair of pressure rollers 24, 25 in such a way that the pretreated surface of the fleece travels in contact with the surface of the roller 24.

A vulcanizable liquid binder, such as rubber latex, in the form of a thick, flowable foam having approximately the consistency of a heavy cream, is placed on the untreated surface of the fleece in the nip of the two rollers 24, 25. This foam is pressed into the fleece at a predetermined pressure as the fleece traverses the constricted passage between the two rollers 24, 25. The pressure exerted by the pressure rollers 24, 25 upon the foam and the fleece can be regulated to cause a complete and uniform penetration of the fleece by the foam, with incorporation into the fleece of a predetermined quantity of solid binder material. Due to the pressure of the rollers 24, 25, some of the foam cells are destroyed and the fleece is reduced in thickness, but numerous, relatively larger interstices are retained between the fibers. The impregnated fleece runs partly around the second pressure roller 25 and then re-enters the drying chamber 22, where it is guided over rollers 26 and 27. During the drying operation, which takes place without pressure, the remaining foam cells collapse and the solid binder material contained in the foam and in the liquid forming the foam, is precipitated in the form of small, filmy particles on the fibers of the fleeces and mainly at the crossing points between adjacent fibers without filling the interstices between the fibers and probably without completely encasing the fibers. The resulting sheet ma-

terial is guided out of the drying chamber 22 over a roller 28 and wound upon a reel 29.

In the course of the impregnating and drying steps described heretofore, the fleece is stretched longitudinally to about five fourths to twice its original length and the weight of fibers per square m. is correspondingly reduced by about 20% to 50%. The amount of stretch increases with the speed at which the material is passed in a continuous operation through the various impregnating and drying stages.

The process according to the preferred embodiment of my present invention, as described so far, is identical with that described and claimed in my copending U. S. patent application Ser. No. 262,941, filed December 22, 1951, which is a continuation-in-part of my co-pending U. S. patent applications Ser. Nos. 102,423 and 102,425, both filed on June 30, 1949.

This process produces a pre-established fibrous sheet material in which the individual fibers F appear to be bonded together at their crossing points by solid filmy binder particles B, while relatively large portions of the fiber surfaces are left uncoated and numerous relatively large interstices are retained between the fibers F (see Fig. 6).

In the next stage of the preferred embodiment of the present invention, illustrated in Fig. 2, reel 29, which carries the pre-established sheet material, is placed on a frame 30, and the sheet material 31 is passed between rollers 32, 33 and then through a salt bath 34. After leaving the salt bath, the sheet material is guided over squeezing rollers 35 and then through a drying chamber 36, whereupon it is wound on another reel 37. During its passage through the drying chamber 36, the water in the salt solution evaporates, leaving a deposit of salt crystals C on the fibers F and on the initial filmy binder particles B cementing the fibers together (see Fig. 7).

In the paste impregnation step (Fig. 3) the sheet material 31 is passed from the reel 37 over guide rollers 38, 39 and then vertically downwardly between two pressure rollers 40 and 41. A vulcanizable binder material of creamy consistency and containing finely dispersed therein a filler material, which subsequently can be washed out for the formation of micropores, is placed in the nip of rollers 40, 41 on both sides of the downwardly moving sheet 31 and pressed into both surfaces of sheet 31 under a pressure to accomplish a substantially uniform penetration of the sheet and the deposit of a filmy layer of binder material on a large part of the salt coated fiber surfaces with substantial preservation of the interstices between the fibers of the prestabilized fiber skeleton. After leaving the pressure rollers 40, 41, the impregnated sheet material 31 is passed over a series of drying cylinders 42, where the impregnation is dried, preferably without being completely vulcanized. Then the sheet material is wound upon a reel 43.

During the vulcanization and washing stage (see Fig. 4), the sheet material is passed from the reel 43 between a pair of rollers 44, 45, and hence through a vulcanizing bath 46 containing, for instance, water at a temperature above 80° C. In the vulcanizing bath the vulcanizable binder particles are vulcanized without pressure and simultaneously the salt crystals formed on the outer surface of the fibers and the first binder particles and under the second binder particles and the micropore forming substances in the second binder particles are washed out, leaving hollow spaces S between the fibers F and the first binder particles B on the one hand, and the second coating particles P on the other hand, and also micropores M in the second coating P (see Figs. 8, 9 and 10). When the sheet material leaves the vulcanizing bath 46, the various binder particles B, P on the fibers F have become completely vulcanized. The sheet material coming from the vulcanizing bath 46 is finally passed through drying chamber 47.

According to Fig. 5, the material coming from reel 43 is treated in a somewhat different manner. It is first passed between grinding rollers 50, 51 and then wound upon reel 52. The material coming from reel 52 is cut by a cutter 53 into pieces of about 1 square m. which are loaded on a car 54. When the car 54 is filled its contents are discharged into a paddle bath 55, which, in this case, serves as vulcanizing bath. Such bath may contain a salt solution at a temperature of about 105°–110° C. Vulcanization in the salt bath is substantially completed in about 20 minutes. Thereafter, the vulcanized pieces are placed into a hot water paddle bath 56 in which the water soluble particles are washed out. The material leaving the bath 56 is passed into a press 57 where the water is pressed out and a preliminary drying is effected. Drying is finally completed in a drying oven 58.

Due to the paddle action during vulcanization and washing, the finished material obtains a surface grain 59, as shown in Fig. 11, which is very similar to natural chamois leather.

As seen in Figs. 8 to 10, in the final product, adjacent fibers F are cemented together at their crossing points by means of solid rubber particles B. Around the fibers and outside of the solid rubber particles B there are deposits of binder material P which have substantially uniformly distributed therein micropores M. Between the fibers F and the solid binder particles B, on the one hand, and the microporous binder particles P, on the other hand, hollow spaces S are formed. These hollow spaces S and the micropores M communicate with the interstices I left between the individual fibers F in the fiber skeleton. Thus a highly porous structure is obtained which has an extraordinary absorptivity due to its numerous interconnected and intercommunicating capillary pores of various sizes and to the swelling properties of the fibers themselves.

The following specific examples may serve to illustrate the invention, but are not intended to limit its scope:

Example 1

A fiber mixture containing about 90% by weight of cotton and 10% by weight of torn rayon was formed into webs of polyposed intermingled fibers, each web having a thickness of about 0.2 mm. and weighing about 15 g. per square m.

Six such webs were laid upon one another at an angle and the resulting multilayer structure was condensed by heat and pressure with slight stretching into a fleece having a weight of about 84 g. per square m.

This fleece was treated on one surface thereof with a foam containing about 10 volume parts of air per volume part of liquid, the latter consisting of a film forming aqueous binder material containing 10% by weight of vulcanizable binder solids and having approximately the following composition:

	Liquid parts by weight	Solid parts by weight
Natural Rubber latex (60%)	167	100
Sodium isobutylene naphthalene sulfonate (wetting agent) solution (50%)	20	10
Other ingredients, such as vulcanizing agents, vulcanization accelerators, antioxidants and the like (dispersions)	22	11
Softened water	791	
	1,000	

Upon drying, about 12 parts by weight of rubber (10 g. per square m.) were deposited on the treated surface of the fleece per 100 parts by weight of fibers in the fleece, thus producing surface cohesion.

Next, a foam was prepared containing three volume parts of air per volume part of liquid from a latex con-

taining about 23% by weight of vulcanizable binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Sodium isobutylene naphthalene sulfonate (wetting agent) solution (50%)	32	16
Vulcanizing agents and other ingredients (dispersions)	28	12.6
Softened water	223	
	455	

This foam was pressed into the fleece through the untreated surface thereof by means of pressure rollers, and the fleece was then dried at moderate temperature without pressure to cause precipitation of solid, filmy coating particles of rubber on the surfaces of the fibers, and mainly at the crossing points between adjacent fibers, to cement the fibers together into a relatively solid fiber skeleton having considerable interstices between the fibers. About 71 parts of solid rubber per 100 parts by weight of fibers were incorporated into the fleece.

The resulting sheet material was next passed through an impregnating bath for the purpose of strengthening the prestabilization. This bath consisted of a 5% dispersion of butadiene styrene polymer containing about 2.5% by weight of (about 50% by weight calculated on the weight of the binder solids) of a wetting agent, such as lauryl alcohol sulfonate. Upon drying, an additional 50 parts by weight of solid binder particles were deposited in the sheet per 100 parts by weight of fibers.

During the prestabilizing stages of the process, the fleece had been stretched lengthwise to about 140% of its original length with an accompanying reduction of 29% in the fiber weight per square m.

The resulting half material had a weight of about 162 g. per square m., of which about 60 g. were fibers, 80 g. vulcanizable binder solids and 22 g. wetting agent solids.

The prestabilized material was now ready for the paste impregnation, which was carried out as follows:

A latex paste was prepared containing about 10% by weight of vulcanizable binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex concentrate (70%)	143	100
Starch water (22%)	687	151
Vulcanizing agents and other ingredients (dispersions)	30	12
Softened water	140	
	1,000	

This paste was pressed into the prestabilized sheet material through both surfaces thereof with a predetermined pressure, and the sheet material was then dried again without pressure. As a result of the paste impregnation, about 158 parts by weight of rubber per 100 parts by weight of fibers were deposited in the prestabilized sheet, together with about 240 parts by weight of starch solids finely distributed throughout the rubber.

The material was then washed carefully at a temperature between about 80 and 85° C., for 2 to 3 hours in a continuous full width washing machine to effect complete vulcanization of all the vulcanizable binder material without pressure and simultaneous elimination of the water soluble starch particles distributed throughout the rubber solids resulting from the paste impregnation. After completion of the vulcanizing and wash-

ing operation, the material was squeezed out between rollers and dried in a drying oven.

The resulting final sheet material had a weight of about 235 g. per square m. and a thickness of about 0.8 mm. It contained about 75% by weight of solid vulcanized binder particles. Its surfaces were uniformly smooth and even. In a standard test, the material was used for the drying of a wet glass panel of 75 x 50 cm., in an air conditioned room maintained at 65% relative humidity and 21° C. The drying time required was 12 seconds, showing that the high amount of microporous rubber incorporated into the sheet produced a relatively good absorptivity. A standard abrasion test on a Schopper abrasion testing machine showed that the material had a high abrasion resistance of 2,300 revolutions.

Example 2

A fiber mixture was prepared to contain 75% by weight of cotton and 25% by weight of ramie. This mixture was formed into thin, loose webs of intermingled fibers, each having a thickness of 0.12 mm. and a weight of about 10 g. per square m. Twelve such webs were combined with pressure and a lengthwise stretch of about 5% into a fleece weighing about 114 g. per square m.

This fleece was first treated by spreading on one surface thereof a foam containing 11 parts of air for each part of liquid, the latter consisting of a 14% natural rubber dispersion of the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex concentrate (73%)	137	100
Wetting agent (40% solution)	50	20
Vulcanization agents and other ingredients (dispersions)	20	9
Softened water	504	
	711	

On drying, 8 g. per square m. (7 parts per 100 parts by weight of fiber) of vulcanizable binder solids were deposited on the surface of the fleece to produce a light surface cohesion.

Prestabilization was completed by pressing into the untreated surface of the fleece a foam containing 4 parts of air for each part of a liquid dispersion containing 24% by weight of binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex concentrate (73%)	137	100
Wetting agent (solution 50%)	36	18
Vulcanization agents and other ingredients (dispersions)	20	9
Softened water	223	
	416	

On drying, about 61 parts by weight of rubber particles were deposited in the fleece mainly at the crossing points between the fibers. Drying was effected without pressure.

The fleece had stretched about 26.5% longitudinally beyond its original length during the prestabilization with a reduction in the weight of fibers per square m., of about 21%, and the resulting half material weighed about 165 g. per square m., of which about 90 g. were fibers, 61 g. were rubber and 14 g. were wetting agent solids.

This half material was next passed through a salt bath consisting of a saturated sodium sulfate solution. Upon drying, the weight of the material rose to 317 g. per square m. of the sheet material due to the deposit of about 152

g. of salt crystals on and in the fibers and on the previously deposited binder particles.

The sheet material was then reinforced by pressing into both surfaces thereof a latex paste containing about 17% by weight of vulcanizable binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex concentrate (73%).....	137	100
Starch solution (23%).....	357	82
Glauber salt.....	82	82
Wetting agent.....	3	3
Other ingredients (dispersions).....	21	10
	600	

On drying, about 110 parts by weight of rubber in the form of coating particles having starch and salt fibers incorporated therein were deposited per 100 parts by weight of fibers, and the material weighed 578 g. per square m.

The impregnated material was washed and vulcanized as described in Example 1, whereupon, after drying, a soft, flexible, smooth-surfaced sheet material was obtained which weighed 250 g. per square m., had a thickness of 0.9 mm. and a rubber content of about 64% by weight. The drying time established by the test described in Example 1 was 9 seconds, the abrasion resistance 2000 revolutions.

Example 3

A fiber mixture containing about 75% by weight of cotton and about 25% by weight of ramie was formed into thin, loose webs of intermingled fibers having each a thickness of about 0.25 mm. and a weight of about 17 g. per square m. Eight such webs were combined cross-wise with pressure and slight stretching into a fleece having a weight of about 126 g. per square m.

A light, stiff foam containing about 12 volume parts of air per each volume part of binder liquid was spread on one surface of this fleece. The foam was prepared from a 14% dispersion of butadiene-acrylonitrile polymer having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile dispersion (37%).....	270	100
Wetting agent (solution 50%).....	66	33
Vulcanizing agents and other ingredients (dispersions).....	34	15
Softened water.....	341	
	711	

Upon drying, about 6.5 g. of vulcanizable binder solids were deposited on the surface of the fleece per square m. (5 parts by weight per 100 parts by weight of fibers), producing a light surface cohesion.

Prestabilization of the fleece was completed by pressing into the untreated surface thereof a comparatively heavy foam comprising 4 volume parts of air per volume part of liquid, the latter containing 24% by weight of binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%).....	270	100
Wetting agent (solution 50%).....	30	15
Other ingredients (dispersions).....	30	12
Softened water.....	85	
	415	

Upon drying without pressure, about 70 parts by weight of vulcanizable binder solids were deposited on the fibers throughout the fleece per 100 parts by weight of fibers, and the resulting half material, which had undergone, during the prestabilization treatment, a longitudinal stretch of about 30% beyond its original length and a reduction of fiber weight per square m. of about 23%, weighed about 185 g. per square m. and contained per square m. about 97 g. of fibers, 73 g. of vulcanizable binder solids and 15 g. of wetting agent solids.

Salt impregnation was effected by passing this half material through a 32% solution of crystalline sodium sulfate and drying without pressure. The sheet material containing the salt impregnation weighed 248 g. per square m.

After completion of the salt impregnation, the sheet material was reinforced by pressing into both surfaces thereof a binder paste containing 15% by weight of vulcanizable binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%).....	270	100
Starch solution (32.5%).....	275	90
Sodium sulfate.....	100	100
Vulcanizing agents and other ingredients (dispersions).....	21	10
	666	

After drying, which was effected without pressure, the sheet material weighed 410 g. per square m. 70 parts of vulcanizable binder solids had been incorporated into the fleece per 100 parts by weight of fibers as a result of the paste impregnation.

At this point, the material, which still contained all the salt crystals from the salt impregnation and all the fillers incorporated during the paste impregnation, was as stiff and hard as a board. In this condition, it was subjected to a surface grinding during which about 33 g. of material were lost. It was calculated that about 10 g. of this loss consisted of vulcanizable binder solids.

After grinding, the material was cut into short pieces of about 1 square m. in size, and these pieces were vulcanized and washed simultaneously in a paddle bath at a temperature of about 95° C. An organic dyestuff was added to the paddle bath to dye the material to the desired yellow color. After completion of the vulcanizing, washing and dyeing operation, the material was removed from the bath, pressed out and dried in a drying oven.

The resulting final sheet material had a weight of about 228 g. per square m. and a thickness of about 0.8 mm. It contained about 58% by weight of vulcanized binder solids. It was soft and flexible and had a very smooth surface and a high absorptivity for water. Its drying capacity, as determined by the test described in Example 1, was about 4 to 5 seconds. Its abrasion resistance was about 1100 revolutions. The material had a color and a surface grain very similar to that of natural chamois leather. In many respects it was suitable as an excellent substitute for this natural material.

Example 4

A fiber mixture containing 75% by weight of cotton and 25% by weight of nylon was formed into thin webs having each a thickness of about 0.23 mm. and weighing 16 g. per square m. Ten such webs were combined with heat and pressure accompanied by a longitudinal stretch of about 6% into a fleece weighing about 150 g. per 75 square m.

This web was sprayed on both surfaces with a 10% latex dispersion having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Wetting agent solution (50%)	4	2
Vulcanizing agent and other ingredients (dispersions)	26	9
Softened water	803	10
	1,000	

Upon drying, about 20 parts of solid rubber were deposited on the two surfaces per 100 parts by weight of fibers (15 g. per square m. on each surface) to produce a relatively strong surface cohesion.

In order to complete the prestabilization, the surface stabilized fleece was next passed through a 10% latex bath of the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Wetting agent solution (50%)	80	40
Vulcanizing agents and other ingredients (dispersions)	33	12
Softened water	720	
	1,000	

When the material emerged from this bath, it was dried without pressure to precipitate on the fibers of the fleece about 42 parts by weight of rubber solids per 100 parts by weight of fibers. During its passage through the successive prestabilization stages, the fleece had been stretched longitudinally by about 54% beyond its original length with a corresponding decrease of the fiber weight per square m. by about 35%.

The prestabilized half material contained per square m. about 97 g. of fibers, 60 g. of solid rubber and 16 g. of wetting agent solids and had a total weight of about 173 g. per square m.

Salt impregnation and dyeing were carried out simultaneously by immersing the prestabilized sheet material in a salt bath consisting of a 32% solution of sodium sulfate containing a lake dye. After removal from the salt bath and drying without pressure, the material weighed 230 g. per square m. due to the deposit of 57 g. of salt crystals per square m.

A pasty binder dispersion was prepared containing about 14.5% by weight of vulcanizable binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Starch solution (32.5%)	271	88
Crystalline sodium sulfate	126	126
Vulcanizing agents and other ingredients (dispersions)	23	10
	690	

The resulting viscous dispersion was pressed into the prestabilized sheet material through both surfaces thereof by means of pressure rollers, and the material was then dried again. The sheet material containing all the fillers and salt crystals weighed 418 g. per square m. About 62 parts by weight of vulcanizable binder solids had been incorporated into the material per 100 parts by weight of fibers as result of the paste impregnation.

The material was next passed through a bath containing an enzyme which converted the starch portion of the

filler to a more water soluble form, and vulcanization and washing were then effected simultaneously in a continuous, full width washing machine at a temperature of about 85 to 90° C.

The sheet material was finally dried and had then a weight of 217 g. per square m., a thickness of 0.7 mm. and a content of vulcanized binder solids of about 55% by weight. Both its surfaces were uniformly smooth.

Example 5

A fiber mixture containing 90 parts by weight of cotton combers and 10 parts by weight of ramie was formed into webs having each a thickness of 0.6 mm. and a weight of 32 g. per square m. Three such webs were combined crosswise with heat and pressure and slight longitudinal stretching into a fleece weighing about 90 g. per square m.

This fleece was first treated by spreading on one surface thereof a very stiff, light foam containing about 13 volume parts of air per volume part of liquid, the latter consisting of a 13% latex dispersion having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (66%)	40	27
Vulcanizing agents and other ingredients (dispersions)	15	5
Softened water	442	
	767	

On drying, about 8.5 parts of solid binder material were deposited on the treated surface per 100 parts by weight of fibers (7.5 g. per square m.) producing a light surface cohesion.

Next, a heavier foam comprising 5 volume parts of air per volume part of binder liquid was pressed into the untreated surface of the fleece in order to complete its prestabilization. This form was made from binder liquid containing 14% by weight of binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (66.6%)	30	20
Vulcanizing agents and other ingredients (dispersions)	17	6.5
Softened water	418	
	735	

On drying, about 70 parts by weight of binder solids were deposited from this foam per 100 parts by weight of fibers. Drying was effected without pressure.

The fleece had stretched lengthwise during the prestabilization treatment by about 32.5% beyond its original length and its fiber weight per square m. had correspondingly decreased by about 24.5%. The prestabilized sheet material weighed about 135 g. per square m. and contained per square m. about 68 g. of fibers, 53 g. of vulcanizable binder solids and 14 g. of wetting agent solids.

This half material was then treated with a 33% solution of sodium sulfate containing a lake dye, from which, after drying, about 45 g. per square m. of salt crystals were deposited on the fibers and the previously incorporated binder solids, raising the total weight of the sheet to 180 g. per square m.

A paste containing 15% by weight of vulcanizable

binder solids was prepared to have the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Starch solution (23%)	278	64
Crystalline sodium sulfate	100	100
Vulcanizing agents and other ingredients (dispersions)	22	9
	670	

This paste was pressed into the prestabilized, salt impregnated material through one surface thereof. After drying without pressure, about 88 parts by weight of vulcanizable binder solids had been incorporated into the sheet per 100 parts by weight of fibers as result of the paste impregnation and the weight of the material had been increased to 320 g. per square m.

The material was washed and vulcanized simultaneously in a continuous, full width washing machine at a temperature of about 90° C. for about 2 hours, then squeezed out and dried.

The finished material had a weight of 179 g. per square m. and a thickness of about 0.6 mm. It contained about 62% by weight of vulcanized binder solids. It had uniformly smooth surfaces. Its absorptivity as measured in drying time by the test described in Example 1 is 4 to 5 seconds. Its abrasion resistance was approximately 900 revolutions.

Example 6

A fiber mixture containing 90% by weight of cotton and 10% by weight of ramie was formed into webs having each a thickness of 0.15 mm. and a weight of about 12.5 g. per square m. Six webs were combined with pressure and about 7% lengthwise stretching into a fleece weighing about 70 g. per square m.

This fleece was first treated by spreading on one surface thereof a stiff, light foam containing about 13 volume parts of air per each volume part of binder liquid. The binder liquid was a 13% dispersion of synthetic rubber having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer (37%)	270	100
Wetting agent solution (50%)	60	30
Vulcanizing agents and other ingredients (dispersions)	10	4
Softened water	430	
	770	

On drying, about 13 parts by weight of binder solids per 100 parts by weight of fibers (9 g. per square m.) were deposited on the treated surface of the fleece, producing a light surface cohesion.

The surface treated fleece was next passed between a pair of pressure rollers, which operated to press into the fleece through the untreated surface thereof a binder foam containing about 6 volume parts of air for each volume part of a 23.5% binder liquid having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (50%)	30	15
Vulcanizing agents and other ingredients (dispersions)	10	4
Softened water	115	
	425	

On drying, about 69 parts by weight of vulcanizable

binder solids were deposited in the resulting sheet material per 100 parts by weight of fibers.

During the prestabilization stages of the process, the fleece was stretched longitudinally beyond its original length by about 33.3% and its fiber weight per square m. was reduced by about 25%. The prestabilized sheet material weighed about 105 g. per square m. and contained per square m. about 52.5 g. of fibers, about 43 g. of vulcanizable binder solids and about 9.5 g. of wetting agent solids.

Salt impregnation was next carried out in a 32% sodium sulfate solution containing a lake dye. After removal of the sheet from the salt bath and drying, which was effected, as in the prestabilization, without pressure, its weight had increased to 126 g. per square m., showing that 21 g. per square m. of salt crystals had been deposited in the sheet.

A binder paste was then pressed into the sheet through both surfaces thereof. This paste contained 15% by weight of vulcanizable binder solids and had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Starch solution (23%)	271	64
Crystalline sodium sulfate	100	100
Vulcanizing agents and other ingredients (dispersions)	25	9
	666	

After drying, the weight of the sheet material had risen to 238 g. per square m. 72 parts by weight of vulcanizable binder solids had been deposited in the sheet per 100 parts by weight of fibers as result of the paste impregnation.

The material was vulcanized without pressure by exposing it for several hours to a stream of hot air and then washed in a continuous, full width washing machine at a temperature of about 60° C. After drying, the finished sheet material had a weight of 133 g. per square m. and a thickness of about 0.4 mm. It contained about 60% by weight of vulcanized binder solids. Its surfaces were uniformly smooth. Its water absorptivity, as expressed in drying time in accordance with the test described in Example 1, was 4 seconds. Its abrasion resistance was 600 revolutions.

Example 7

Denatured hemp was formed into loose, light webs having each a thickness of about 0.4 mm. and a weight of about 22 g. per square m. Six such webs were combined with pressure and heat and slight longitudinal stretching into a fleece weighing about 124 g. per square m.

This fleece was first treated by spreading on one surface thereof a flowable foam containing about 9 volume parts of air per volume part of a 13% synthetic rubber dispersion of the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agents solution (50%)	40	20
Vulcanizing agents and other ingredients (dispersions)	20	8
Softened water	446	
	776	

About 6.5 parts by weight of vulcanizable binder solids were deposited on the treated surface per 100 parts by weight of fibers (8 g. per square m.) when the fleece was dried.

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Next, a heavy, creamy foam containing about 3 volume parts of air per volume part of liquid was pressed into the untreated surface of the fleece by means of pressure rollers. The binder liquid used for the preparation of the foam contained 23% by weight of binder solids and had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (66.6%)	30	20
Vulcanizing agents and other ingredients (dispersions)	20	8
Softened water	118	
	438	

On drying, about 72 parts by weight of vulcanizable solids were deposited throughout the fleece per 100 parts by weight of fibers. Drying was effected at a temperature of about 100° and continued for several hours until a substantially complete vulcanization of binder solids had occurred, without application of pressure.

During the prestabilization stages of the process, the fleece underwent a longitudinal stretch beyond its original length by about 28% and the fiber weight per square m. was reduced by about 22%. After completion of the prestabilization, the resulting sheet material weighed about 193 g. per square m. and contained per square m. about 97 g. of fibers, 76.5 g. of vulcanized binder solids and about 19.5 g. of wetting agent solids.

The prestabilized sheet material was next impregnated with a latex paste containing about 20% of vulcanizable binder solids by pressing such paste, by means of pressure rollers, into both surfaces of the sheet. The latex paste had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Starch solution (22%)	151.3	33.3
Sodium chloride	66.7	66.7
Vulcanizing agents and other ingredients (dispersions)	12	7
Softened water		
	500	

After drying, the impregnated sheet had a weight of 309 g. per square m. About 60 parts by weight of vulcanizable binder solids per 100 parts by weight of fibers had been incorporated in the sheet as result of the paste impregnation.

It was then cut into pieces of about 1 square m. each, and these pieces were vulcanized for about 30 minutes in a paddle bath containing a saturated sodium chloride solution at a temperature of about 105° C.

Directly after leaving the vulcanizing paddle bath, the material was passed without intermediate drying into a second paddle bath in which it was washed in a stream of water at about 75° C., until all the water soluble components had been washed out. Finally, the material was removed from the bath, squeezed out between rollers and dried in a drying oven.

The finished material had a weight of 231 g. per square m. and a thickness of 0.8 mm. It contained about 58.5% by weight of vulcanized binder solids. It was flexible and had excellent water absorptivity and a surface grain similar to that of natural chamois leather.

Example 8

A fiber mixture containing 90% by weight of cotton and 10% by weight of ramie was formed into loose, light webs having each a thickness of 0.25 mm. and a weight of about 17 g. per square m. Six such webs were combined with heat and pressure and light lengthwise

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stretching into a fleece weighing about 95 g. per square m.

This fleece was first given a surface impregnation by spreading on one surface thereof a light foam containing about 10 volume parts of air per volume part of binder liquid. The binder liquid consisted of a 13% latex dispersion of the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Wetting agent solution (66.6%)	15	10
Vulcanizing agents and other ingredients (dispersions)	45	19
Softened water	544	
	771	

After drying of the foam, the treated surface carried about 10 parts by weight of binder solids per 100 parts by weight of fibers in the fleece (9.5 g. per square m.) and was lightly coherent.

A foam comprising about 5 volume parts of air per volume part of liquid was then pressed by means of pressure rollers into the fleece through the untreated surface thereof. The foam was made from a dispersion containing 16% by weight of binder solids and having the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Wetting agent solution (66.6%)	31	21
Vulcanizing agents and other ingredients (dispersions)	45	19
Softened water	382	
	625	

On drying, about 31 parts by weight of rubber solids were deposited throughout the resulting sheet material per 100 parts by weight of fibers. The fleece was stretched longitudinally during the prestabilization stages of the process to about 36% beyond its original length with a corresponding reduction of fiber weight per square m. of about 26%, and the prestabilized sheet material contained per square m. about 70 g. of fibers, about 29 g. by weight of solid rubber and about 6 g. of wetting agent solids, the total weight of the material being 105 g. per square m.

The material was next treated with a 30% solution of Glauber salt and dried, causing deposition of 63 g. of salt crystals per square m.

The sheet material, which now weighed 168 g. per square m., was next treated with a latex paste which was pressed into both surfaces of the sheet. This paste contained about 10.5% by weight of solid rubber and had the following composition:

	Liquid parts by weight	Solid parts by weight
Natural rubber latex (60%)	167	100
Starch solution (23%)	435	100
Methyl cellulose (21.5%)	130	28
Glauber salt	128	128
Vulcanization agents and other ingredients (dispersions)	93	36
	953	

After drying of the paste impregnation, 72 parts by weight of vulcanizable binder solids had been deposited per 100 parts by weight of fibers and the weight of the sheet was 346 g. per square m.

The sheet material was then washed for 2 hours in a continuous, full width washing machine at a temperature of about 90 to 95° C. and finally squeezed out and dried.

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The finished material had a weight of 149 g. per square m. and a thickness of 0.5 mm. It contained 54% by weight of natural rubber particles. Its surfaces were uniformly smooth. Its absorptivity, as measured in time by the test described in Example 1, was 4 to 5 seconds. Its abrasion resistance was about 700 revolutions.

Example 9

Pure wool was formed into a single web of polyposed, intermingled fibers, said web having a thickness of about 1 mm. and weighing about 50 g. per square m.

This web was passed between pressure rollers, causing it to stretch lengthwise by about 10% and, then, it was sprayed on both surfaces with a 15% latex dispersion having the following composition:

	Liquid parts by weight	Solid parts by weight
Neoprene latex (60%)	100	60
Vulcanizing agents, accelerators and antioxidants (dispersions)	20	8
Softened water	280	
	400	

The fleece was dried to produce surface cohesion. After drying, it contained about 33 $\frac{1}{3}$ parts by weight of rubber disposed on the surfaces of the fleece per 100 parts by weight of fibers (7.5 g. per square m. on each surface).

A foam was prepared to contain 8 volume parts of air per volume part of a 35% latex having the following composition:

	Liquid parts by weight	Solid parts by weight
Neoprene latex (60%)	583	350
Wetting agent solution (50%)	210	105
Vulcanizing agents and other ingredients (dispersions)	50	29
Softened water	148	
	1,000	

The foam was pressed into the fleece through both pretreated surfaces thereof by means of pressure rollers, and the fleece was then dried at a moderate temperature without pressure to cause precipitation of filmy coating particles on the surfaces of the fibers and mainly at the crossing points between adjacent fibers. About 80 parts by weight of solid binder material were incorporated into the fleece per 100 parts by weight of fiber.

Next the fleece was inserted for two hours into water having a temperature of about 85° C., to effect a vulcanization of the binder solids deposited on the fibers and a washing out of the wetting agent solids. At the end of this period, the resultant sheet material was removed from the bath and dried on drying cylinders.

The intermediate sheet material, which was about 50% longer than the original web, and contained about $\frac{2}{3}$ of the original weight of fibers per square m. had a weight of about 64 g. per square m., of which about 30 g. were fibers and 34 g. were vulcanized binder solids.

This intermediate material was then treated by pressing into both surfaces thereof an aqueous paste containing about 15% by weight of a vulcanizable binder material and having the following composition:

	Liquid parts by weight	Solid parts by weight
Neoprene latex (60%)	250	150
Starch solution (32.5%)	461	150
Glauber salt	150	150
Vulcanizing agents and other ingredients (dispersions)	139	53
	1,000	

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After drying without pressure, about 80 parts by weight of vulcanizable binder solids per 100 parts by weight of fibers had been incorporated into the sheet as result of the paste impregnation, and the weight of the sheet was 136 g. per square m. The neoprene particles introduced into the sheet during the paste impregnation were vulcanized by passing the sheet through a continuous, full width washing machine containing a saturated sodium chloride solution at a temperature of about 108° C. The material was then dried and cut into pieces of about 1 square m. each which were treated in a paddle bath at about 80° C. to effect a washing out of the fillers incorporated with the neoprene deposits resulting from the paste impregnation. Finally, the sheet was squeezed out and dried.

The final product weighed 88 g. per square m., had a thickness of about 0.3 mm. and contained approximately 66% by weight of solid vulcanized binder particles. It had a uniform, leather-like surface grain.

Example 10

Spun rayon was formed into thin webs having each a thickness of about 0.15 mm. and a weight of 13 g. per square m. Eighteen such webs were combined with pressure and heat, accompanied by a light longitudinal stretching, into a fleece weighing about 222 g. per square m.

This fleece was first treated by spreading on one surface thereof a light, stiff foam containing about 12 volume parts of air per volume part of a 13% binder dispersion having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene styrene polymer dispersion (36%)	278	100
Wetting agent solution (50%)	60	30
Vulcanizing agents and other ingredients (dispersions)	25	10
Softened water	407	
	770	

When the foam was dried, about 4 parts by weight of binder solids were deposited on the treated surface per 100 parts by weight of fibers in the fleece, (9 g. per square m.), producing a light surface cohesion.

A thick, creamy flowable foam was then prepared containing two volume parts of air per volume part of binder liquid. The latter was a 23% dispersion of the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene styrene polymer dispersion (36%)	278	100
Wetting agent solution (50%)	60	30
Vulcanizing agents and other ingredients (dispersions)	25	10
Softened water	72	
	435	

This foam was pressed by means of pressure rollers into the untreated surface of the fleece, and the fleece was then dried, causing deposition of about 46 parts by weight of vulcanizable binder solids per 100 parts by weight of fibers. Drying was effected in a drying chamber at a temperature of about 100° C., for about 25 minutes to cause a light pre-vulcanization of the vulcanizable binder particles. During the prestabilization treatment, the fleece was stretched longitudinally by about 26.5% beyond its original length while its fiber content per square m. was reduced by about 21%.

The resulting half material weighed 290 g. per square m. and contained per square m. 176 g. of fibers, 88 g. of solid binder material and 26 g. of wetting agent solids.

Salt impregnation was then carried out by immersion

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of the half material in a saturated solution of sodium chloride which contained a small quantity of finely distributed undissolved salt. A dye was added to the salt bath to impart to the final product the desired yellow coloration corresponding to that of natural chamois leather. After leaving the salt bath, the sheet material was dried to cause a deposit of salt crystals on the surface of the fibers and on the previously deposited binder particles. About 150 g. of salt crystals were deposited per square m. of the sheet material, raising the weight of the sheet material to 440 g. per square m.

Thereafter, the sheet material was passed vertically downward between a pair of pressure rollers having their axes disposed in a common horizontal plane, and an aqueous pasty dispersion of vulcanizable binder solids was pressed into both surfaces of the prestabilized sheet. The paste had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene styrene polymer dispersion (36%)	278	100
Cornstarch solution (32.5%)	274	90
Glauber salt	50	50
Vulcanizing agents and other ingredients (dispersions)	36	12
Softened water	62	
	700	

The total solid content of the dispersion was about 35% by weight and its content of vulcanizable binder solids was about 14% by weight. After drying of the paste impregnation on drying cylinders, the sheet material had a weight of 608 g. per square m. About 40 parts by weight of vulcanizable binder solids had been incorporated into the sheet per 100 parts by weight of fibers during the paste impregnation stage.

Thereafter the material was subjected to a surface grinding which produced a smooth, even and fiber free surface, while reducing the weight of the material by about 30 g. per square m.

The sheet was washed in a continuous, full width washing machine for about two hours at a temperature of approximately 95° C., and then dried, cut into pieces of about 1 square m. each, washed again in a paddle bath for 30 minutes at 85° C., and finally dried again.

The finished material had a weight of about 318 g. per square m., a thickness of about 1.5 mm. and contained about 47% by weight of vulcanized binder solids. It had a surface grain similar to that of natural chamois leather.

Example 11

A fiber mixture containing 80% by weight of cotton and 20% by weight of wool was formed into loose, light webs having each a thickness of about 0.4 mm. and a weight of about 19 g. per square m. Six such webs were combined with pressure and slight longitudinal stretching into a fleece, weighing about 105 g. per square m.

The fleece was first treated by spreading on one surface thereof a foam containing about 10 volume parts of air per each volume part of an 8% aqueous binder dispersion having the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (50%)	54	27
Vulcanizing agents and other ingredients (dispersions)	21	7
Softened water	905	
	1,250	

Upon drying, about 4.5 parts by weight of vulcanizable

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binder solids per 100 parts by weight of fibers (5 g. per square m.) were deposited on the treated surface of the fleece, producing a light surface cohesion.

Next, a heavier foam containing about 5 volume parts of air per volume part of a 14% aqueous binder dispersion was pressed by means of rollers, at moderate pressure and relatively low speed, into the untreated surface of the sheet. The binder dispersion had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (50%)	100	50
Vulcanizing agents and other ingredients (dispersions)	21	7
Softened water	309	
	700	

When the foam was dried without pressure, about 21.5 parts by weight of vulcanizable binder solids were deposited throughout the fleece per 100 parts by weight of fibers.

The fleece was stretched lengthwise during the prestabilizing stages of the process to about 125% of its original length with reduction in its fiber weight per square m. of about 20%, and the prestabilized sheet material contained per square m. 84 g. by weight of fibers, 22 g. by weight of vulcanizable binder solids and 10 g. of wetting agent solids, the total weight of the sheet at this point being 116 g. per square m.

This half material was next treated with an 8% solution of polyvinyl alcohol and then dried. About 12 g. of water soluble solids were deposited per square m., raising the weight of the sheet to 128 g. per square m.

Thereafter, the sheet material was treated with an 8% aqueous dispersion of a vulcanizable binder material in the form of a thin paste which was pressed into both surfaces of the sheet and which had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Starch solution (32.5%)	275	90
Sodium sulfate	100	100
Vulcanizing agents and other ingredients (dispersions)	25	10
Softened water	580	
	1,250	

After drying, the material weighed about 346 g. per square m. About 70 parts by weight of vulcanizable binder solids had been incorporated per 100 parts by weight of fibers during the paste impregnation.

The material was washed in a continuous, full width washing machine at a temperature of about 90° C., for approximately 2½ hours and then dried.

The final sheet material had a weight of 165 g. per square m., a thickness of about 0.7 mm. and contained about 49% by weight of vulcanized binder particles. Its surfaces were uniformly smooth.

Example 12

A fiber mixture containing 50% by weight of cotton and 50% by weight of rayon was formed into loose, light webs having each a thickness of about 0.5 mm. and a weight of about 26 g. per square m. Twelve such webs were combined with pressure and heat and slight longitudinal stretching into a fleece weighting about 300 g. per square m.

This fleece was first treated by spreading on one surface thereof a flowable foam containing about 10 vol-

ume parts of air per volume part of a 14% synthetic rubber dispersion of the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (50%)	120	60
Vulcanizing agents and other ingredients (dispersions)	20	10
Softened water	290	
	700	

About 3.5 parts by weight of vulcanizable binder solids were deposited on the treated surface per 100 parts by weight of fibers (10.5 g. per square m.) when the fleece was dried.

Next, a heavy, creamy foam containing about 3 volume parts of air per volume part of liquid was pressed into the untreated surface of the fleece by means of pressure rollers. The binder liquid used for the preparation of the foam contained 25% by weight of binder solids and had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (37%)	270	100
Wetting agent solution (66.6%)	90	60
Vulcanizing agents and other ingredients (dispersions)	20	10
Softened water	20	
	400	

On drying without pressure, about 72.5 parts by weight of vulcanizable solids were deposited throughout the fleece per 100 parts by weight of fibers. During the prestabilization stages of the process, the fleece, which passed rapidly through the several stages, underwent a longitudinal stretch to about double its original length and the fiber weight per square m. was reduced by about 50%. The prestabilized half material weighed about 330 g. per square m. and contained per square m. about 150 g. of fibers, 114 g. of vulcanizable binder solids and 66 g. of wetting agent solids.

The prestabilized sheet material was then treated with a 32% solution of sodium sulfate and dried, causing a deposition of 82 g. of salt crystals per square m.

The sheet material which now weighed 412 g. per square m., was next treated with a latex paste which was pressed into both surfaces of the prestabilized sheet. This paste contained about 17% by weight of binder solids and had the following composition:

	Liquid parts by weight	Solid parts by weight
Butadiene acrylonitrile polymer dispersion (60%)	133	80
Polyvinyl chloride dispersion (50%)	40	20
Starch solution (32.5%)	252	82
Sodium sulfate	82	82
Vulcanizing agents and other ingredients (dispersions)	33	12
Softened water	60	
	600	

After drying of the paste impregnation on drying cylinders, 57 parts by weight of binder solids per 100 parts by weight of fibers (86 g.) were incorporated, and the total weight of the material increased to 639 g.

The sheet material was then vulcanized in a hot air stream at approximately 120° C., for about 20 minutes and thereafter cut into pieces of about 1 square m. each and washed in a paddle bath for 30 minutes at 85° C. After removal from the paddle bath the material was squeezed out and dried.

The finished sheet material had a weight of 350 g.

per square m., a thickness of about 2.5 mm. and contained about 57% by weight of vulcanized binder solids. It had a surface grain similar to that of natural leather.

It should be understood that the foregoing examples are not intended to limit the scope of my invention, and that various modifications and changes are possible within this scope.

I claim:

1. A process for the manufacture of highly water absorbent, flexible, porous, fibrous sheet material of high tensile strength and abrasion resistance, which process comprises first prestabilizing a loose fleece of intermingled, polyposed, fine, cardable fibers containing at least a major amount of fibers capable of swelling in water, by a treatment including the steps of uniformly through impregnating such fleece with a dilute aqueous vulcanizable rubber latex and condensing the fleece to a sheet, drying the sheet without pressure to cause deposition of about 20 to about 133 parts by weight of nonporous rubber particles per 100 parts by weight of fibers throughout the fleece, and mainly at the crossing points between the fibers, in such a manner that the fibers are cemented together at their crossing points and numerous relatively large interstices are retained between the fibers in the plane of the sheet, and, thereafter, reinforcing the resulting prestabilized sheet material by pressing into it, through at least one surface thereof, a vulcanizable rubber latex in the form of a heavy, flowable aqueous suspension containing about 8% to 20% by weight of vulcanizable rubber solids, and between about 100 parts and 275 parts by weight of a filler per 100 parts of rubber solids, said filler being selected from the group consisting of a high molecular carbohydrate substance and mixtures of said carbohydrate substances with not more than about twice their weight of water-soluble alkali metal salts, drying again to cause deposition on the fibers and on the previously deposited non-porous rubber particles of additional vulcanizable rubber particles having colloidal filler material dispersed therethrough, the quantity of said coating particles being sufficient to effect a reinforcement of the fiber skeleton but insufficient to fill the interstices between the fibers, subjecting the material to an elevated temperature without pressure to effect substantially complete vulcanization of the vulcanizable rubber material, then treating the sheet material with water to eliminate the filler material, and finally drying to produce a sheet material stabilized by nonporous rubber particles and reinforced by microporous rubber coating particles and in which the micropores in the reinforcing coating particles communicate with the interstices between the fibers.

2. A process as claimed in claim 1, in which the prestabilization is carried out so as to incorporate about 26 to 85 parts by weight of vulcanizable rubber solids into the fleece per 100 parts by weight of fibers.

3. A process as claimed in claim 1, in which the rubber latex employed for the prestabilization of the fleece is substantially free of fillers of the type which can be subsequently eliminated by washing with water to form pores.

4. A process as claimed in claim 1, in which the reinforcing paste impregnation is carried out in a manner to cause incorporation of about 40 to about 160 parts by weight of vulcanizable rubber solids into the sheet per 100 parts by weight of fibers.

5. A process as claimed in claim 1, in which the starting fleece has a weight of about 45 to about 300 grams per square meter.

6. A process as claimed in claim 1, in which the carbohydrate substance of the filler incorporated into the rubber latex paste is selected from the group consisting of the water-soluble and water-solubilizable starches.

7. A process for the manufacture of highly water absorbent, flexible, porous, fibrous sheet material of high tensile strength and abrasion resistance, which process

comprises first prestabilizing a loose fleece of intermingled, polyposed, fine, cardable fibers containing at least a major amount of fibers capable of swelling in water, by a treatment including the step of uniformly through impregnating such fleece with a dilute aqueous vulcanizable rubber latex binder free from pore-forming material and condensing the fleece to a sheet, drying without pressure to cause deposition of non-porous rubber particles throughout the fleece, thereby cementing said fibers mainly at their crossing points while retaining numerous relatively large interstices between the fibers in the plane of the sheet and stabilizing the sheet to form a prestabilized sheet material, second, applying to said prestabilized sheet material an aqueous solution of a pore-forming agent substantially free from rubber and drying said sheet material to cause deposition of said pore-forming agent uniformly throughout said sheet, reinforcing said sheet material in a third treatment by pressing into said sheet material a heavy, flowable aqueous suspension containing further vulcanizable rubber solids admixed with further pore-forming agent, drying again to cause deposition of further vulcanizable rubber particles interspersed with particles of further pore-forming agent throughout said sheet material, said further vulcanizable rubber particles effecting a reinforcement of the fiber skeleton without filling the interstices between the fibers, vulcanizing the reinforced sheet material at elevated temperature without compression, thereafter treating the vulcanized sheet material with water to dissolve out the particles of pore-forming agent from the second and third treatments, and finally drying to produce a sheet material stabilized by the non-porous rubber particles and reinforced by microporous rubber coating particles in which the micropores in the reinforcing rubber coating particles communicate with the interstices between the fibers and with the pores previously filled by the pore-forming agent of the second treatment.

8. A process as claimed in claim 7, wherein the dilute vulcanizable rubber latex employed for the prestabilization is pressed into at least one surface of the fleece in the form of a stable flowable foam.

9. A process as claimed in claim 8, wherein the latex foam contains up to about 60 parts of a wetting agent per 100 parts of vulcanizable rubber solids.

10. A process as claimed in claim 7, in which the prestabilization of the initial fleece includes a preliminary application to one surface of said fleece of a foamed adhesive and drying to effect sticking together of the fibers disposed on the surface of the fleece at their crossing points with preservation of the interstices between the fibers.

11. A process as claimed in claim 7, in which the prestabilization of the initial fleece includes a preliminary application to one surface of the fleece of a light stable foam containing about 9 to 12 parts of gas per volume part of an aqueous rubber latex containing between about 8% and 15% by weight of rubber solids, the dilute vulcanizable rubber latex of the prestabilization being applied to the other surface of the fleece in the form of a heavy flowable foam containing about 2 to 8 volume parts of gas per volume part of an aqueous rubber latex containing about 14% to 35% by weight of vulcanizable rubber solids.

12. A process as claimed in claim 7, in which vulcanization of the reinforced sheet material is effected by exposing the sheet material to a stream of hot air.

13. A process as claimed in claim 7, wherein the vulcanization is effected in an aqueous paddle bath, the sheet material being paddled during vulcanization to thereby complete vulcanization and produce a surface grain similar to that of natural leather.

14. A process for the manufacture of highly water absorbent, flexible, porous, fibrous sheet material of high tensile strength and abrasion resistance, which process comprises first prestabilizing a loose fleece of intermingled,

polyposed, fine, cardable fibers containing at least a major amount of fibers capable of swelling in water, by a treatment including the steps of applying to one surface of said fleece a light stable foam containing about 9 to 13 parts of gas per volume part of an aqueous rubber latex containing between about 8% and 15% by weight of rubber solids and drying to effect sticking together at their crossing points of the fibers disposed on said surface with preservation of the interstices between the fibers, applying to the other surface of the fleece a heavy flowable foam containing about 2 to 8 volume parts of gas per volume part of an aqueous rubber latex containing about 14% to 35% by weight of vulcanizable rubber solids, drying without pressure to cause deposition of about 20 to about 133 parts by weight of non-porous rubber particles per 100 parts by weight of fibers throughout the fleece and vulcanizing the sheet, to thereby form a prestabilized sheet material wherein the fibers are cemented together at their crossing points with retention of the interstices between the fibers, in a second treatment drenching said prestabilized sheet material with a concentrated aqueous solution of a pore-forming agent free from rubber and drying to cause deposition of said pore-forming agent uniformly throughout said sheet material in an amount constituting by weight about one-tenth to about one-half of the dried sheet material, and in a third treatment reinforcing said sheet material by pressing into the latter a further vulcanizable rubber latex in the form of a heavy, flowable aqueous paste containing about 8% to 20% by weight of vulcanizable rubber solids, and between about 100 parts and 275 parts by weight of a dissolved further water-soluble pore-forming agent per 100 parts of rubber solids, drying again to cause deposition of further vulcanizable rubber particles interspersed with particles of further pore-forming agent throughout said sheet material, said further vulcanizable rubber particles effecting a reinforcement of the fiber skeleton without filling the interstices between the fibers, vulcanizing the reinforced sheet material at elevated temperature without compression, thereafter treating the vulcanized sheet material with water to dissolve out the particles of pore-forming agent from the second and third treatments, and finally drying to produce a sheet material stabilized by the non-porous rubber particles and reinforced by microporous rubber coating particles in which the micropores in the reinforcing rubber coating particles communicate with the interstices between the fibers and with the pores previously filled by the pore-forming agent of the second treatment.

15. A porous, flexible sheet material of a water absorptivity, abrasion resistance and tensile strength comparable to that of chamois, comprising a skeleton consisting of fine cardable polyposed fibers and containing a major proportion of water-swellaible fibers, said skeleton having substantially vulcanized, flexible, water-insoluble, non-porous, filmy rubber particles adhering to the fibers and cementing the fibers together at their crossing points without filling the interstices between the fibers, and also substantially vulcanized, flexible, water-insoluble, microporous rubber particles adhering to the fibers and to the non-porous rubber particles under fibers, said microporous rubber particles reinforcing said fiber skeleton without filling the interstices between the fibers, additional spaces being provided between the fibers and the solid binder particles on the one hand and the microporous binder particles on the other hand, said micropores communicating with the relatively large open interstices between the fibers and with said additional spaces.

16. A porous sheet material as claimed in claim 15, having a thickness of about 0.3 mm. to 2.5 mm.

17. A porous sheet material as claimed in claim 15, containing about 47% to 75% by weight of substantially vulcanized rubber material and about 53% to 25% by weight of fiber material.

18. A porous sheet material as claimed in claim 15,

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containing per 100 parts by weight of fibers about 33 to about 135 parts by weight of non-porous, substantially vulcanized rubber particles and about 40 to 160 parts by weight of microporous, substantially vulcanized rubber particles.

19. A porous sheet material as claimed in claim 15, having a weight of approximately 85 g. to 320 g. per square m.

20. A porous, flexible sheet material of a water absorptivity, abrasion resistance and tensile strength comparable to that of chamois, which comprises a skeleton consisting of fine cardable polyposed fibers and containing a major proportion of water-swellaible fibers, said skeleton having substantially vulcanized, flexible, water-insoluble, non-porous, filmy rubber particles adhering to the fibers and cementing the fibers together at their crossing points without filling the interstices between the fibers, and substantially vulcanized, flexible, water-insoluble mi-

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croporous rubber particles adhering to the non-porous rubber particles on the fibers, said microporous rubber particles reinforcing said fiber skeleton without filling the interstices between the fibers, the micropores in said microporous particles communicating with the relatively large open interstices between the fibers.

References Cited in the file of this patent

UNITED STATES PATENTS

1,958,821	Haarburger	May 15, 1934
2,006,687	Riddock	July 2, 1935
2,097,417	Neiley	Oct. 26, 1937
2,327,540	McQuiston	Aug. 24, 1943
2,330,314	Schwartz	Sept. 28, 1943
2,355,521	Ganz	Aug. 8, 1944
2,537,631	Greenup et al.	Jan. 9, 1951
2,574,849	Talalay	Nov. 13, 1951