FIG. 1

FIG. 2a

FIG. 2b

FIG. 2c

FIG. 3

APPLY SURFACE COAT-ETC.

FORM PAPER WEB

IMPREGNATE

MECHANICALLY SHRINK

APPLY SURFACE COAT-ETC.

CALENDER

BOND WITH NON-WOVEN
The present invention pertains to an artificial leather or coating base characterized by its leather-like feel, texture and warmth. More particularly, it is concerned with the manufacture of a laminated coating base comprising an impregnated and compressively shrunk web of short, cellulosic fibers adhesively bonded to a dimensionally stabilizing mat of relatively long fibers. This invention is specifically directed to the manufacture of an artificial leather of a weight and performance fully equivalent to upper shoe leather, and to shoes fabricated therefrom.

Many substitutes for leather have been proposed and have come into general use. Leather has been replaced by plastic films, by coated fabrics, and by coated or uncoated papers. The substitute products are usually stronger, more abrasion resistant, more waterproof, more resistant to flexing, and, in most cases, have more uniform properties.

Synthetic materials wear better and are more practical than leather for heavy duty service such as in bus and streetcar upholstery and have been readily accepted for these reasons. In other markets, such as wall coverings, camera cases, automobile upholstery and book covers, leather has lost its market to coated fabrics, films and papers on the basis of cost besides performance. Synthetic materials are available in continuous lengths and wide widths at a much lower price than leather and in attractive colors and finishes which in many cases outweigh leather.

Some consumers, however, still demand the feel, texture and warmth of real leather. The synthetics presently available cannot match the mellow, supple feel or the interesting natural texture of real leather and have not entirely replaced natural leather for this reason.

Artificial leathers have made initial inroads into the leather market for shoe uppers, leather coats, jackets, gloves and slippers. In all these cases where leather comes in contact with the body either directly or as an outer garment which flexes when the body moves, leather has an important advantage in the way it bends and flexes and conforms to the body without feeling stiff or confining.

It has been stated in the past that one reason why synthetics cannot compete with leather is that leather has superior moisture vapor transmission properties over the synthetics, which are usually substantially impermeable plastic films or heavily impregnated coated webs. While there may be some truth to this claim, it has been known for years that completely impervious rubber footwear can be worn with comfort providing it is not too stiff and unyielding. Soft leather without finishing materials, for example, as in Indian moccasins, probably does promote comfort because of its permeability, but modern shoes with synthetic linings and moisture resistant finishes can hardly be considered to be readily permeable to moisture and yet they are quite comfortable to wear.

The present invention is based upon duplicating in a fibrous web system the physical properties and construction of leather which account for its supple feel and excellent flexibility. This leather-like feel is obtained in a fibrous web system by a combination of mechanical techniques using a wide range of fibers and binders or impregnants.

The present invention is based upon the discovery that the properties of natural leather can be simulated by means of a composite or multi-layered construction of fibrous webs in which outer layers of compressively shrunk short cellulosic or synthetic fibers bound with an elastomeric binder are intimately laminated with an elastomeric adhesive to a strongly dimensionally stabilizing layer of a woven or nonwoven fabric made from relatively long textile-length fibers.

The process of the present invention permits the manufacture of uniform sheets of artificial leather in wide widths which have the mellow feel and lively flexibility of real leather, particularly in the lighter weights. Many of the previous known types of artificial leather are stronger and more wear- or water-resistant than natural leather, but none are as soft and leather-like as the present product.

This invention is particularly directed to the manufacture of an artificial upper shoe leather of novel construction and to shoes fabricated therefrom. The artificial upper shoe leather of this invention has the requisite properties of toughness, stitch resistance, flexibility, piping resistance and extensibility which permit it to be handled in conventional shoe assembly operations such as lasting and impart to it the feel and performance of natural leathers.

The artificial leather base of this invention can also be used to replace natural leather in the manufacture of luggage, brief cases, camera cases, hand bags and the like, as will be appreciated by those skilled in the art.

The preferred artificial leather product of this invention is a laminate comprising a dimensionally stabilizing nonwoven web of relatively long randomly disposed fibers to which is adhesively secured a top ply of a biaxially extensibilized impregnated cellulosic web, the whole having a caliper in the range of 0.025 to 0.090 inch which corresponds to an upper shoe leather thickness of about 2 to 6 "ounces" (1 "ounce" equals 1/64 inch).

The term "cellulosic web" refers particularly to a web made by wet-method paper-making techniques from conventional cellulosic pulps wherein there is some hydration bonding of the relatively short fibers in the web, but the term is to be taken as including webs derived from furnishers based in whole or in part on equivalent synthetic fibers. By equivalent synthetic fibers are meant synthetic fibers which can be formed into webs by wet-method paper-making techniques.

It is known that compressive shrinking or extensibilizing of webs made from relatively short fibers by paper-making techniques will increase the elongation and energy absorption of the webs (see United States Patent 2,624,245). Cellulosic webs which have been compressively shrunk do not in themselves meet many of the criteria for a leather replacement. If made from short fibers, they do not have the strength and stitch resistance required. If shrunk only in one direction, they resemble leather in that direction only. If shrunk in two or more directions, they become very soft and leather-like in feel provided they are shrunk at least 5 percent and preferably to 15 to 25 percent in both directions.

Compressively shrunk cellulosic webs, however, have
too low a modulus to be useful as a leather substitute. In other words, they are too easily stretched out again after shrinking and once stretched do not return to the earlier length of shape. Clothing or shoes made out of such materials would grow in size with continued use and become baggy and shapeless in a short time. Webs compressively shrunk in both directions and then impressed with an elastomer or similar binder have improved strength and modulus. Saturation with an impression binder, however, cures the defects of too easy extension and insufficient recovery. Furthermore, although sheets of saturated material shrunk in cross directions or biaxially shrink if properly coated and compounded, have the look and feel of real leather, their tensile strength and stitch resistance are inadequate.

The use of long fibers, such as cotton or hemp, in impressed cellulose webs is well known to improve the strength and stitch resistance of artificial leather papers, but saturated webs containing long fibers do not respond well to compressive shrinking. The fibers are too difficult to displace and the properties of real leather are not obtained. Furthermore, the degree of strength and stitch resistance needed cannot be reached with fibers 1/4 inch or less in length which are the longest which can be handled in conventional paper-making equipment.

Although the use of long fibered pulps does not solve the problem, the addition of long fibered pulps to sulfate (kraft) or sulfite furnishes does improve the properties of this invention, and they may constitute up to 60 percent of the paper-making stock. The results desired, however, are not obtained unless some portion of the finished artificial leather base contains fibers of textile make and length, as described below, and some portion contains short hydrated cellulose or synthetic fibers having an average length under 1/4 inch.

In the skins of animals the fibers of collagen are arranged almost completely at random and are interwoven in all three dimensions. Paper-making processes are incapable of producing such a random arrangement, i.e., the fibers are randomly arranged in only two directions. Even the processes for making so-called random webs of nonwoven fabrics arrange the fibers at random in only two dimensions. There is no substantial number of fibers oriented perpendicular to the surface of the sheet in either paper of nonwoven materials. It is rare to find a fiber which is tilted out of the plane of the sheet more than 5 degrees for any portion of its length.

Compressively shrinking of fairly short fibered webs having originally an open pore structure does produce a substantial amount of orientation in a plane perpendicular to the plane of the paper (the Z direction) and this is the best method currently known for producing such changes in fiber orientation. Processes are also known to curl, twist and bend fibers before the paper web is formed. Mercerization of pulp as described in United States Patents 1,857,100 and 2,088,524 is an example. The amount of "Z-orientation" produced from mercerized fibers is rather low and to date has not been sufficient to give a noticeably leather-like feel to saturated webs. Such fiber are useful, however, for making a porous, open-textured sheet which responds well to compressive shrinking and can be used in this invention.

If the outer plies of the artificial leather of this invention are not compressively shrunk, the resulting laminate is relatively inflexible even when it is made with soft, flexible fibers bound with a soft and stretchy elastomer. The fibers of such sheets all run parallel to the surface of the laminate and when they are stressed by bending they crumple and the bonds between the fibers are ruptured irreversibly, producing internal splitting and wrinkling of the sheet called "piping." Piping is one of the principal defects of artificial leathers made from paper bases. However, if the fibers are compressively shrunk either before or after saturation, the fibers are more randomly oriented and can accommodate bending and twisting without rupture of the bonds between the fibers and without delamination of the layers of the fibers. The layer structure of the paper no longer exists to the degree which was present before compressive shrinking because of the Z orientation imparted to the fibers and the entire structure of the sheet is much more like that of real leather. Some piping still occurs, as it does in leather, but this piping is reversible and the wrinkled appearance of the surface disappears as soon as the sheet is bent back to its original position.

The center layer of the reinforcing woven or unwoven fabric need not be compressibly shrunk to obtain good stitch resistance. These layers are advantageous to give a final extensibilizing treatment to the entire laminated structure after all the layers have been assembled, shrinking it at least 1 percent, if one wishes to emulate a very thin and flexible variety of leather.

It is preferred to cross-laminate the cellulose web layers more than one is used, but it is not necessary that they be exactly 90 degrees out of register. To simulate the grain of leather, i.e., its extensibility, and to have more strength in one direction than in the other, it is advisable to laminate the layers with the angle between them being between 45 and 90 degrees.

This invention will become clear from the following examples and descriptions of the drawings attached to and forming a part of this specification.

In the drawings:

FIGURE 1 illustrates an artificial leather fabricated in the manner of this invention;

FIGURES 2(a), 2(b) and 2(c) depict different types of extensibilized cellulose webs that can be used in the construction of the artificial leather, with 2(a) illustrating extensibilization in the machine direction, 2(b) illustrating extensibilization in both the machine and cross directions, and 2(c) illustrating extensibilization in two directions at an angle between the machine and cross directions;

FIGURE 3 schematically illustrates one method of manufacturing the artificial leather or coating base.

Referring to FIGURE 1, the artificial leather in its simplest form comprises a biaxially shrunk and impressed cellulose web ply 1 and a reinforcing or dimensionally stabilizing long-fibered web or as highly stress 3 allowing bending of the sheet as the outer plies; thus, a nonwoven can be used without special treatment provided it is not too thick. However, if it is desired to simulate an extremely soft and flexible leather like kidskin, it is desirable to use rather thin layers of both the extensibilized cellulose web and the reinforcing mat. It is also advantageous to give a final extensibilizing treatment to the entire laminated structure after all the layers have been assembled, shrinking it at least 1 percent, if one wishes to emulate a very thin and flexible variety of leather.

More than two plies can be used, of course, and this is preferred for many applications. Thus, a second extensibilized and impressed cellulose web can be adhesively secured to the under side of lamina 2. The top ply 1 and/or the bottom cellulose web ply, if used, could consist of two or more extensibilized and impressed cellulose webs preferably cross-laminated as previously indicated. Lamina 2 may also consist of two or more plies of a nonwoven cross laid to whatever degree is necessary to develop optimum strength in the composite. The combination of extensibilized cellulose web and long-fibered web or mats may have any desired thickness and may be further strengthened by being secured to woven cloth, felt and similar webs.

The laminated composition without a coating thereon can have a beam weight (24 x 36 inches—500 sheets) in the range of 150 to 1200 pounds and a thickness in the range of 25 to 90 mils. It is preferred that the coating base have a piping radius less than 1/4 inch, an ultimate tensile greater than 50, preferably greater than 100 pounds.
per inch width, and extensibility (ultimate) in the range of 20 to 150 percent and a recovery after elongation to 50 percent of its elongation at break in the range of 35 to 95 percent, all as measured either across the width or along the length of the sheet. Overall, the impregnated cellulose web can contain 10 to 220 weight percent on fibers of an impregnant. A particularly preferred impregnated cellulose web contains from 20 to 200 weight percent of the impregnant based on the weight of the fibers. More preferably, it contains 60 to 150 weight percent of the impregnant. In a still more preferred embodiment, the impregnant is employed in amounts from about 50 to 120 weight percent and a slack mercerized cotton fabric is utilized in the laminated structure. The cellulose web can constitute 10 to 90, preferably 25 to 50, percent of the weight of the fibers in the laminant and the remaining 90 to 10, preferably 75 to 50, percent of the fibers are the relatively long stabilizing fibers in woven or nonwoven form.

Referring to FIGURE 3, the artificial leather is made by first forming a cellulose web in step 20 in any convenient manner; for example, with a Fourdrinin or Rotoformer (trademark of Sandy Hill Iron and Brass Works) paper-making machine. While the wet cellulose web can be dried prior to the compressive shrinking and then cross-linked to secure the desired degree of fiber plasticity for compressive shrinking, it is preferred to work with cellulose webs that have not been dried after their formation to the point where hydration bonding is complete. The web can be impregnated by "beater addition" or can be impregnated after it has been formed. As shown, it is impregnated separately in step 21. The cellulose web can be saturated before or after the compressive shrinking, although the former is preferred. It is also preferred to use an elastomer impregnant that is in the form of a latex and to maintain the impregnant in a gel or somewhat mobile form during the extending treatment of the paper web. The cellulose web received from the paper-forming machine can be impregnated by dry or wet saturation techniques. Beater addition is understood to refer to the preparation of a slurry of fibers and the addition of the latex to the fibers prior to forming a sheet.

As shown in the drawing, the impregnated cellulose web from step 21 is compressively shrunken 5 to 25 percent in step 22. It is possible to design a cellulose web such that some embossing in only one direction is required to give the web the properties desired, particularly if cross-section shapes of the cellulose web are to be used. It is much preferred, however, to biaxially shrink the cellulose web because superior performance is obtained. The biaxial shrinking of the cellulose web can be carried out by first shrinking the web in one direction using the technique described in United States Patent 2,624,245 and then shrinking it in the cross direction using the same technique. Alternatively, the cellulose web can be compressively shrunken in two directions in one pass through a machine of suitable design such as is described in South African Patent 2,520/58 issued to Claypak, Inc.

The impregnated and extended cellulose web before binding to the reinforcing long-fibered mat has, preferably, an extensibility greater than 50%, preferably 50 to 200 percent, before break, a tensile strength at 15% elongation of 50 to 150 pounds per inch width and a recovery after elongation to 50 percent of its elongation at break in the range of 35 to 80 percent all as measured after drying and either in the machine or cross-machine direction. Its wet strength is preferably 60 to 90 percent of its dry strength, and its piping radius is less than ¼ inch.

In step 23 a nonwoven fabric made from randomly disposed relatively long textile fibers is laminated to the compressively shrunken and impregnated cellulose web using any convenient type of stretchy adhesive. The laminate is then calendered to uniform thickness in step 24 although it may not be necessary to do this in some applications. This is followed in step 25 by the application of any desired type of surface coating on the outer cellulose web ply.

The cellulose web is preferably made from strong, flexible wool pulp fibers, such as bleached kraft pulp made from spruce or hemlock. Satisfactory products can also be made from unbleached kraft and from bleached and unbleached sulfite fibers mixed with strength imparting fibers. Examples of suitable mixtures are kraft and hemp, kraft and jute, and kraft, hemp and a small amount of groundwood. Admixtures of nylon, rayon, methyl terphthalate-ethylene glycol polymers, acrylonitrile polymers, and similar synthetics in fiber form, in amounts up to 50 percent of the furnish, yields a stronger outer ply.

In areas where soft wood kraft fibers are not available, fibers such as bamboo, bagasse, and esparto can be used. The use of different fibers will produce detectable differences in strength, feel and pliability as known to those skilled in the paper-making art. As long as the fibers can be used to make a cellulose web which can be saturated and which can be compressively shrunk, they are useful in making the outer cellulose web ply of the artificial leather. The fibers used in the paper-forming processes by the wet method are necessarily less than about ½ inch in average length.

Certain fibers are well known to be soft, flexible and absorbent and are usually chosen for the manufacture of saturated papers. Such fibers are highly purified kraft or sulfite pulps having a high alpha cellulose content. These fibers make a bulky sheet which bends easily without cracking or piping and which absorbs the impregnant quickly. In many cases a mercerized or alkali-treated fiber may be chosen for the base sheet because such fibers are known to be curbed and kinked and to make sheets of saturated paper with good tear resistance and high resistance to folding and wear.

The selection of furnish for forming the cellulose web is well known in the art and is not part of this invention.

The long fibers used for making the inner woven or nonwoven plies of the composite construction should have an average length greater than ½ inch and should be as strong and as extensible as possible. Good results can be obtained with cotton fibers. It is preferred to use, however, the stronger and more extensible web constructions made from fibers such as nylon, methyl terphthalate-ethylene glycol polymers, acrylonitrile-vinyl chloride polymers and similar synthetics. Weaker synthetic fibers, such as cellulose acetate, normally should not be chosen for the inner ply.

It is preferred to cut the woven inextensible fabrics on the bias wherever possible before laminating in order to avoid losing the flexibility and extensibility desired for the artificial leather construction.

Any of the conventional elastomeric or resinous impregnants can be used to bond the fibers of the cellulose web and of the long-fibered mat. For example, natural rubber and synthetic rubbers, such as butadiene-styrene, butadiene-acrylonitrile, neoprene and the like can be used. See also those saturants described in the following United States Patents: 2,410,078; 2,416,232; 2,438,195; 2,441,523; 2,692,253; 2,760,884; 2,799,596; 2,848,344; 2,848,105; 2,899,353; 2,905,584; and 2,857,109. Polyurethane emulsions are also particularly suitable as impregnants.

The elastomers or resins will be compounded with the usual ingredients, such as antioxidants, fillers, thickeners and curing agents. In order to make a more water resistant artificial leather, a thermosetting resin can be co-cured with the synthetic rubbers. For example, a commercial Buna N latex (butadiene-acrylonitrile in ratios of 70/30 to 55/45) can have added to it ½ to 10 weight percent of a water soluble phenolic resin or
from 2 to 15 weight percent of a water soluble melamine-formaldehyde resin. These saturants can be cured after drying for several minutes at 250 to 425° F. The resulting product is extremely strong and tough when wet. Its wet strength can be adjusted by changing the amounts of curing agent and conditions or cure until the wet strength is 70 to 90 percent of the dry strength with the product still remaining supple and flexible.

Strong, tough, and weather resistant fiber layers can be made by saturating with a neoprene latex and curing with zinc oxide or one of the other standard curing combinations for neoprene latex.

Ethylene-propylene copolymers, ethylene-vinylacetate copolymers and other special copolymers made by grafting or substitution on a preformed elastomer chain or by condensation with an active group to form polymeric side chains can be used as saturants.

The elastomeric saturants can be used both in the cured and uncured state and are compounded with the usual compounding ingredients. Normally it is cheaper and more convenient to use latexes or water dispersions to saturate the fibrous webs, but solutions and melts can be used in some cases.

The cellulosic web can be saturated with the elastomer prior to the extensibilizing treatment in any convenient manner. The web can be saturated wet as it comes out of the paper-making machine or, if the web has been dried, it can be dry saturated. The web can be tub sized and, if only a small amount of impregnat is to be used, coating methods can be used to put the impregnant in the web. The amount of elastomer used will depend upon the type of the elastomer and the web but, in general, will preferably be in the range of 80 to 120 weight percent based on the dry fibers.

It has been found that there is a particular advantage in extensibilizing webs impregnated with an elastomer latex system while the latex is in gel form, i.e., it has not been set to a nonfluid state by drying. It appears that if the elastomer is maintained in gel form greater fiber mobility is permitted during the extensibilizing treatment with the consequence that the treatment is more effective and better elastomer bonds are formed which allows a lower amount of impregnant to be used.

The compressive shrinking is accomplished by compacting and rearranging the fibers through compression of the cellulosic web between two complementary surfaces. One of the surfaces at the time of contacting the web is an expanded elastic adherent surface and the other is a stable nonadherent surface such as a steel bar or roll. After being gripped between these surfaces, the elastic surface is caused to contract which results in shrinkage of the web. This shrinkage is best carried out at a web temperature in the range of 210 to 300° F. and under sufficient compression perpendicular to the surfaces of the web to prevent more than a 5 percent increase in the thickness of the impregnated cellulosic web. It is preferred to work with fresh cellulosic webs taken directly from the paper-making machine without substantial removal of other than loosely held water. Hydration bonding of the web has not been completed and the web fibers are therefore more amenable to the compacting and rearranging afforded by the extensibilizing treatment than is the case when the web has been conventionally dried. Generally speaking, improved results are obtained by working with fresh cellulosic webs the water content of which has been maintained above 60 weight percent since the time of web formation.

The conventional extensibilizing method, i.e., as set out in United States Patent 2,824,245, results in compressive shrinking of the cellulosic web in only one direction. This is illustrated in FIGURE 2(a). Dotted line 6 indicates the machine direction of the cellulosic web 5 as it comes off the paper-making machine. In a conventional shrinking process, the cellulosic web would be fed into the extensibilizing machine in the machine direction such that compressive shrinking results as indicated by the heavier arrows 7.

This unidirectionally extensibilized sheet can be compressed in the cross direction by passing it through the extensibilizing machine in that direction. The results are indicated in FIGURE 2(b). Here the cellulosic web 8 has a machine direction 9 imparted to it by the paper-making machine. It has been compressively shrunk as described in connection with FIGURE 2(a) in the direction as indicated by 10 and then turned 90 degrees and passed through the extensibilizing machine such that it is also shrunk in the cross direction as indicated by the arrows 11.

As mentioned previously, it is preferred to work with cellulosic webs that have been biaxially compressed and shrunk. The term "biaxial" includes the shrinking of webs in two or more directions. The biaxial compression and shrinking can be accomplished in the manner illustrated in FIGURE 2(c) by using a machine that has the compacting rolls arranged in an angle to the passage of the cellulosic web through the machine. (See South African Patent 2,520/58 issued to Clupak, Inc.) Thus, the cellulosic web 12 having a machine direction as indicated at 13, is passed in that direction through an extensibilizing machine which has two sets of compression members arranged at right angles to the web and to themselves such that biaxial compressive shrinking results in one pass as indicated by the arrows 14 and 15.

The cellulosic web after the extensibilizing treatment, if it has not at this point been impregnated, is impregnated and, if necessary, is dried. It is then bonded to a dimensionally stabilizing mat formed of long fibers. The adhesive used to laminate plies can conveniently be the same material used to saturate the fibers. It can also be a standard flexible latex adhesive based on natural rubber, neoprene or some other synthetic rubber. The adhesive chosen should be strong enough to resist delamination and should be as flexible as possible to avoid stiffening of the laminate. It should also be compounded with conventional compounding ingredients—antioxidants, antiozonents, fillers, thickeners and in some cases curing agents, to perform its function properly.

After bonding the nonwoven to the cellulosic web and forming the number of plies desired, the laminate or composite is then pressed or calendered and/or heat treated, if necessary. The pressing or calendering will serve to give a uniform thickness to the laminate and can also be used to coat the outer surface of the outer paper web.

The coating base or artificial leather base so obtained could be used as such but it will usually be treated with a surface coat that simulates a leather finish. This coat can be applied by doctoring, spraying, brushing, hand swabbing or similar methods. Exactly the same materials and techniques used to finish leather give well bonded, long lasting finishes on the artificial leather of this invention.

EXAMPLE I

The following cellulosic webs were made on a Rototherm paper machine in a conventional manner. Web A—80

A furnish of a soft, highly purified, bleached sulfate pulp made from southern pine was prepared. This pulp has a high alpha cellulose content. The furnish was lightly beaten to a Canadian standard freeness of about 630 cc. of water, 0.2 weight percent of a water soluble melamine formaldehyde colloid resin was added (Parex 607—American Cyanamid Co.). A sheet having a basis weight of about 80 lb. (24 x 36 inches—500 sheets)
Web A—125

The same furnish as above was formed into a sheet having a basis weight of about 125 lbs. and a thickness of about 27 mils.

Web AK—94

A saturating web was made from the high alpha content bleached sulfate southern pine pulp as described above, but in this case 60 percent by weight of the southern kraft pulp was replaced with an unbleached kraft which had been treated with alkali under mercerizing conditions so that the fibers were twisted, bent, and then dried at 15 mils. This web is a commercially available unbleached kraft known as Solka 10A (International Paper Company) made from Canadian spruce pulp. This sheet was also treated with 0.2 weight percent of the wet strength resin. The pulp was beaten to a Canadian standard freeness of 700 cc., which was just sufficient to make it possible to form a good sheet and avoid cutting the fibers any more than was necessary. The product obtained from this pulp is particularly porous and easily saturated, and forms a saturated sheet of high elongation. The pulp was formed into a 94 lbs. sheet of 15 mil thickness.

Web AK—125

The same pulp as used to form Web AK—94 was formed into a web having a basis weight of 125 lbs. and a thickness of about 26 mils.

Web KM—72

A furnish was made by mixing 65 percent of an unbleached, Finish soft wood kraft (Sunilla) with 35 percent of the above mercerized pulp (Solka 10A). This mixture was beaten to Canadian standard freeness of 675 cc. and formed into a porous open sheet having a ream weight of 72 lbs. which saturates easily. About 0.2 weight percent of the melamine wet strength resin was included in the furnish.

Web M—38

This was a sheet of manila hemp paper formed from bleached fibers reclaimed from manila hemp rope (Flex rope—John A. Manning Co.). This paper has a basis weight of about 38 lbs. and is approximately 0.004 inch in thickness. It is easily saturated and gives a product with high strength, both dry and wet. The machine direction tensile strength of the sheet is about the same both before and after saturation and falls in the range of 50 to 65 lbs. per inch of width. The cross machine tensile and tear resistance is rather low since most of the fibers in this sheet run parallel to the machine direction.

The different plies for constructing the artificial leather samples were obtained by impregnating and extensibilizing the cellulosic webs as follows:

Ply A—80—18

Web A—80 was saturated with a butadiene-styrene latex, the rubber of which had a butadiene-styrene ratio of about 50/50. Two percent of Sinto-white Crystals (Monsanto Chemical Co.) were added to the latex as an antioxidant to improve the heat resistance and life of the rubber. In order to avoid degradation by traces of copper, manganese or iron ions, approximately 1/4 percent of the sodium salt of ethylene diamine tetracetic acid was added to the latex based on the dry weight of the rubber. Conventional stabilizers and coloring agents were also added. The concentration of the latex was such that about 40 lbs. of latex solids were picked up by each 100 lbs. of paper. The saturated sheet was dried and slit to the proper width and then passed through an extensibilizing machine and compressively shrunk 18 percent in three passes in the machine direction only.

The extensibilizing machine used in these experiments was a laboratory model employing a reinforced rubber belt 12 inches wide, one inch thick and having an internal circumference of 62 inches. The belt was passed around three vertical rolls, each 3 inches in diameter, and then over a fourth tension roll, exactly as illustrated in United States Patent 2,704,729. The top roll of the three vertical rolls was adjustable to permit varying the compression on the belt as it entered between the top and the middle rolls, which permitted control of the percent shrink per pass. Generally, the belt was compressed above 10 percent for these experiments. The middle roll was the driven roll and was heated to about 250° F. by superheated steam. The bottom roll was spaced about 2 inches from the middle roll. The cellulosic web samples were introduced into the nip between the belt and the top of the middle roll and removed from the belt underneath the middle roll. The webs were given 1 to 3 passes in these experiments to obtain the desired degree of shrink. About 7 percent shrink could be obtained in the first pass, an additional 5 percent was usually secured in the next pass, an additional 4 percent or so could be obtained in the third pass. The rate used was 4 yards per minute.

Ply A—80—18 x 15

Pieces were cut from Ply A—80—18. These were turned 90 degrees and shrunk in the cross direction using three passes through the machine to obtain a shrink of 15 percent. The resulting sheet was extremely soft and flexible and its surface as smooth and uniform but covered with very fine shrink marks or fissures reminiscent of a leather surface. It had the suppleness and feel of leather but lacked leather's strength and elasticity. If it were stretched, it elongated without returning to its original shape when the stretching force was removed. When soaked in water, much of the original shrink was lost.

Ply A—125—15

A similar product was made by saturating Web A—125 with the S-BC latex to a rubber pickup of 40 percent. After drying, rewetting, and compressive shrinking to 15 to 18 percent in the machine direction, this sheet had a thickness of 22 mils and was very soft and flexible.

Ply A—125—15 x 15

Pieces cut from Ply A—125—15 were shrunk 15 percent in the cross machine direction. This produced a very limp and leather-like product.

Ply AK—94—18

Web AK—94 was saturated with a Buna N-phenolic latex. The rubber used was a copolymer of acrylonitrile and butadiene having a butadiene/acrylonitrile ratio of 65/35 (Hyac 1562—B,—B. F. Goodrich Chemical Co.). The latex was compounded as follows:

Buna N latex (Hyac 1562)—100 parts by weight, Phenolic resin (Durez 14791) —2 weight percent, Antioxidant (Santo-white crystals) —2 weight percent, Copper inhibitor (Versene) —0.25 weight percent.


2 The Dow Chemical Company.
The latex was diluted to approximately 28 weight percent solids and at this dilution each 100 lbs. of cellulose web absorbed approximately 60 lbs. of latex solids. The product was dried and cured by exposing to a temperature of approximately 400° F. for about 2 minutes. The resulting product after drying had an open texture and a somewhat fuzzy surface because of the mercerized fibers present. The caliper was reduced and the surface improved by three passes through the extensibilizing machine to give a shrink in the machine direction of 18 percent. The resulting extensibilizing sheet had a very good tear resistance, good elongation, and responded well to the shrinking process.

Plv AK-94—18 x 18
Samples cut from Plv AK-94—18 were also shrunk in the cross machine direction to a shrink of 18 percent.

Plv KM-72—15
Web KM-72 was saturated with the above Buna N latex and dried by exposing to a temperature of approximately 400° F. The resulting sheet was strong, tough and tear resistant. Its tensile strength and tear strength when wet were about 80 percent of its dry strength.

Rolls of this cured, saturated cellulose web were compressed into a hard sheet. In order to shrink this web it was necessary first to wet the sheet thoroughly and uniformly and then redry it to a moisture content of between 30 and 40 percent. Two passes through the machine shrunk the web 15 percent in the machine direction and produced a limp and flexible ply which had excellent strength and water resistance.

Plv KM-72—15 x 15
Pieces were cut from Plv KM-72—15 and shrunk in the cross machine direction. After two passes the sheets had shrunk 15 percent in the cross machine direction. These sheets had the look and feel of pigskin or kid leather and were covered with tiny wrinkles and fissures which gave the surface a pleasing texture and appearance. These sheets were easily elongated and had no capability to retract after the tension was removed.

Plv M-38—A—125—12
Web M-38 made from manila hemp fibers did not readily respond to compressive shrinking. Saturation with a Buna N latex of a formula similar to that above gave a very strong, semi-transparent sheet which tore easily along the machine direction and had a harsh feel. Three passes through the compressive shrinking machine only reduced the length by 8 percent. The resulting sheet was much softer but did not have the surface smoothness and suppleness of the webs made from kraft or sulfite pulps.

Nonwoven

The nonwoven ply used to construct the artificial leathers of this example was an isotropic nonwoven web of nylon fibers laid down on a "Rando Webber" machine and saturated with an acrylic adhesive (Lantueck 2011–03 Wellington Sears Co.). This material has a thickness of about 16 mils and the fibers have an approximate length of about ½ to 1 inch. It has a weight of about 2½ ounces per square yard. It is a very strong and elastic material which helps to stabilize the soft and stretchy top and bottom plies made of the cellulose webs and increases the strength and tear resistance—particularly the stretch resistance—of the composite without bulk or stiffness.

Table I lists the constructions of the various plies that were assembled for testing and gives some of their physical properties. All of the samples were brushed with a natural rubber adhesive on the reverse side of the top and bottom plies and assembled. They were pressed in a hot platen press until nearly dry, and the drying was completed by letting the samples dry overnight at room temperature.

<table>
<thead>
<tr>
<th>Example</th>
<th>Plys</th>
<th>Construction</th>
<th>Thickness (Inches)</th>
<th>Total Bond Weight (Pounds)</th>
<th>Tensile MD x CD (lbs/inch width)</th>
<th>Elongation MD x CD (Percent)</th>
<th>Stitch Hold MD x CD (Percent)</th>
<th>Gurley Moist MD x CD (Milligrams/ Inch width)</th>
</tr>
</thead>
</table>


1 (39 x 39 x 39 inches.)

A leather-like sheet with interesting texture was made from this sheet by wetting one surface with natural rubber latex and laminating it to Web A-125 which had been saturated with the S-BR latex as described above. The sandwich of the two varieties of webs with wet adhesive latex between them was fed to the compressive shrinking machine and after two passes had shrunk 12 percent. The sheets were adjusted to a moisture content of about 20 percent before the adhesive was applied. After two passes through the extensibilizing machine, the heat and pressure of compressive shrinking had partially dried and firmly united two webs. Furthermore, the surface composed of the hard and stiff fibers of manila hemp had taken on the same minutely fissured appearance which the softer fibers assumed readily in the extensibilizing process. This laminated sheet also had a much softer and more leather-like feel than any attained by attempting to shrink the rope paper alone. It was apparent that by backing up the rope paper with a soft fiber web the work of the compressive shrinking machine had been facilitated and the web more easily softened. On close examination, it was also apparent that the two webs had attained a very close degree of association amounting to interpenetration at the line where the adhesive joins the two webs. The two were so firmly attached that it was impossible to separate them without destroying one or the other.

As a result of this experiment with manila hemp paper, it is part of this invention to manufacture some varieties of the outside plies of the artificial leather by extensibilizing to an additional shrink of at least 1 percent, two, three or more webs of saturated fibers which have been partially shrunk in advance, completing both the laminating and shrinking in one final pass through the machine which performs part or all of the function of drying the adhesive.

Four of the laminated artificial leathers were made into uppers for men's shoes. These samples were carried through all of the steps in the shoe making process up to the point where the welt was to be sewed on and the outer
sole and heel attached. The shoes were fabricated on standard equipment in a regular shoe factory. No special instructions were given to the operators and no complaints were received from any of them. In the case where one sample broke during the "pulling over" operation, the operator felt the machine had not adjusted properly to the weight of the material. No other troubles were noted.

Drying by being pressed for 14 seconds at about 175° F. and 500 lb. per square inch pressure.

A lacquer emulsion coat, also pigmented, was then sprayed on. After drying the sprayed sample was again plated at about 250° F.

The coated sample was fabricated into 8C men’s shoes. This was done by introducing the artificial leather sample into a commercial assembly line. The shoe making operations went remarkably smoothly. Pulling over, which is the most critical operation in lasting the shoe, gave no problem and it appeared that the sample performed as well as natural leather. After the soles and heels were attached and trimmed, the shoes were re-finished with a pigmented coat and a clear spray coat, as is conventional, to cover scuffs and finger marks. The artificial leather uppers had a very attractive grain on the finished shoes. The shoes after being worn for some time did not crack or become misshapen. They responded to repeated polishings in the same manner as shoes made from natural leather.

EXAMPLES III AND IV

The following cellulose web is made on a Rotoformer paper machine in a conventional manner.

Web

A furnish of a commercial unbleached Kraft sulfate pulp made from a blend of Douglas fir and hemlock is prepared. The furnish had an 85–87 percent alpha cellulose content. The furnish was mechanically curled in a standard curling machine. The furnish was lightly beaten to a Canadian standard freeness of about 770 cc. About 0.2 weight percent of a water soluble melamine formaldehyde acid colloid -resin was added (“Parez 607”—American Cyanamid Co.). A sheet having a basis weight of about 108 lbs. (24 x 36 inches—500 sheets) and a thickness of approximately 40 mils was prepared from this furnish, dried and cured.

Impregnated sheets

The above web was saturated with a 97½ percent carboxylated styrene/butadiene latex, (solids 40 percent—“Good-rite” 2750 x 15, Goodrich Chemical Company), 2 percent water-soluble phenol formaldehyde resin and ½ percent of the sequestering agent ethylene diamine tetraacetic acid. The concentration of latex was such that about 157 lbs. of latex solids were picked up by each 100 lbs. of paper. The saturated sheet was dried and slit to the proper width and then passed through an extensilizing machine and compressively shrunk 14 percent in two passes in both the machine and cross-direction. The extensibilizing machine used was the aforementioned laboratory model.

The resulting impregnated web was then laminated to a slack mercerized cotton fabric. The slack mercerized cotton fabric had a thickness of 16 mils and a weight of

<table>
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<th>Table II</th>
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<tr>
<td><strong>Shoe Operation</strong></td>
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<tr>
<td>Die Cutting</td>
</tr>
<tr>
<td>Sewing</td>
</tr>
<tr>
<td>Stitch resistance</td>
</tr>
<tr>
<td>Skiving</td>
</tr>
<tr>
<td>Folding</td>
</tr>
<tr>
<td>Fitting (sewing lining and upper material)</td>
</tr>
<tr>
<td>Assembling (dying counter and inserting last)</td>
</tr>
<tr>
<td>Pulling over</td>
</tr>
<tr>
<td>Heel Nailing (pulling heel tight around last and nailing to insole)</td>
</tr>
<tr>
<td>Glue lasting</td>
</tr>
<tr>
<td>Toe lasting</td>
</tr>
</tbody>
</table>

1 Both slightly loose at vamp.

Although the stitch resistance is reported to be only fair on the samples made without nonwoven fabric (comparative Examples A and B) as an interior ply, the shoes did not break or pull stitches during the lasting operations. Although hand webs were not made into completed footwear, it was perfectly clear that they could be finished into shoes and the final operations were omitted only to save time. These experiments well demonstrate the value of the nonwoven nylon interior ply to improve the strength and stitch resistance of the laminated artificial leather and to assist in establishing the cellulosic exterior plies.

**EXAMPLE II**

An artificial leather was constructed in accordance with this invention and fabricated into pair of size 8C men’s shoes. The cellulosic web was made on a Rotoformer from a furnish comprising 40 percent of an alkali treated unbleached Kraft (Solka 10A) and 60 percent of a high alpha content bleached sulfate, southern pine pulp. It had a ream weight of 80 pounds and a caliper of 17 mils. It was dried and then saturated with 98 percent Hycar 1562—2 percent Durez 14798. The saturated web was then extensilized in the previously described machine to a 21 percent shrink in the machine direction. Samples cut from the extensilized web were then cross extensilized in the cross machine direction to a 24 percent shrink. Two of the biaxially extensilized sheets were laminated to an inner web of a nonwoven consisting of nylon fibers (Lantuck 3011) which had a thickness of 18 mils and a weight of about 3 ounces per square yard. The top and bottom plies were cross laminated so that the machine direction of the top ply was parallel to the cross direction of the bottom ply. The adhesive used was a natural rubber latex. This 3 ply construction was then pressed at a temperature of 230° F. from an original thickness of 56 mils to a final thickness of 41 mils. It had the following properties: Gurley stiffness, 5685 x 5404 (CD); tease, 132 x 130; piping, less than ½ inch in both directions; elongation, 90 x 100 percent; and an internal ply strength, 188 lb. per square inch.

The artificial leather laminate so obtained was finished with a coating used to prepare natural leather. It was swabbed by hand with applicators consisting of pile fabric tacked to a board. The coating used was a water based mixture of a black dye pigment and acrylic resin binder. The swabbed sample was dried with hot air. Two coats were put on in this way and the sample was plated after frying.
about 5½ oz. per square yard. The adhesive used was a natural rubber latex. The two-ply construction was then pressed at a temperature of 230° F. from an original thickness of 40 mils to a final thickness of 35 mils. The resulting product was quite flexible, had piping less than ¼ inch in both directions, an elongation of over 50% in each direction, and a delamination resistance of around 60 oz. inch of width.

The artificial leather laminate so obtained was finished with a coating used to prepare natural leather. It was swabbed by hand with applicators consisting of a pile fabric tackied to a board. The coating used was a water-based mixture of a black dyed pigment and acrylic resin binder. The swabbed sample was dried with hot air. Two coats of putty in this way and the sample was dried after drying being pressed for about fifteen seconds at 180° F. and 500 lbs. per square inch pressure. A lacquer emulsion coat, also pigmented, was then sprayed on. After drying the sprayed sample was again plated at about 250° F.

The resulting product closely resembled natural leather and had substantially the same properties as natural leather. The resulting product is suitable for the formation of artificial leather products.

The above described procedure is repeated with the exception that the cellulosic web is impregnated with 107 percent of the impregnating agent rather than 157 percent as in the previous procedure.

The product is very similar to the above product with the exception that it has a lower delamination resistance, somewhat poorer flex life and was slightly lower in tensile strength.

**EXAMPLE V**

An artificial leather was made in accordance with this invention and fabricated into a pair of size 9D man's shoes. The cellulosic web was made on a Rotof former from furnish comprising of 50 percent bleached Canadian kraft (which previously been treated with caustic (15 percent) to chemically cur the fibers) and 50 percent bleached sulfate hemlock pulp. About 0.2 weight percent of a water soluble melamine formaldehyde acid colloid resin was added ("Parez 607", American Cyanamid Company). It had a dry weight of 130 lbs. and a wet weight of 30 lbs. It was dried and then saturated with a latex compound consisting of 97.5 percent carboxylated styrene/butadiene latex, (solsids 35 percent—"Good-rite" 2570 x 15, Goodrich Chemical Company), 2 percent of a water soluble phenol formaldehyde resin and ½ percent of ethylene diamine tetraacetic acid sequestering agent. The level of impregnation was 100 percent based on the weight of the dried fiber.

The saturated web was then extensified in the previously described machine in two passes to a 15 percent shrink in the machine direction. Samples cut from the extensibilized web were then cross extensified in the cross machine direction to a 15 percent shrink. Two of the biaxially extensibilized sheets were laminated to an inner web of a slack mercerized cotton fabric having a thickness of 16 mils and a weight of about 5½ oz. per square yard. The adhesive used was a neoprene solvent cement ("Supergrip-67")—United Shoe Machinery Co.). The two ply construction was then pressed at a temperature of 250° C. from an original thickness of 55 mils to a final thickness of 45 mils. It had the following properties: Gurley stiffness 3600 x 2900 (MD x CD); tensile 111 x 56; piping less than ¼ inch in both directions; elongation 43 x 44 percent and a slant tear strength of 20 x 20.

The artificial leather laminate so obtained was finished employing a soft carboxylated butadiene/acrylonitrile latex ("Tylac 5040", International Latex Corp.). For each 100 parts of latex mixture 1 percent of carbon black (at 35 percent solids), 3 percent casein and 2 percent of a sulfur vulcanizing agent is added. The resulting product was cured for three minutes at 225° F.

The resulting artificial leather was then sprayed with a commercial nitrocellulose lacquer. The coating was dried at room temperature for about five minutes at which time it is substantially dry.

The coated sample was fabricated into a pair of 9D man's shoes. This was done by introducing the artificial leather sample into a commercial assembly line. The shoe making operations went very smoothly. Pulling over, which is the most critical operation in testing the shoe, gave no problems and it appeared that this sample performed equally as well as natural leathers. After the soles and heels were attached and trimmed, the shoes were refinished with a pigment coat and a clear spray coat, as is conventional, to cover scuffs and finger marks. The artificial leather shows a very attractive grain on the finished shoes. The shoes after being worn for three months did not crack or become mis-shapen. They responded to repeated polishing in the same manner as shoes made from natural leather.

Artificial leathers were also made from the following nonwovens: Pellon V592 (The Pellon Co.)—polyamide fibers bonded with neoprene rubber—30 mils thick, tensile of 24 x 15 (MD x CD) lb. per square inch, as measured in the laboratory; Pellon 9900—W—polyamide fibers bonded with a nitrile rubber—25 mils thick, tensile of 9.5 x 8.0 (MD x CD) lb. per square inch, as measured in the laboratory; Webril EM-313 (The Kendall Co.)—Dynew fibers (Union Carbide and Carbon Corp.)—textile fibers formed from a copolymer of vinyl chloride and acrylonitrile) and Vinyon fibers (Union Carbide and Carbon Corp.)—weight of 1.2 ounces per square yard, 31/2 mils thickness.

The above nonwovens are air laid. An artificial leather was also made from a nonwoven consisting of a mixture of sisal and nylon textile fibers and formed wet by paper making techniques. It had a ream weight of 131.4 lb., a thickness of 17 mils, and a tensile of 17.0 x 10.5 (MD x CD) lb. per square inch.

The artificial leather based on the Webril EM-313 nonwoven was fabricated into a pair of men's shoes that gave particularly satisfactory performance. The top ply of the artificial leather consisted of a cellulosic web made in the manner of the above described Ply KM-72—15 x 15. The outer bottom ply consisted of a similar cellulosic web having a 30 lb. ream weight, cross-layed with respect to the top ply. The inner stabilizing ply consisted of two cross-layed Webril EM-313 nonwovens webs. A natural rubber adhesive was used.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. An artificial leather base comprising a compressibly shrunk cellulosic web impregnated with an elastomeric binder consisting essentially of short paper-making fibers adhesively secured to a dimensionally stabilizing mat of fibers of textile length.

2. The artificial leather base of claim 1 having a ream weight (24 x 36 inches—500 sheets) in the range of 150 to 1200 pounds and a thickness in the range of 25 to 90 mils, within the range of 10 to 90 percent of the fibers thereof being contributed by said cellulosic web and 90 to 10 percent by said mat.

3. The artificial leather base of claim 2 having an ultimate tensile greater than 50 pounds per inch width, an ultimate extensibility in the range of 20 to 150 percent in any one direction, and a recovery after an elongation of 50 percent of its elongation at break in the range of 35 to 95.

4. An artificial leather base comprising at least two outer plies of compressively shrunk cellulosic webs im-
pregnated with an elastomeric binder, said webs consisting essentially of short, paper-making fibers, said webs being secured to at least one intermediate ply of a dimensionally stabilizing mat of fibers of textile length.

5. An artificial leather comprising the artificial leather base of claim 1 coated with a leather simulating surface and having a thickness in the range of 2 to 6 ounces.

6. A shoe, the upper leather of which consists of the artificial leather of claim 5.

7. A coating base comprising a dimensionally stabilizing mat of relatively long bonded fibers adhesively secured to an outer ply of a biaxially extensibilized cellulosic web impregnated with an elastomeric binder consisting of relatively short paper-making fibers and containing from 20 to 200 weight percent of the impregnant, said coating base having a caliper in the range of 0.025 to 0.090 inch, a ream weight in the range of 150 to 1200 pounds, an ultimate tensile greater than 50 pounds per inch width, and an extensibility in the range of 20 to 150 percent.

8. The coating base of claim 7 wherein said paper-making fibers consist of up to 50 percent of synthetic fibers, and wherein said mat is nonwoven.

9. The coating base of claim 7 when extensibilized to a shrink of at least 1 percent.

10. The coating base of claim 7 wherein said outer ply comprises two cross-laid independently extensibilized impregnated cellulosic webs.

11. The coating base of claim 7 wherein the impregnated cellulosic web contains from 60 to 150 weight percent of the impregnant.

12. The coating base of claim 7 wherein the impregnated cellulosic web contains from 80 to 120 weight percent of the impregnant.

13. A coating base which comprises a slack mercerized cotton fabric adhesively secured to an outer ply of a biaxially extensibilized cellulosic web impregnated with an elastomeric binder consisting of relatively short paper-making fibers and containing from 20 to 200 weight percent of the impregnant, said coating base having a caliper in the range of 0.025 to 0.090 inch, a ream weight in the range of 150 to 1200 pounds, an ultimate tensile greater than 50 pounds per inch width, and an extensibility in the range of 20 to 150 percent.

14. The coating base of claim 13 wherein the impregnated cellulosic web contains from 60 to 150 weight percent of the impregnant.

15. The coating base of claim 13 wherein the impregnated cellulosic web contains from 80 to 120 weight percent of the impregnant.

16. A process for preparing a coating base which comprises impregnating a cellulosic web consisting of relatively short paper-making fibers, with from 20 to 200 weight percent of an elastomeric impregnant, biaxially extensibilizing the web, and adhesively securing the impregnated cellulosic web to a slack mercerized cotton fabric.

17. The process of claim 16 wherein the cellulosic web is impregnated with from 60 to 150 weight percent of the impregnant.

18. The process of claim 16 wherein the cellulosic web is impregnated with from 80 to 100 weight percent of the impregnant.

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