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MANUFACTURE OF SUBSTITUTE LEATHER

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This invention relates to the manufacture of fibrous materials and more particularly to an improved substitute leather. This application is a continuation in part of prior application Serial No. 697,691, filed November 11, 1933.

Heretofore it has been proposed to manufacture imitation leather products by treating a base of cellulose with specially prepared compositions. One such proposal comprised the saturation of rope paper with an aqueous solution of glue and glycerin and the supplementary affixation of the impregnant with formaldehyde in a second bath.

Such a product presents inherent disadvantages of such a nature as to very materially limit or restrict its use. For example, this product possesses only a limited flexibility and is lacking in the characteristic softness or pliability of leather. Furthermore, it tends to dry out in an arid atmosphere with a decided loss of tensile strength. Due to its physical characteristics it presents substantially negligible wearing and tearing qualities when made up in thicknesses less than three-one-hundredths of an inch.

Another artificial leather product which has been made consists of cellulose webs, each impregnated with rubber latex or rubber dissolved in a solvent, and then laminated to form a finished article of the desired thickness.

This general concept of utilizing paper with rubber has also been extended to a process which involves the incorporation of rubber latex with the pulp in the paper beater followed by the molding of the pulp on the paper board machine.

In view of their composition such rubber impregnated products do not possess the physical characteristics which would render them a reasonable substitute for leather.

I have found as a result of considerable experimentation in this field that it is possible to closely approximate the non-fibrous constituents of natural leather by a carefully controlled synthesis, and further that the synthesized leather-like constituents may homogeneously and permanently be incorporated in a suitable fibrous base to produce as a final product a material which in physical characteristics closely resembles leather.

An object of the present invention therefore is to produce a new and improved composition of matter.

Another object is to provide a new composition of matter having the essential characteristics and qualities of leather.

A further object is to provide a novel fibrous base material.

A still further object is to provide an improved process of treating fibrous material to form new products therefrom.

Yet another object is to provide a novel, potentially tannable composition.

With these and other equally important objects in view, the invention comprehends the concept of coating, saturating or impregnating fibrous base material with a specially prepared composition and after such treatment converting it into other form by reason of which the so treated fibrous material presents the main characteristics of leather.

In carrying out the present invention, as indicated hereinbefore, a major concept is to simulate as closely as possible the composition of leather. There is thus employed as starting materials simple and conjugated proteins. According to the present invention, such materials are definitely partially hydrolized in acid, alkaline or enzymatic solutions. Such a treatment gives a product which is, so to speak, potentially tannable.

In order to avoid the disadvantages inherent in prior art products, there is then embodied in the potentially reactive proteolytic material a substance or substances in amounts so controlled as to impart permanent pliability or softness to the finished product, as well as to substantially preclude material changes due to humidity or dryness.

With this given concept in view, it will be appreciated that a number of different compositions are available. As illustrative of such materials, there is employed, in the preferred process, a composition which, for the sake of a term, will be called a greased softener. This preferred ingredient may be prepared by mixing polyhydric alcohols, such as glycerol, sorbitol, and/or glycol, sulphonated oils, saponified water-miscible oils or fats, a suitable fatty acid such as oleic acid, and any desired essential oil, such as birch oil. This composition, when uniformly disseminated through the mass, provides a permanent softener and lubricant in the final product. Another and equally important function which this additive composition serves is to render the final leather-like product amenable to cellulose lacquer finishing.

In carrying out the manufacture of the improved product, as will be explained more fully hereinafter, the partially hydrolized protein matter and greased softener are thoroughly and homogeneously incorporated or mixed, as by agitation, trituration and so forth.

It will be appreciated from the foregoing dis-

cussion that a number of specifically different formulae may comprise the impregnating or saturating solution and are within the scope of the present invention in so far as they utilize the principles herein disclosed. For example, a saturant may be made up according to the following formula:

Solution A

	Parts by weight
Animal hide glue of high viscosity and jelly strength	150
Cheap bone glue of low viscosity and jelly strength	25
Commercial casein	25
Blood albumen	15
Sodium carbonate	3
Tri-sodium phosphate	9
Slaked lime	1
Sodium or potassium sulphate	15
Zinc oxide	15

The above materials in dry form are mixed in a large kettle which is provided with heating means. After thorough mixing of the dry ingredients, there is then added approximately 1200 parts by weight of cold water. The materials are continuously stirred until absorption is completed and the bath heated so as to raise the temperature slowly up to between 170° F. and 180° F. and the mass held at substantially this temperature for a period of approximately an hour.

It will be observed that under these conditions the protein or collagen-like constituents are advisedly and definitely partially hydrolyzed in aqueous alkaline media to produce new products, that is to say the amino acids, such as glycine, leucine, aspartic acid and glutamic acid which form the basic network of true collagen. In these circumstances the amino acids being partially freed from the original protein are thus made potentially available for tanning, as is the case in natural leather tanning. In other words such definite and partial hydrolysis establishes a chemical system simulating that obtaining in the natural leather tanning.

There may then be prepared a separate greased softener component which may have the following composition:

Solution B

	Parts by weight
Commercial crude or yellow glycerin (between 28° and 30° Bé.)	60
Commercial sorbitol	40
50% sulphonated castor oil	50
Oleic acid	30
Birch oil	3

This solution B is made up by adding the castor oil, oleic and birch oil separately and sequentially to the polyhydric alcohols with constant stirring.

Solutions A and B are then thoroughly mixed and adjusted with phosphoric acid to the pH desired for a particular operation in a manner more particularly to be described.

As has been indicated, the definite, partial hydrolysis of the protein starting material may be effected in acid solution or by means of suitable enzymes. In the case of acid hydrolysis, however, the albumin is omitted from the main protein-containing batch. This main batch may be hydrolyzed in the presence of a suitable acid, such as acetic acid, at a pH of 3.0 at approximately 170° F. for substantially an hour. The albumin constituent is separately degenerated or hydrolyzed with ammonia solution. After hydrolysis of the above mentioned main batch the product is adjusted with a suitable alkali to a pH of substantially 6.8 and the separately hydrolyzed albumin is added thereto. The batch is then finally adjusted to the desired pH.

When enzymatic hydrolysis is utilized the conditions of temperature and hydrogen ion concentration are similarly adjusted to optimum values.

The saturant solution may be used in any desired or approved manner to impregnate and/or saturate fibrous base material. After saturation the proteolytic material and softener are coagulated or set in and on the fibers and in the interstitial spaces of the fibers by contacting the impregnated material with a suitable tanning bath. In the preferred mode of operation, the tanning bath or solution comprises any of a number of known tanning agents, including vegetable tannin, alkaline formaldehyde, mineral salts or tanning oils. Upon the addition of the tanning or coagulant agent, there is an immediate or spontaneous coagulation or irreversible gelatinization effected.

In conducting two stage operations, namely saturation of a sheet followed by tanning, the hydrogen ion concentration of the saturant is correlated with the particular tannage employed. For example in one method of operation a fibrous sheet is first saturated and then the impregnated product is tanned with a formaldehyde solution. In this operation, prior to saturation, the saturant bath is first adjusted to pH 6.8. After saturation in such a bath the sheet is then contacted with a tanning solution consisting essentially of 10 parts of formalin and 100 parts of water. This tanning solution is adjusted to a pH of substantially 8.6 and then used for converting or tanning the impregnated sheet. The quantity of tanning solution employed is controlled so as to insure an excess of formaldehyde based on the total protein content of the saturant. When the saturated sheet is contacted with such a solution, as for example by continuous passage through a bath of the solution, immediate coagulation is effected.

As indicated hereinbefore the two stage treatment may be effected by using other tanning agents. For example vegetable tanning may be utilized. In this case the saturant is first adjusted to substantially pH 4.8. After saturating a sheet with this solution, the sheet may be contacted with a vegetable tanning agent as for example a solution of 25 parts of quebracho or sumac extract in 100 parts of water. This tanning solution is adjusted to substantially pH 4.8 and then utilized for conversion of the impregnated material.

Chrome tannage may be utilized similarly. In this operation, as in vegetable tanning the saturant is first adjusted to pH 4.8 and then used for saturation. The tanning solution may comprise, for example, 30 lbs. of potassium dichromate, 40 lbs. of sulphuric acid (52° Bé.), 75 lbs. of sodium thiosulphate and 10 lbs. of sodium chloride in 500 lbs. of water. This solution is adjusted with alkali to substantially pH 4.8 and then employed to convert the impregnated product.

In some circumstances it is desirable to carry out, in effect, a single stage treatment, i. e. one in which the fibrous base material is saturated with a solution containing the tannable proteolytic material and a potentially available tanning agent. Under the concept of the present invention this may be done by adding a retarding agent to the tanning solution and then incorpo-

rating the latter to the saturant. For example, a tannable saturant may be made up by first adjusting the saturant bath to pH of 7.8 to 8.0 and then mixing therewith the desired amount of hexa-methylene tetramine or a solution of equimolecular proportions of ammonia and formaldehyde in the proportion of substantially 7 per cent to 8 per cent of aldehyde content on the weight of the total proteins. Similarly mineral and vegetable tannages may be incorporated in the saturant by first adjusting the saturant to pH 4.8 and the tannage, with ammonia to pH 7.2. It will be observed that when a fibrous mass, which is saturated with such solutions, is subjected to heat, as in the drying step, the retarding agent, namely the ammonia, is volatilized and the pH of the material is automatically lowered to that point at which coagulation takes place spontaneously so that the collagen-like constituents are homogeneously, uniformly and irreversibly tanned in situ.

It will be observed that the described bath of liquor, comprehends the main constituents of the non-fibrous portions of leather, and is in such physical condition that it may readily impregnate or saturate even relatively closely felted or woven materials. Now according to the present improvement, a mix having the characteristics described is utilized to coat, saturate or impregnate any suitable fibrous base such as, unsized sheets composed of animal, vegetable or mineral fibers or any predetermined mixture of such fibers. Particular fibrous materials which may be employed in the manufacture of novel products are tanned and untanned leather, rope, jute, kraft pulp, sulphite pulp, wood pulp, cord, linen, silk, wool, wood alpha cellulose, asbestos, or any desired mixture of these and similar materials.

While as pointed out hereinafter the invention specifically includes the saturation of leather and/or cellulose materials in set form, it will be appreciated that it also comprehends the impregnation of disaggregated material which, after treatment with the impregnant and fixing agent, may be molded in any desired shape or form.

It will be understood of course that, if desired, other ingredients may be added to the main bath or liquor to achieve the additive effect of such ingredients. Thus, for example, to the main bath may be added rubber latex, solvent rubber in ammonia solution, resins, rubber accelerators and anti-oxidants, vulcanizing agents, mineral fillers, or film strengtheners, such for example as zine oxide, dyestuffs and other similar products.

It will be appreciated that the actual impregnation of the fibrous base material may be effected by employing a number of specifically different apparatus. The equipment employed will naturally depend largely upon the physical state of the fiber which is to be treated. Depending upon the characteristics of the fiber base employed and the demands of the final product, impregnation and fixing may be carried out either intermittently or continuously. Due to the effectiveness of the penetration and the completeness of the coagulation or gelatinization caused by the tanning agent, a very wide permissible flexibility of manipulative technique is presented.

In one preferred form of operation for the manufacture of artificial leather in sheet or continuous form, it is possible to utilize, as a starting material, rolls or sheets of leather and/or cellulose. Thus, the rolls of fibrous material, which may comprise unsized leather and/or cellulosic fiber such as paper, woven or felted textile products, or combinations of these, are unwound from a suitably positioned unwind stand and passed through a tank containing the saturant. This tank is provided with means to maintain the impregnant at substantially 150° to 120° F. and, if desired to insure an agitated or turbulent condition. Such tank, for example, may be fifteen or more feet long, six or more feet wide and approximately three feet deep. Preferably it is equipped with a false bottom for steam heating the bath. The tank may also be provided with individually driven squeeze rolls, which function not only to improve the impregnation by the saturant, but also to remove excess liquor from the sheets and to maintain the bath in more or less agitated condition.

These dimensions, which have proven satisfactory in practice, are given merely to indicate the desirability of providing a relatively long period of travel of the sheets in the bath. Obviously the same results can be achieved by providing a deeper tank and passing the sheets through it in a sinuous course. In the manner well known to those skilled in the art, the sheets may be pulled through the bath by the squeeze rolls or drying cylinders or cans.

It will likewise be appreciated that, if desired, the web of fibrous material may be preliminarily subjected to the action of a wetting agent to increase subsequent impregnation or penetration by the saturant. After the material has been completely saturated, it may then, as noted above, be subjected to the action of the setting agent, namely the tanning solutions described. With this type of treatment it will be appreciated that a continuous throughput of material is insured. If desired, the saturated base may be allowed to age for a predetermined period of time before being subjected to the action of the tanning agent. This short aging or curing period insures a more uniform concentration of the impregnant. While in some circumstances a brief aging period may be preferred, it is to be clearly understood that it is not absolutely essential for, as noted above, the material may be effectively saturated and fixed or transformed in a single continuous operation. It will likewise be understood that a partial curing may be achieved even in a continuous process by providing a relatively long period of travel under dehydrating and accelerating conditions, between the impregnating tank and the fixing bath: also a mulling period may be established after the tanning and prior to final drying.

After the fixed or coagulated tanned base sheet has been treated on the drying cans, it may thereafter be wound upon rolls or formed into sheets. Thereafter the treated base may be finished by the application of surface coatings, such as cellulose ester base or other lacquers, surface coloring materials, embossing, burnishing and the like.

As indicated hereinbefore it is possible to incorporate dispersed rubber in the saturant. It is found that in order to obtain the full advantages of the beneficial effects of the use of rubber, it is preferable to embody it in the mix in a special manner. When so incorporated, it is found that the rubber may readily be utilized, even when the main mix or composition includes chromium salts. For the incorporation of rubber, it is preferred to select a solution of rubber

latex with, if desired, natural proteins, resins, sugars, and so forth. Preferably the rubber composition may contain between 30% and 40% of rubber.

For this incorporation there is separately prepared a solution of the following composition:

	Lbs.
Ammonia preserved latex (containing between 35% and 40% of rubber)	645
Degenerated hemoglobin	65
Water	300

This solution may be made up by first preparing a stock hemoglobin solution by dissolving the hemoglobin in four times its own weight of cold water containing from 5% to 10% of ammonium hydroxide. In these circumstances, therefore, the hemoglobin decomposes into globin and hematin. To this cold hydrolized solution is then added, with constant stirring, the rubber latex. The latex solution, as noted above, may contain any suitable adjuvant, such as natural proteins, resins and the like.

The proteinated latex, as above prepared, is then combined with the main solution comprising a mixture of partially hydrolized protein and softener, and the mixture thoroughly stirred. The entire batch, which at this point is at a temperature of between 110° F. and 120° F., is constantly agitated and heated so as to maintain it at a temperature of between 120° F. and 130° F. This combined saturant may be employed, as hereinbefore described in place of the softened hydrolyzed protein mixture and the tanning agents in either of the two methods described.

While improved substitute leather products may be produced by the process described, it is particularly to be noted that a salient feature of the invention, which is considered to be novel per se, is the special compounding of and treatment with rubber latex. As indicated hereinbefore, it has been proposed to impregnate cellulosic materials, particularly paper, with rubber latex. In such methods, however, it was substantially impossible to obtain a uniform and intimate dispersion of the latex in relatively massive products such as the harder formed sheets of paper. The method of compounding the rubber latex according to the present invention by, in a sense, proteinating it or otherwise treating it to insure a stable peptization and then using this peptized latex to impregnate the fibers, is quite different from prior processes. In the earlier proposals, latex was initially converted into impregnating material by creaming and removal of the serum natural with it.

In sharp contradistinction to such processes, in the present method the latex is finely dispersed and peptized in a degenerated or decomposed hemoglobin solution or other equivalent peptizing medium. Without attempting accurately to define the mechanism of this process, it would appear that the globin and/or hematin in fact act as a protective colloid for the rubber and insure its colloidal status. This peptized colloid or dispersion of rubber, being afterwards dispersed in a protein bath, readily penetrates the fibers and interstitial spaces of the fibers.

It is particularly to be noted that because of the relatively small quantity of rubber employed and because of the high degree of dispersion of the rubber through the impregnated mass the collagen-like characteristics of the product is preserved that is to say, the ultimate products are leather-like and not rubber-like.

Consonant with the current theory that peptization or the protective effect may result from the adsorption of one colloid on another, it would appear that the lowering of the surface and interfacial tension due to this adsorption increases the wettability or penetration of the rubber colloid particles, and hence explains the very definitely improved impregnating characteristics of this material.

In addition, the hydrolized hemoglobin solution or its equivalent, in contact with the colloidal rubber particles of the latex, prevents increase in viscosity when this same latex is subsequently combined with the partially hydrolized protein. It further insures definite control and suspension of the rubber when the entire compounded saturant is heated to effect more efficient penetration into the fibrous base, particularly when composed of leather fibers.

Other materials of a protein and/or carbohydrate origin may be utilized in lieu of the hemoglobin but only when they are completely hydrolized to a point where a continuous colloidal liquid phase is chemically established and the destruction of all the original jellifying or pasting qualities insure. In other words, hemoglobin, albumen, animal glue and gelatin, marine products, casein, starches and vegetable gums, agar, Irish moss, alginates and the like, hydrolized by acids or alkalies as required to destroy jellying properties through the formation of amino acids and other by-products, can be employed to effect the rubber dispersion of the character desired. Other methods of securing this peptization utilizing proteolytic materials are available. Thus, for example, it has been found that chloral hydrate prevents the setting of glue. Hence, glue can be employed in the present invention to peptize the rubber. In such circumstances chloral hydrate to the extent of from 5% to 10% of the weight of the glue is employed for preventing jellification of the latter when it is used as a protective colloid or peptizing agent for rubber latex of emulsified aqueous solutions of rubber. It will be appreciated that this principle of using the chloral hydrate to prevent jellification of the glue may be used to prepare noncoagulating rubber dispersions in acid solution or for use in concentrating rubber of natural latex, or for peptizing vulcanizants for later combination with latices, emulsified rubber, and so forth. It is preferred however, to use hemoglobin because of its known efficiency, economy and expeditions reaction for the process outlined.

While the best results are obtained by using rubber latex, it is possible in some circumstances to utilize a solution of rubber in a suitable solvent, provided this is made up and peptized or protected in the manner described. When employing a true rubber solution, alone or in conjunction with rubber latex, it is advisable to insure its fine subdivision by passing it through a colloid mill. It is to be noted particularly at this point that a relatively large amount of rubber may be incorporated in the impregnant bath but minor amounts are preferred. This, it will be appreciated, is most likely due to the very fine dispersion of the rubber as a result of the effective peptizing action of the special stock solution and lowered interfacial tension therein.

While the treatment has been described with respect to a continuous roll or sheet of paper or similar material, it is clearly to be understood that it is by no means limited, in its potential use, to this material. The impregnant or sat-

urant operates effectively upon any character of filler, such as those mentioned hereinbefore. Similarly, the major concept herein described may be adapted for incorporation in existing processes. Thus, in view of the viscosity characteristics of the saturant, it will be appreciated that the saturant, upon proper dilution, may be utilized in an agitating machine of the type of a paper beater and the material fixed or gelatinized thereafter at any desired stage of the treatment. In short, the composition made up in accordance with the present invention may be, with slight modifications, made applicable to any existing process where natural or artificial fibers are matted, felted or woven, or otherwise fabricated into finished articles.

Likewise, it will be appreciated that, while the invention has been described with respect to the manufacture of substitute leather, it is to be understood that the materials made according to the process need not necessarily be leather-like products. For example, it is within the contemplation of the invention to utilize the present improvement in the manufacture of fabricated articles which involve a fiber base and in which it is desired to bond such fibers under such conditions as to improve their strength, toughness and wearing qualities. Thus, it is within the contemplation of the invention to use the ingredients described herein in conjunction with other saturants or impregnants, such as asphalt base materials, emulsions and so forth, for the production of such articles as friction clutches, brake bands and the like. Obviously, if the uses to which the articles are to be put so require, additional fillers, such as ground resinoids, natural resins, inorganic powders and the like may be incorporated. Similarly, depending upon the requirements of the finished product, the relative percentage of the ingredients herein set forth may be varied to conform the final article to such requirements. Hence, for example, where it is desired to obtain substitute leather having a relatively high degree of softness or pliability, the percentage of the greased softener may be increased within reasonable ranges. Furthermore, if desired, other lubricants, whether oleaginous or non-oleaginous, such as graphite, soapstone, insoluble soaps and the like, may be employed. It will be appreciated that in making finished articles under the present process, solid materials may readily be suspended in the impregnating bath so as to cause their adhesion to or incorporation in the fiber base.

It is to be understood that the particular treatment of fibrous materials herein described is given as merely illustrative of one method of modifying a raw material to obtain a product of improved physical characteristics. The described treatment may be associated and properly correlated with other treatments to further and advantageously modify the characteristics of fibrous starting materials; in other words, impregnating and tanning agents herein described may be used alone, as stated, upon fibrous material, or may be employed in conjunction with other agents to produce improved fiber base products.

It is particularly to be observed that the fundamental concept of the present invention is the production of a substitute leather. For this purpose, the chemical status of the tannable constituents of hides is duplicated is so far as possible. In operating under the invention, as will now be appreciated, a fibrous matrix is impregnated with a chemical system which closely approximates that of hides or skins immediately prior to tanning. In natural leather tanning the essential operations, apart from the preliminary quasi-mechanical steps, such as removal of hair and adipose tissue, involves the removal of the elastin of the skin and the partial hydrolysis of the collagen. This partial hydrolysis results in the formation of a certain percentage of proteoses, peptones, polypeptides and amino acids. In natural leather tanning therefore the system which is tanned comprises a protein nucleus of unconverted collagen and an associated network of specifically different, but balanced amounts of proteoses, peptones, polypeptides and amino acids. The combination of the tanning material with such a system produces leather. In the ultimate product, namely the leather, the physical characteristics such as pliability, strength and the like are largely determined by the respective amounts or balance between the different portions.

The present invention is based upon an extensive research, the purpose of which was, as noted, to simulate or substantially duplicate the physico-chemical status of animal skins or hides immediately prior to tanning. As noted this comprises establishing a fibrous base and saturating this with a special chemical, matrix-forming system, made up of balanced amounts of proteins and hydrolytic protein conversion products such as proteoses, peptones, polypeptides and amino acids including glycine, leucine, aspartic and glutamic acids. After saturating, the products is converted or tanned to a leather-like mass. It is to be observed that this specially produced chemical system or saturant which is employed not only parallels that of tannable hides qualitatively but also quantatively. For this reason, it is particularly to be observed, there is preferably employed as starting material a number of specifically different protein materials, (e. g. bone glue, animal hide glue, albumin, casein, etc.) which upon controlled hydrolysis produces the substantial balance of the several proteolytic materials such as exist in natural collagen. With such a balance definitely and positively established, the tanning process, as explained, proceeds as in the case of natural or true leather and equivalent end products are thus produced.

This concept is carefully to be distinguished from the simple step of tanning a given protein material, such as glue, with a tanning agent, such as formaldehyde. While it has long been known that glue may be combined with, say, formaldehyde, it is also known that the resulting product is a hard, brittle material which cannot be plasticized satisfactorily. Such a material is not within the concept of the present invention.

The proteins, as is known, are hydrolyzed, so to speak, step by step, yielding in turn bodies of decreasing complexity, namely: the proteoses, peptones, polypeptides and finally simple amino acids.

In the present invention therefore a starting material comprised of different proteins is definitely hydrolyzed for such a predetermined time and under such controlled conditions of temperature and pressure as to insure the formation of a balanced amount of the several proteolytic materials described. Thus, operating under the invention, that is to say, by hydrolyzing the stated protein mixture at a temperature of substantially 170° F., for a period of an hour, and under definitely alkaline conditions (pH 12) a

definite controlled conversion of the character described takes place. This manifestly produces an amino acid network different from that obtainable from any one protein. The resulting product, under these conversion conditions, then comprises from substantially 20 percent to substantially forty percent of a balanced amount of peptones, polypeptides and simple amino acids and from sixty percent to eighty percent of substantially unconverted proteins and proteoses.

It will be appreciated that while alkaline hydrolysis has been described, as a specific example, the same result may be secured with acid hydrolysis as, for example, by hydrolyzing the protein starting material with an acetic acid solution (pH 3.0) at substantially 170° F. for a period of about an hour.

I claim:

1. An article of manufacture comprising a cellulosic base impregnated with glycine-like hydrolytic products of proteolytic material and finely dispersed rubber latex, each of which has been coagulated in situ.

2. A method of preparing artificial leather which comprises saturating cellulosic material with a solution of albuminous materials which have definitely been hydrolyzed at temperatures of the order of 170° F. and in the presence of a suitable reagent and tanning materials in which peptized rubber latex is homogeneously dispersed and then subjecting the saturated cellulosic material to the action of a coagulant.

3. A method of preparing artificial leather which comprises saturating felted cellulosic material with a solution of protein material which has definitely been hydrolyzed under the action of heat and an appropriate reagent and tanning materials in which finely dispersed rubber latex is homogeneously incorporated, allowing the saturated material to age and then subjecting the material to the action of a coagulant which fixes components of the impregnating solution in insoluble form in and between the fibers.

4. A method of producing leather-like compositions which comprises subjecting a mixture of proteins to hydrolysis at a temperature sufficiently high and for a time sufficiently prolonged to produce a substantial amount of amino acids, saturating a fibrous base with the hydrolyzed material and then subjecting the saturated product to the action of a tanning solution.

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