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COMPOSITION AND METHOD FOR SURFACING LEATHERS AND LEATHER SUBSTITUTES BASED ON FILLED POLYURETHANE LATEX

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ABSTRACT OF THE DISCLOSURE

Formation of leather-like surfacing from coating compositions comprising aqueous dispersions of polyurethane latex containing 10 to 50 percent by weight of a tough, flexible, organic particulate filler such as as leather dust, organic spheroids, or the like, having an average diameter of 10 to 75 microns, the slurry having a mayonnaise-like consistency and a viscosity of about 30 to 2500 poise and being suitable for coating of substrates such as imperfect leather, leather splits, woven or non-woven fabrics, or polymeric films.

This is a division of U.S. patent application Ser. No. 755,436, filed Aug. 26, 1968 and now abandoned.

This invention relates to the finishing of leather and leather substitutes. More particularly it relates to the formation of a surfacing over leathers, such as splits and imperfect topgrained leathers, fabrics, and leather substitute base materials.

In the leather processing industries, the choicest pieces of leather are selected with care for uses where top grade hides are used, for example in handbags, high quality men's shoes', etc. The remaining hides which are scarred or otherwise defective are used in lower grade applications where possible. A large amount of very thick hides are split to remove the topgrain surface for use in high quality applications, the remaining part of the hide, referred to as a "split," has no smooth grain surface, but rather has an open rough fibrous surface on both sides. Even with a great deal of buffing and the best known treatments for finishing, it has not hitherto been possible to form a surface on splits which would make the same acceptable in high quality applications.

Various synthetic substrates are now available which can provide the strength, stretchability and toughness of leather, but which do not have a truly leather-like appearance. Such synthetic substrates include cloth, polymer impregnated needle-punched heat-shrunken nonwoven webs, and certain leather fiber-polyurethane water laid sheets. If water vapor transmission is not necessary in the finished leather substitute, the substrate can be an impermeable plastic film such as one, for example, from polyvinyl chloride.

Many leather substitutes have been produced or proposed in recent years, using some of these synthetic substrates, but most of these, for example, those having polymeric surfaces, are difficult to finish with conventional and economical aqueous based leather finishes. Poor adhesion of the finish is often experienced, and a non-leather-like appearance often results.

Most of these newer leather substitutes are made by applying a coating from an organic solvent or a mixture

of a solvent and a non-solvent (usually water) to a suitable substrate, followed by extracting the solvent from the coating with the non-solvent. Such coatings have the disadvantages associated with the use of an organic solvent and in addition, some of them are cumbersome, costly, and difficult to make.

It is an objective of the present invention to provide on irregular leathers, fabrics, and leather substitute base materials, a surfacing capable of being finished by conventional leather finishing coatings and techniques of conventionally finished topgrained leathers. It is a further objective of this inventiion to apply such a surfacing from an aqueous polymer dispersion or latex system. Further, in accordance with this invention, compositions are provided which employ polyurethane-urea latices as the binder for the coating composition. Substrates surfaced in accordance with the invention have excellent appearance and flex durability, and can be formed with good moisture vapor transmission characteristics.

Briefly summarized, the present invention provides compositions and processes for coating or surfacing leathers or leather substitutes to smooth out surface irregularities, which surfacing is receptive to conventional leather finishes, and thus can be further finished, if desired, without substantially altering conventional leather tannery procedures. Leathers and leather substitutes can be surfaced in accordance with this invention to provide both smooth finishes having the appearance of natural leather and velvet-like suede appearing sheet materials. The invention utilizes a thicknened polyurethane latex which contains a tough, flexible organic particulate filler such as leather dust or polymeric particles. The particulate fillers used in the practice of the invention are in the size range of about 10 to 150 microns and preferably 15 to 75 microns. The filler particles may range in shape from irregular ground up particles to more uniform spheroidal shapes resulting from suspension polymerization. The filler is preferably harder and less elastic than the elastomer of the latex and thus contributes to the leather-like, as contrasted to plastic or rubber-like, appearance and feel of the coatings. The addition of 10 to 60% by weight (based on the total solids content of the latex) of the filler not only increases the breathability of the coating, but also provides a surface surprisingly receptive to conventional leather finishes. The thickened latices used in the practice of the invention have a viscosity in the range of 30 to 2500 poise, and can best be described as having a "mayonnaise-like" consistency. They are applied to the substrates by known methods, such as knife coating, roll coating, spraying, casting or brushing. The composition can be coated directly on the substrate, or can be first applied to a release surface and then transferred to the substrate.

In a preferred embodiment the filler is in the form of small, brightly colored elastomeric spheres which provide a flat, velvet-like appearance to the coatings. These preferred coatings are startlingly attractive in appearance, particularly when used for forming women's shoes. For dark colored finished sheet materials, it is preferred to use leather dust as the filler, because products are obtainble which closely resemble natural leather in texture and appearance.

The elastomeric polyurethane latices useful in forming the coatings of the present invention consist of polyether polyurethane, polyester polyurethane, polyurethane-urea,

or other urethane latices having the hereinafter specified minimum physical properties. As is known to those skilled in the art, polyurethanes can also be prepared from polyester-ether polyols or various mixtures of polyesters and polyether polyols with each other and/or poly amines. For convenience, these will all be referred to herein as "polyurethane latices." Examples of the suitable latices are those disclosed in U.S. Patent 2,968,575, issued Jan. 17, 1961 (Mallonee), and U.S. Patent 3,264,134 issued Aug. 2, 1966 (Vill and Suskind), or British Patent 1,078,202 published Aug. 9, 1967. The preferred polyurethanes are those formed from the reaction product of an organic diisocyanate with a polyoxyalkylene glycol or polyol chain extended with a compound having at least two active hydrogen atoms, for example water or a polyamine, such as piperazine, dimethyl piperazine, hydrazine, methylene bis-3-chloro-4-aniline, 2,4-tolylene diamine, ethylene diamine, polyoxyalkylene diamines or the like. Alternatively polyoxyalkylene glycols or dimercaptans may be used as chain extending agents. Coatings for leather substitutes having outstanding charatceristics can be prepared by using chain-extended polymers formed by the reaction of isocyanate terminated prepolymers of polyoxyalkylene glycols and organic diisocyanates with the above-noted diamines or water to provide a polyurethane having a number average molecular weight of at least about 10,000 and having the hereinafter specified physical properties.

The polyurethanes which result in useful leather substitutes must be elastomeric and resistant to creep or flow at ambient temperatures. They generally have been found to have a brittle temperature of about −10° C. or lower, and preferably −30° C. or lower. The polyurethane should have a tensile of at least 300 p.s.i. (21 kg./cm.^{2}), more preferably at least 1000 p.s.i. (70 kg./cm.^{2}), and should have an elongation at break of at least 300 percent, preferably at least 600 percent. The modulus (stress at 100 percent elongation) should be between 50 (3.5 kg./cm.^{2}) and 1000 (70 kg./cm.^{2}) p.s.i., and preferably between 100 and 500 p.s.i. (7 to 35 kg./cm.^{2}) for shoe uppers. These properties can be measured on the polymer as isolated and formed in any suitable manner into a coherent shape, such as a film, and the resulting form, e.g. cast film, may be heated or hot pressed prior to testing to insure the effective removal of solvent, etc. However, it should be understood that the above properties are merely illustrative of those displayed by elastomeric polyurethanes useful in the practice of the invention, since the measurements obtained on any given test sample may vary with the technique used to prepare the sample for test purposes. For example, the properties may be altered by the presence of residual amounts of emulsifying agents, incomplete solvent removal, additional heat curing occurring during or after film formation, physical working of the film, or the presence of moisture. Therefore, the above values are representative of the properties measured on samples of the preferred elastomeric polyurethanes. Test samples should be prepared by using conditions as similar as practically possible to those encountered in manufacturing the coatings of the invention.

As noted above, the chain extension of isocyanate-terminated prepolymers provides one method of forming polymers useful for the invention. For example, prepolymers bearing terminal isocyanate groups may be prepared by adding one or more polyoxyalkylene polyols, polyoxyalkylene diamines or hydroxy terminated polyesters to an excess of organic diisocyanate, and by carrying out their reaction in a temperature range from about room temperature to about 100° C. Another procedure is to react the diisocyanates with an excess of polyoxyalkylene glycol, polyester glycol or polyoxyalkylene diamine so as to prepare the dimerized glycol or diamine, and then cap this material with isocyanate groups, i.e. add it to an excess of diisocyanate to form a prepolymer having terminal isocyanate groups. Reactive prepolymers such as these may subsequently be converted to the desired polyurethanes of this invention by reaction with compounds having at least two reactive hydrogen atoms. By "active hydrogens" as the term is used herein, is meant hydrogens which display activity according to the Zerewitinoff test described in J.A.C.S. 49, 3181 (1927). Typical groups are hydroxyl, carboxyl, primary or secondary amino, and mercapto groups.

Various organic diisocyanates may be used in the preparation of prepolymers for use in the invention. Because of their ready availability and the fact that they are liquid at room temperature, mixture of the 2,4- and 2,6-toluene diisocyanate isomers are preferred. Other preferred diisocyanates are 4,4′-diphenylene methane diisocyanate, and 3,3′-dimethyl 4,4′-diphenyl diisocyanate. Further examples of useful aromatic diisocyanates include paraphenylene diisocyanate, meta-phenylene diisocyanate, 4,4′ - diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 4,4′-diphenyl ether diisocyanate, 3,3′-dimethoxy 4,4′-diphenyl diisocyanate, 4-chloro-1,3-phenylene diisocyanate and xylylene. Suitable aliphatic or cycloaliphatic diisocyanates include the simple alkylene diisocyanates such as hexamethylene diisocyanate as well as more complex materials such as bis(2-isocyanatoethyl) fumarate, bis(2-isocyanatoethyl) carbonate, bis(2 - isocyanatoethyl) 4-cyclohexene-1,2-dicarboxylate, bis(2-isocyanatoethyl)-1,4,5,6,7,7′-hexachloro-5-norbornene-2,3-dicarboxylate.

Polyoxyalkylene glycols or polyols used in preparing such prepolymers have molecular weights generally ranging from about 300 to about 5000 and preferably from about 400 to about 3000, the more resilient polymers normaly being obtainable from higher molecular weight glycols. Examples of such polyoxyalkylene glycols are polyoxyethylene glycol, polyoxypropylene glycol, polyoxytetramethylene glycol, and higher polyoxyalkylene glycols. These polyether glycols are prepared by well known ring opening or condensation polymerizations. When these polyols contain recurring oxyethylene groups, the total weight fraction of such oxyethylene groups should be controlled since this structure tends to confer water sensitivity to the finished product. Other suitable polyols include castor oil, hydroxyl terminated polybutadiene and hydroxyl terminated vinyl polymers, preferably in the 500–5000 molecular weight range.

Polyoxyalkylene diamines prepared from polyglycols, such as polyoxypropylene glycol, may also be used to prepare useful polyureas or polyurethane-ureas, as described in U.S. Patent 3,179,606. Such diamines usually have molecular weights from about 500 to about 10,000.

Polyester glycols or polyols may be used alone or together with polyether glycols or polyols in the preparation of the prepolymers for use in this invention. Polyester glycols or polyols may be prepared for example by reacting dicarboxylic acids, esters or acid halides with simple glycols or polyols. Suitable glycols include ethylene, propylene, diethylene, dipropylene, tetramethylene, decamethylene glycols, 2,2-dimethyl-1,3-propane diol, and cyclic glycols, such as cyclohexanediol. Polyols such as glycerine, pentaerythritol, trimethylol propane, and trimethylol ethane, may be used in limited amounts to introduce chain branching into the polyester. These hydroxy compounds are reacted with aliphatic, cycloaliphatic or aromatic dicarboxylic acids or lower alkyl esters or ester forming derivatives thereof to produce polymers bearing terminal hydroxyl groups, and being characterized by molecular weights in the same approximate range as for the aforementioned polyoxyalkylene glycols; preferably the molecular weights are from about 400 to about 4000, and more preferably from about 1000 to about 2000. Examples of suitable acids are, for example, succinic, adipic, suberic, sebacic, phthalic, isophthalic, terephthalic and hexahydro terephthalic acids and the alkyl and halogen substituted derivatives of these acids.

The formation of a prepolymer can be carried out with or without solvents, although the presence of solvent may

often facilitate mixing and handling. Common solvents which are inert to isocyanates may be used, such as toluene, xylene, etc. Chain extension of the prepolymer may be partially carried out in solution before emulsification. In this connection small difunctional molecules, such as diethylene glycol or diamines, may be used as chain extending agents to increase the density of polar sites in the finished polymer and thereby increase such physical properties as the modulus and tensile strength. Correspondingly, the prepolymer may be partially reacted with other glycols or other difunctional or trifunctional materials in such amount that the finished reaction product still retains isocyanate termination.

The prepolymer is finally emulsified in water and extended with water or polyamine during the emulsification process, as in the procedures of Mallonee U.S. Patent 2,968,575, or Wyandotte British Patent 880,665, or Vill and Suskind U.S. Patent 3,264,134. Other suitable latices will be apparent to those skilled in the art.

In some cases the filler particles may be prepared directly during the emulsification-polymerization step, by carrying out the emulsification step with reduced agitation. In this way, a mixture of small latex size particles and larger (than 10 micron) spheroidal particles may be formed in one procedure. Alternatively, two separate latices can be prepared, one having larger, preferably harder particles, and the other having smaller, preferably more rubbery particles.

The prepolymers before chain extending may be modified with other ingredients such as plasticizers, dyes, pigments, minor amounts of other compatible polymers, or agents which provide light, heat, or oxidative stability, and the like, as long as the elastomeric character of the polyurethane is not lost.

As an alternate to the use of a di- or polyisocyanate, phosgene chemistry may be used directly to prepare the prepolymers. For example, as is well known, phosgene may be reacted with a diamine to form an isocyanate terminated prepolymer. In a similar way carbonate esters may be reacted with diamines to produce isocyanate terminated prepolymers.

In order to have microporous polymeric films or coatings with the greatest stability of the microporous structure at ambient temperatures, it is desired that the polymeric material should be crosslinked since this will reduce its thermoplasticity. Such crosslinked products also have better flex durability and are more resistant to solvent, and have many other advantages. The amount of crosslinking required will depend on the average chain length of the polymeric material involved. The crosslinking should not be enough to reduce the ultimate elongation at break to less than 300%. Polyurethanes having a crosslink density of about 1 crosslink per 5,000 to 1 per 15,000 atomic weight units of polymer are preferred. Less crosslinking is required in the case of very high molecular weight polymers. Chain branching of the polymer can also be achieved by high temperature heating of the prepolymer or the final polymer.

The polyurethane latices useful for these coatings may be anionic, cationic, or nonionic, but for most purposes anionic latices have been found to be easiest to work with and the most useful.

In making these coatings on a porous substrate, it is preferred to add a thickening agent to the latex so that the final viscosity of the coating material is in the range of more than 5000 cps. and preferably more than 10,000 cps. Such thickened materials are applied easily to permeable substrates and form uniform coatings.

Suitable thickening agents include finely divided silica, polyacrylic acid thickeners, methylcellulose, carboxyl methylcellulose, polyvinyl pyrrolidone, and the like.

When thickened latices are coated in accordance with the invention on an open porous surface such as cloth with a single thick coating in such a way that surface irregularities are covered, the resulting coated film is smooth and free from many imperfections that would normally arise if a multiplicity of thin coats were applied to the same substrate. In addition, the use of a thickened latex reduces the amount of impregnation of, or penetration into, the substrate to an insignificant amount. Furthermore, in pigmented or filled systems, where the added material is of large particle size and which would normally have a tendency to settle, the use of the thickened latex keeps the particles in uniform suspension such that a uniform coating of good appearance is obtained in contrast with those obtainable from a low viscosity latex.

Leather dust obtained for example, by collecting ground, tanned leather, such as from the grain side of chrome tanned kips, can be sorted to a satisfactory size by removing that which does not pass through a 40 mesh screen. Use of about 10–40% leather dust based on total weight of the dried coating gives good results and the use of about 25% is preferred. Such coatings, if not perfectly smooth, can be readily buffed to give a surface strongly resembling a top quality leather. When applied to a leather split the product has exceptional appearance, hand and break, and in addition can be finished with conventional leather finishes.

Films made from the mixture of filler particles such as leather dust and polyurethane latex have surprisingly been found to have a much higher modulus than films of the latex alone.

Colored polyurethane or other rubbery spherical particles, usually in amounts of 25–60% of the total solids weight, may also be mixed into the thickened polyurethane latex. Coatings from such mixtures have a fine suede-like, non-glossy, pleasing appearance. When a mixture of colors are used to give a composite color, such as red, yellow, and blue to give brown, an especially pleasing appearance is obtained.

As mentioned earlier, colored polyurethane spheres can be made simultaneously with the preparation of the latex by using a pigmented prepolymer and mild agitation during the emulsification procedure.

Many resins are in the right particle size range to be useful as fillers in the preparation of these products. Colored particles can be made by grinding colored resins, for example polyvinyl chloride, to the right size or by precipitation from a solution. Some polyvinyl chloride may be used along with other particles to contribute scuff resistance to the resulting coating.

A preferred embodiment of this invention is the use of a water-immiscible, high boiling, non-solvent organic liquid, finely dispersed in the thickened latex coating composition to contribute a desirably high moisture vapor permeability to the resulting coating. Such liquids usually have a boiling point of about 150°–300° C., such that on drying, the water from the latex can be evaporated first and then the organic liquid, so that on evaporation microporous channels will be left through the coating to permit the transmission of water vapor.

The organic liquid should not be a solvent for the polyurethane or of the particulate filler. Suitable organic liquids for this use include mineral spirits having a boiling point above 150° F., hexadecene, dodecene, dodecyl chloride, and the like.

Alternatively, microporosity can be achieved by freeze coagulation of the polymer or other known techniques.

The microporous polymeric materials applied to such substrates usually have a thickness after drying of 3 to 30 mils and preferably from about 5 to 15 mils. The coatings may be applied to suitable substrates by knife coating, spray coating, roller coating, brushing, extrusion, or by any other suitable technique.

It is possible to form unsupported films by process of this invention and the latex polymer can be reinforced by fiber additives to improve tear and tensile strength. In this case the films are usually cast on a glass or stainless steel support which allows the fim to be easily released

after the drying operation. Such films may be laminated to a suitable substrate, if desired.

Often it is desirable to add a fibrous material to the latex polymers used in the process of this invention to reinforce the polymer after coating. Such fibrous materials are usually used in small amounts sufficient to give the reinforcing required. Higher amounts may be used if the fibers are of such a fine nature that they do not unduly change the hand or texture of the finish coating.

EXAMPLE I

Chrome tanned leather buffing dust (Trostel Tanning Company) was passed through a wire screen having 0.4 mm. openings by mechanical shaking. 180 grams of the leather dust from this screening was added to 450 grams of mineral spirits and mixed by hand until all of the leather dust had absorbed some of the mineral spirits (boiling point 160–200° C.). 60 grams of oleic acid, U.S.P., was added to the above mixture and agitated by hand. 60 grams of ammonium hydroxide, at 28% concentration, was added to the mixture and mixed by hand for several minutes. The oleic acid and ammonium react to form ammonium oleate, a surface active agent which assists in wetting of the leather by the mineral spirits and dispersal thereof in the latex. The resultant paste-like mixture was then allowed to stand for several minutes. 450 grams of tap water was then added to the mixture and agitated with an air motor at a relatively slow speed. 1040 grams of 51.4% total solids anionic polyurethane latex (Wyandotte Chemicals Corporation's X–1028 Latex) was added to the mixture while the mixture was being continuously agitated with the air motor. Another 500 grams of tap water was then added to further reduce the viscosity. 9 grams of a dry sodium salt of a condensed naphthalene sulphonic acid (Rohm and Haas Company's Tamol N) was added to the final mixture and allowed to mix for approximately 15 minutes. The mixture was then agitated in an Eppenbach Home-Mixer for 15 minutes at a fairly fast speed (Variac Setting—70). The mixture was allowed to cool to room temperature (72° F.), then sprayed with an airless spray gun with a spray tip orifice of .015 inch (0.38 mm.) and with an air gauge pressure of 60 pounds onto a chrome tanned leather split that had been swab-coated with a thin layer of an emulsified reaction product of organic diisocyanate and polyalkylene ether glycol chain extended with water to an approximate thickness of .045 inch (1.14 mm.). The viscosity of the coating mixture was 18,600 centipoise at 70° F. The sample was then put into a 120° F. forced air oven for 16 hours. The sample was then buffed with 400 grit sandpaper to smoothness and a final coating thickness of approximately .015 inch (0.38 mm.).

A commercially available aqueous acrylic type finishing system was then sprayed on the sample in three coats.

The sample has a smooth leather-like appearance. The water vapor transmission rate of the coated sample was found to be 420 grams of water transmitted through 100 square meters per hour. A 40 mm. by 70 mm. rectangle was cut out of the sample and placed on a flexing machine (Bally). The coated sample flexed over 70,000 times before the specimen failed. The same figure was obtained for the uncoated leather split.

EXAMPLE II

Example I was repeated except the Tamol N was omitted. The mixture had a viscosity of 27,000 centipoise and sprayed well, but several imperfections were noted in the coating.

The W.V.T. of this coated leather split was 550 grams. The flex life was 700,000.

EXAMPLE III

In a pint jar the following materials were hand mixed in squence:

30 grams of chrome tanned leather dust which has been passed through a screen having 0.4 mm. openings (40 mesh) and which had particles mostly in the 10–50 micron size range
75 grams of mineral spirits (B.P. 160°–200° C.)
10 grams of oleic acid
70 grams of 10% aqueous sodium hydroxide, and
21 grams of tap water.

After the mixture was homogeneous, 209 grams of Wyandotte E–411 polyurethane latex (90 grams of solids) was added.

The mixture was then stirred for 30 seconds with a high shear mixer. It had sufficient viscosity so that when stirred, the surface remained deformed.

After centrifuging to remove air bubbles, the mixture was knife coated on cotton cloth at a 40 mil wet thickness. The coating was dried at 65° C. for 16 hours and heated at 150° C. for 30 minutes.

The coated cloth had a water-vapor transmission rate (WVT) of 16.4 grams per square meter per hour, and was flexed 1.28 million flexes o na Newark leather flexer (commercially available from Newark Leather Finish Co.), at which point the test was stopped, showing no sign of failure. A similar coating, made with ammonium hydroxide in place of sodium hydroxide, was viscous but would flow out after being stirred. A coated cloth had a WVT of 9.7 gms./m.^{2} per hour. It likewise flexed for 1.28 million flexes without failure.

Water vapor transmission is measured by covering a cup containing water with the test sample and measuring weight loss to an external atmosphere of 50% relative humidity and 21° C. over a 24 to 48 hour period.

EXAMPLE IV

A 42.3% solids polyether-polyurethane latex was formed by emulsifying in water a prepolymer prepared by reacting 21.0 moles of 2000 average molecular weight polyoxypropylene diol and 5.4 moles of 425 average molecular weight polyoxypropylene triol with 58.5 moles of toluene diisocyanate (TDI) (80.20 ratio of 2,4: 2,6 isomers) at 85° C. for three hours to an isocyanate equivalent of 928. This composition had one triol unit for each 10,000 hypothetical atomic weight units in the formulation. A film, dried, heated at 150° C. for 20 minutes, and then held cooled to 21° C. at 50% relative humidity had the following physical properties; measured with an Instron Tensile Tester using ⅛ inch (.317 cm.) wide dumbbell sample and a jaw separation rate of 20 inches (50.8 cm.) per minute:

Tensile strength: 980 #/in.^{2} (69 kg./cm.^{2})
100% modulus: 120 #/in. (8.4 kg./cm.^{2})
Percent elongation at break: 970%

Coatings dispersions were prepared using this latex and two filler levels of 40 mesh chrome tanned leather dust as in Example III. One part of tanned leather dust was mixed with 2½ parts of mineral spirits (B.P. 160–200° C.) and ½ part each of oleic acid and concentrated aqueous ammonia. This mixture was added to the above latex to give mixtures having 10% and 25% leather dust based on solids. The mixture was stirred briefly with a high speed blender followed by centrifuging to remove air.

Viscosities, measured with a Brookfield Model RVW Helipath Viscometer at 25° C., were

	Poise
10% leather dust sample	285
25% leather dust sample	4750

Knife coatings (0.1 cm. orifice) were made from each on untreated cotton cloth and on polyester film. The coatings on cloth were dried in a 65° C. forced air oven. The coated polyester films were air dried. Both were fused at 150° C. for 30 minutes, followed by reconditioning at 21° C. and 50% relative humidity. The coatings made on polyester film were stripped off and tested for tensile, modulus, and elongation. The coated cloth samples were

checked for flex durability and water vapor transmission.

The following results were obtained:

Percent leather dust	Tensile lbs./in.²	100% modulus, lbs./in.²	Percent elongation	WVT, g./m.²/hr.	Flex durability (Newark)
10	340 (24 kg./cm.²)	250 (17.6 kg./cm.²)	510	4	No failure at 4,000,000.
25	260 (18.3 kg./cm.²)	260 (18.3 kg./cm.²)	100	2.5	Do.

The two coatings both accepted standard aqueous leather finishes, and the finished coatings had a similar appearance. Those with 25% leather dust loading were more leather-like to the touch than were the 10% leather samples.

EXAMPLE V

A coating dispersion was prepared from the following formulation as in Example IV:

	Grams
40 mesh chrome tanned leather dust	30
Mineral spirits	75
Oleic acid	15
Concentrated NH_4OH (28–30% NH_3)	15
Water	38
Latex described in Ex. IV at 42.4% solids	212

The viscosity of the mixture was found to be 455 poises. The mixture was knife coated (0.1 cm. orifice) onto a needle punched polypropylene non-woven web which had been sized and filled with a polyurethane latex (Wyandotte E–207) and which had a thickness of about 60 mils (.15 cm.).

The coating was then dried at 65° C. for several hours followed by a fusion cycle at 150° C. for 45 minutes and reconditioning at 50% relative humidity at 21° C.

The coated non-woven web was flexed on a Bally flex tester and failed after 147,000 cycles.

This construction can be finished with conventional leather finishes and has adequate strength, abrasion resistance and flex durability to be used for upholstery or shoe uppers. It had excellent break, similar to that of high quality leather.

EXAMPLE VI

Four cationic latices were prepared using the procedure of Suskind U.S. application Ser. No. 311,227 (French Patent 1,410,546, delivre Aug. 2, 1965). The polymers were designed to have an average of one mole of triol for 15000, 10,000, 7500 and 5000 hypothetical average atomic weight units, designated as numbers 1, 2, 3, and 4, respectively, and were prepared from the following formulations:

Number 1

	Grams
(A) 1968 average molecular weight diol	300
(B) 424 average molecular weight triol	10.66
(C) TDI (80/20 2,4-/2,6-isomers)	66.3
(D) Methyldiethanolamine (MDEOA)	7.54

Number 2

(A) Diol	300
(B) Triol	16.66
(C) TDI	73.6
(D) MDEOA	7.80

Number 3

(A) Diol	300
(B) Triol	22.9
(C) TDI	81.9
(D) MDEOA	8.08

Number 4

(A) Diol	300
(B) Triol	37.0
(C) TDI	98.6
(D) MDEOA	8.71

Charges A, B and D were weighed into bottles and mixed until homogeneous. Then Charge C was mixed in, the bottles capped and placed on a roll mixer and allowed to exotherm for 2 hours, after which they were placed in a 65° C. oven for 2.5 hours and then back on the rollers for 40 hours at room temperature. Each of these was then emulsified in water containing acetic acid with the aid of a high speed mixer and allowed to stand several days before using. The emulsification charges and percent solids of the latices are in the table below:

Number	Parts			Percent solids
	Prepolymer	Water	Acetic acid	
1	384.5	557	11.6	34.2
2	398.06	600	12.0	36.7
3	411.88	618	12.4	42.3
4	444.31	668	13.4	36.3

Coating dispersions were prepared from each of the four latices by mixing 30 grams of 40 mesh chrome tanned leather dust with 75 grams of mineral spirits (B.F. 160–200° C.), 15 grams water and enough latex to give 90 grams of polymer solids. Enough water is used above to give a total weight of 425 grams. The ingredients were mixed with a high shear mixer followed by centrifuging to remove any entrapped air bubbles.

A 0.1 cm. (wet) knife coating was made on untreated cotton cloth from each of the above, dried at 65° C. for 3 hours, fused at 150° C. for 30 minutes and then reconditioned at 50% relative humidity and 21° C.

Number	Hypothetical crosslink density	WVT, g./m.²/hr.	Viscosity, poises	Newark flex, cycles to failure
1	1/15000	5	5,500	5,300
2	1/10000	5.3	1,900	668,000
3	1/7500	4.6	250	668,000
4	1/5000	4	2,900	5,300

With this system, a hypothetical crosslink of 1 triol to 7500–10,000 atomic mass units polymer is preferred to give maximum flex durability.

EXAMPLE VII

400 grams of the polyether-polyurethane prepolymer of Example IV (at 75% solids, 25% toluene) was emulsified in 500 g. of water using a high speed mixer for 3 miutes. 3.71 grams of 64% hydrazine was added and emulsification continued for another 15 seconds. The latex was allowed to stand for several days after which the toluene was azeotroped out under vacuum. The latex had a solids content of 42.4%.

A film prepared from the latex had the following properties:

Tensile strength: 1110 #/in.² (78 kg./cm.²)

Modulus (stress at 100% elongation): 160 #/in.² (11.3 kg./cm.²)

Percent elongation at break: 660%

A coating dispersion was prepared with the above latex and 25% of 40 mesh chrome tanned leather dust as in Example III. The viscosity was 430 poises.

A coating on cloth made as before had a WVT of 4 grams/m.²/hr. and flexed 2½ million cycles on a Newark flexer without failure. This coating composition is similar to that of Example II, except that diamine was used for chain extension. Its higher modulus gave somewhat improved scuff resistance.

EXAMPLE VIII

A series of latices were prepared as in Example IV but using different amounts of triol. Coating compositions,

made up as in Example IV were applied to cloth, and after drying and heating were tested for flex durability.

	Hypothetical atomic weight units per mol of triol	Newark flex to failure, cycles
a	50,000	1,000
b	32,000	1,000
c	18,000	18,000
d	13,000	650,000
e	10,000	>1,800,000
f	8,000	>1,300,000
g	6,000	>2,000,000
h	4,000	800,000

The coated cloth of sample d was heated an extra hour at 150° C. and then required 1,270,000 flexes before failure occurred. The coated cloth of sample h was heated an extra hour at 150° C. and then withstood 2 million flexes without failure.

EXAMPLE IX

A polyester-polyurethane latex was prepared by emulsifying 1500 grams of isocyanate capped hydroxyl terminated polyester (Witco P611) diluted to 75% solids with toluene in 2260 grams of water. The toluene was azeotroped out under vacuum. The resultant latex was at 53.3% solids. A coating dispersion was prepared using this latex by the following formulation:

	Grams
Chrome tanned leather dust (40 mesh screened)	30
Mineral spirits	75
Oleic acid	15
Concentrated NH_4OH	15
Latex at 53.3% solids	169
Water	50

The viscosity after mixing was 375 poise. A 0.1 cm. knife (wet) coating was made on untreated cotton cloth, dried at 65° C., put through a fusion cycle of 150° C. for 30 minutes and 200° C. for 10 minutes, followed by reconditioning at 50% relative humidity and 21° C. It has a WVT of 4 g./m.²/hr. This coating could be finished with conventional leather finishes and has exceptional scuff and abrasion resistance. Thus, it has special utility where rough handling is encountered such as in luggage.

EXAMPLE X

A latex was prepared as in Example IV, except that just prior to emulsification, the prepolymer was diluted with toluene, certain pigments were added, and the mixture was put through a stone mill to obtain adequate dispersion. The latices obtained had large and small particles. The largest particles were spheroids about 80μ in diameter which served as a particulate filler.

Pigment				Grams			WVT of resulting coating
Latex	Color	No.	Vendor	Prepolymer (75% solids)	Pigment	Water	
1	Red	9273	Drakenfeld	1,600	90	2,200	
2	White	RA	Titanox	1,600	90	2,200	
3	Blue	F18029	Ferro	1,600	90	2,200	
4	Yellow	1079	Reichhold	1,600	90	2,200	10.6
5	Black	10R	Cabot	1,600	30	2,200	5.5
6	Buff	F17126	Ferro	1,600	90	2,200	8
7	Green[1]						8.3

[1] Mixture of above latices.—7.3% red; 10.4% white; 41.8% blue; 32.2% yellow: 8.3% black.

Toluene was removed from the resultant latices by azetroping at reduced pressure. They were thickened with a polyacrylic acid thickener and the pH was adjusted to 6.5–7.0 to obtain thickening. The mixtures had viscosities of approximately 200 poise. The surface of the mixture remained deformed when stirred.

A 40-mil knife coating on cloth was made of each thickened latex and dried at 65° C. for one hour and then 45 minutes at 150° C.

The surface of the coatings was non-glare due to the presence of the crosslinked spheroidal particles. Mixtures of the pigmented latices were also made. These surfaces were likewise non-glare, and had an attractive velvet-appearance due to distinguishable particles of the various colors. These coatings are especially desirable in women's and children's shoes and in upholstery and wearing apparel where the velvety, suede appearance and bright colors contribute to style.

EXAMPLE XI

Coating dispersions were prepared using the latex of Example IV and blue pigmented crosslinked polyester-polyurethane spheres having a particle size of 10 to 75 microns, mostly about 20–25 microns.

The following formulations were used:

10% SPHERES

	Grams
Blue urethane spheres	12
Latex at 43.2% solids	250
2% polyacrylic acid thickener	50
Aqueous ammonia	1

25% SPHERES

Blue urethane spheres	30
Latex at 43.2% solids	208
2% polyacrylic acid thickener	70
Aqueous ammonia	1

50% SPHERES

Blue urethane spheres	60
Latex at 43.2% solids	139
2% polyacrylic acid thickener	45
Aqueous ammonia	0.5

After thorough mixing, the compositions had viscosities of 200, 150, and 260 poise, respectively. Coatings (0.1 cm. wet) were made from each on untreated cotton. The coated cloth samples were dried at 65° C., followed by heating at 150° C. for 30 minutes. Free film samples were also cast, air dried and then heated at 150° C. for 30 minutes. The following properties were observed:

Free film						Cloth coating	
Tensile		100% modulus		Percent elongation	WVT, g./100 m.²/hr.	Newark flex	
Lbs./in.²	Kg./cm.²	Lbs./in.²	Kg./cm.²				
400	28	120	8.4	610	6.5	No failure at 4,000,000.	
1,390	99	140	9.9	630	6	Slight failure at 2,000,000.	
390	27.4	240	16.9	330	5	Failed at 60,000.	

The coatings made with 25% and 50% of polyurethane spheres were non-glossy, compared to that containing 10% polyurethane spheres. They had an attractive velvety suede-like appearance.

EXAMPLE XII

A coating dispersion was prepared using the latex of Example IV with wood flour as the filler. The wood flour had a particle size range of 20 to 100 microns. The following ingredients were blended thoroughly in a high shear mixer and then passed through a stone mill at a 0.005" setting to form a composition having a viscosity of 210 poise:

	Grams
Wood flour	30
Mineral spirits	75
Oleic acid	20
NH_4OH (28–30% NH_3)	10
Latex at 43.2% solids	208
Sulfonated naphthalene-formaldehyde resin (Tamol Sn)	4
2% aqueous polyacrylic acid thickener	100

Knife coatings were on untreated cotton cloth and free films were made as in Example IX.

Free film					Cloth coating	
Tensile		100% modulus		Percent elongation		
Lbs./in.²	Kg./cm.²	Lbs./in.²	Kg./cm.²		WVT	Newark flex
270	19	270	19	140	9.4	Failed at 74,000.

This coating is receptive to conventional aqueous leather finishes, as noted in previous examples, using leather dust.

EXAMPLE XIII

A coating dispersion was prepared using the latex of Example IV and urea formaldehyde spheres having a particle size of 20–40 microns in the following proportions:

	Grams
Urea formaldehyde spheres	30
Latex at 43.2% solids	208
2% aqueous polyacrylic acid thickener	120
Concentrated aqueous ammonia	1

The viscosity after mixing was 710 poise.

Free films and knife coatings on untreated cotton cloth were made as before.

Free film data					Cloth coating data	
Tensile		100% modulus		Percent elongation		
Lbs./in.²	Kg./ m.²	Lbs./in.²	Kg./cm.²		WVT	Newark flex
310	22	280	20	160	9.4	Slight failure at 2,000,000.

This coating had good scuff resistance and was very receptive to conventional aqueous leather finishes.

EXAMPLE XIV

Dispersions were prepared from the latex of Example IV and finely divided, orange pigmented polyvinyl chloride resin having particles of 10 to 150 microns in size.

(A)

	Grams
Filler particles	30
Latex at 43.2% solids	208
2% aqueous polyacrylic acid thickener	150
Concentrated aqueous ammonia	1

(B)

	Grams
Filler particles	60
Latex at 43.2% solids	139
2% polyacrylic acid thickener	75
Concentrated aqueous ammonia	1

The viscosity was 150 poise for the first, and 75 poise for the second. Coatings and free films were made.

	Free film data					Cloth coating data	
	Tensile		100% modulus		Percent elongation		
	Lbs./in.²	Kg./cm.²	Lbs./in.²	Kg./cm.²		WVT	Newark flex
A	230	16	140	10	500	7	No failure at 4,000,000
B	150	10.6	140	10	360	7.6	Do.

The coatings had an attractive velvety appearance and had very good scuff resistance. They have adequate flex durability for use in shoe uppers or upholstery material.

EXAMPLE XV

A polyether-polyurethane prepolymer was prepared by reacting 9.76 moles polyoxypropylene triol of 423 average molecular weight, 52.8 moles of polyoxypropylene diol of 1970 average molecular weight, and 52.8 moles of polyoxypropylene diol of 1016 average molecular weight with 243 moles of toluene diisocyanate (90/20 mixture 2,6/2,4 - isomers) 85° C. for 4.5 hours of methyldiethanol. This prepolymer was then emulsified with a high speed mixer using the following formula to form a cationic latex:

	Parts
Prepolymer	42.3
Acetic acid	1.2
Deionized water	56.5

A synthetic leather substrate was prepared by dispersing 308 grams of chrome tanned leather fibers (Lorum Fiber Co. Y–020–015 fibers at 9% H_2O) in 2.5 gallons of water with the aid of a small paper beater. This was transferred to a 30-gallon chest equipped with agitation and diluted to a total slurry volume of 50.4 liters with 15° C. water. To this 1.7 grams of brown dye and 10.5 grams of sulfonated naphthalene-formaldehyde resin were added and allowed to mix in. Then 2090 grams of the cationic polyurethane latex described above at 40.2% solids was added, followed by 8.4 grams $Al_2(SO_4)_3$, 42.0 grams Na_2CO_3 and 420 grams 1.2% aqueous ammoniated Karaya Gum to precipitate the latex. One-fourth of this flocculated polymer-leather slurry was transferred to a 20 x 20" (50.8 x 50.8 cm.) handsheet mold; 35 grams of ¼" (0.64 cm.) long x 2 denier nylon fibers predispersed in water was added. This was then mixed to uniformly disperse the leather fibers, nylon fibers, and polymer floc particles, followed by drainage through a 30-mesh (0.59 mm. opening) wire screen. The wet web produced was removed, pressed between blotter paper, and dried at 110° C. for 30 minutes. The dried sheet was

buffed to insure uniform thicknesss, and was found to have the following properties:

WVT—21 grams/m.²/hour
Bally flex—very small surface cracks at 547,000 flexes

This sheet makes a very desirable substrate for any of the previously described coatings to give strong, tough leather substitutes.

A topcoat dispersion was prepared using the latex of Example IV and the orange polyvinyl chloride particles of Example XIV as a filler. The following ingredients were used:

	Grams
Latex at 42.5% solids	236
Orange polyvinyl chloride particles	100
2% aqueous polyacrylic acid thickener	25
Concentrated aqueous ammonia	1

To 200 grams of the above, 50 more grams of 2% aqueous polyacrylic acid thickener was mixed in followed by centrifuging. The viscosity was 75 poise. An 0.1 cm. (wet) knife coating was made on the above described synthetic leather substrate, dried at 65° C. for 40 hours, and then fused at 150° C. for 30 minutes, followed by reconditioning at 21° C. and 50% relative humidity. The water vapor transmission was 6 grams/m.²/hour.

What is claimed is:

1. A method for surfacing a flexible, sheet-like substrate comprising:

(a) preparing an aqueous dispersion by blending together, in an aqueous medium,film-forming rubbery polyurethane latex particles less than 10 microns in diameter, said rubbery polyurethane latex particles, when cast and fused to form a film, having a tensile strength of at least 300 p.s.i., an elongation at break of at least 300%, and a modulus at 100% elongation of 50–1000 p.s.i., and a non-fibrous particulate filler, the particles of said filler being in the size range of about 10 to about 150 microns and averaging 10–75 microns in size, said particles comprising 10–60% by weight of the total of said rubbery polyurethane latex particles and said particulate filler, said total being 10–70% by weight of said aqueous dispersion, said aqueous dispersion having a viscosity of 30 to 2,500 poise;

(b) coating the aqueous dispersion obtained according to step (a) onto a flexible substrate; and

(c) drying the resulting coating.

2. A process acording to claim 1 including the further steps of buffing said coating and applying an aqueous leather finish thereto.

3. A process according to claim 1 wherein said filler is leather dust.

4. A process according to claim 1 wherein said filler comprises elastomeric spheroids.

5. A process according to claim 1 wherein said polyurethane comprises the reaction product of an organic polyisocyanate and a polyoxyalkylene polyol.

6. A method according to claim 1 wherein said substrate sheet is split leather.

7. A method according to claim 1 wherein said substrate is a cloth.

8. A method according to claim 1 wherein said substrate comprises a non-woven fabric.

9. A method according to claim 1 wherein said particulate filler particles are harder and less elastic than said rubbery latex particles.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,745,041 Dated July 10, 1973

Inventor(s) Albert E. Raymond

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 10, after "techniques" and before "of conventionally" insert -- to present a smooth high quality surface comparable to those -- .

Column 3, line 5, "poly amines" should be -- polyamines -- ; and line 69, "diisocyanates" should be -- diisocyanate --.

Column 8, line 21, "o na" should be -- on a -- ; line 40, "80.20" should be -- 80:20 -- ; line 51, "120 #/in." should be -- 120 #/in.^{2} -- ; and line 62, "RVW" should be -- RVF -- .

Column 10, line 26 (at the end of the line), "B.F." should be -- B.P. -- ; and line 51 (first word), correct the spelling of -- minutes -- .

Column 13, line 58 (in the second column of the Table under the heading "Tensile"), change "Kg./m^2" to -- Kg./cm.^{2} -- .

Column 14, line 10 (in the second column of the Table), correct the spelling of -- Tensile --; lines 29-36 (in Example XV) have been omitted, and should be inserted in the printed patent as follows: After "4.5 hours" insert -- to an isocyanate equivalent weight of 864. The prepolymer was then diluted to 94% solids with toluene and cooled to 50° C. followed by the addition of 34 moles -- ; and line 37, change "methyldiethanol" to -- methyldiethanolamine -- .

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,745,041 Dated July 10, 1973

Inventor(s) Albert E. Raymond

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, line 3 (after "WVT") change the dash (--) to an equal (=) sign; and
line 4 (after "Bally flex") change the dash (--) to an equal (=) sign.

Column 16, line 7, correct the spelling of -- according -- .

Signed and sealed this 25th day of December 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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