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ARTIFICIAL LEATHER

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This invention relates to sheet material suitable as a leather substitute and more particularly to improved artificial leather products and their manufacture.

Most artificial leathers now known to the art, chiefly nitrocellulose or rubber-coated fabrics, are deficient in durability and in resistance to light, heat, or oxygen for many important leather uses. Furthermore, nitrocellulose coated fabric suffer from the disadvantage of high inflammability, while rubber products are generally available only in a restricted range of colors due to the discoloration caused by compounding agents and necessity for heat curing. Synthetic resin coatings have been proposed, but are fragile, tacky or lacking in durability.

This invention has as an object an artificial leather which is free from the above mentioned objections and which possesses good pliability, a leather-like hand, and preferably also a decorative surface. A further object resides in methods for manufacturing my improved artificial leather product. Other objects will appear hereinafter.

These objects are accomplished in the manner more fully described hereinafter which comprises subjecting a sheet of synthetic linear polyamide to cold working and then subjecting the cold worked sheet to sufficient heat and pressure to alter its surface without melting the sheet or materially changing its linear dimensions.

I have discovered that cold-worked synthetic linear polyamide sheets when subjected to heat and pressure, as by a plate press, have a leathery feel or hand and a pleasing appearance not possessed by sheets comprising polyamides which have not been subjected to both cold working and plate pressing. They are also markedly superior in resistance to cracking failure on repeated flexing. These results have been found to depend upon neither cold working nor press plating singly, but upon the combination of these two processing steps. For example, after being subjected to 40,000 flexes in a Schiltknecht flex machine, a polyamide sheet which had been elongated 111 per cent by cold rolling and then plate pressed at 90° C., showed only one break, whereas another sheet of the same composition which had been similarly rolled but not plate pressed showed six breaks. As a further example, a different polyamide sheet which had been cold rolled 100 per cent in one direction and then plate pressed at 93° C. showed no failure after 100,000 flexes, whereas another sheet of the same composition which had not been rolled

but which had been plate pressed began to fail at 60,000 flexes.

A marked superiority is also noted in the definition of the decorative effect secured when cold worked sheets comprising polyamides are embossed as compared to the pattern produced when unworked sheets are embossed under identical conditions; such definition includes improved sharpness, depth, and clarity of pattern.

The above mentioned polyamides which will be referred to in more detail later are of the general types described in Patents 2,071,250, 2,071,253, and 2,130,948.

The term "cold working" as used herein includes all processes wherein compressive or tensile stress is applied to the polyamide sheet causing it to elongate in one or more directions and thereby producing a substantial increase in the surface dimensions of the sheet. Convenient means for carrying out cold working include passing a sheet of polyamide composition between rolls under high pressure to effect elongation or applying a tensile stress exceeding the yield point of the material across the sheet to effect elongation and resultant increase in area. The first method is referred to more specifically as cold rolling and the second as cold drawing. Cold working is preferably applied at temperatures below 50° C. Cold working results in the orientation of polymer crystallites along one or more preferred axes, these axes being in the direction of those dimensions principally increased by the operation of cold working. The tensile strength of the sheet is enhanced by cold working, particularly along the axes of orientation. Best results are obtained by cold working until elongations of at least 50-200 per cent are obtained, although considerable improvement is brought about in the subsequent heat and pressure step by elongations throughout the range from 10 per cent to 50 per cent. The sheets are preferably elongated in two mutually perpendicular directions, since such sheets when subjected to the subsequent heat and pressure step exhibit leather-like hand superior to those of sheets elongated in only one direction.

The "heat and pressure" treatment which is applied to the cold worked sheet is an operation of compressive impressing at elevated temperatures, whereby the surface characteristics of the sheet are modified without increasing materially the linear dimensions, i. e., the surface dimensions, of the sheet. This process is customarily carried out by subjecting the polyamide sheet to

heat and pressure between plates. The time of treatment is short, generally not over one minute and usually for a few seconds only. The plates may be smooth in which case the sheet takes on a polished appearance, or one or both of the plates may be engraved with the desired pattern. When a pattern is introduced the operation can be referred to as embossing. In the heat and pressure treatment of the cold worked polyamide sheet, the upper temperature limit is determined by the temperature at which the polyamide composition melts. The temperature selected for this treatment is, in general, between 20 and 100° C. lower than the melting point of the polyamide or polyamide composition of which the sheet is composed. In general, however, the temperatures will be above 60° C. The optimum temperature is a characteristic of each polyamide or polyamide composition used and is determined by subjecting small strips of the cold worked sheet to pressure between two plates, one of which is engraved, to a range of temperatures and selecting that temperature which gives the best decorative effect. The pressures are selected sufficiently high to secure accurate delineation of the pattern without causing lateral flow of the polymer compositions and increasing the area of the sheet. In general, the pressures used in the heat and pressure operation are much lower than the compressive force used in bringing about elongation in cold rolling.

The polyamide films or sheets used in the practice of this invention may be prepared by several methods. Since the polyamides melt without appreciable decomposition in the substantial absence of oxygen, it is possible to form a sheet directly from the molten polymer composition. In this process the sheet obtained from the molten polymer composition may be tempered by rapidly chilling. For this purpose, the composition can be extruded as a sheet into a cooling atmosphere or into a suitable quenching liquid, as for example water or other inert nonsolvents for the polyamide composition, or the polyamide composition can be extruded directly onto a rotating wheel maintained at a temperature substantially below the melting point of the composition. The sheets may also be obtained by molding the polyamide material into a block under heat and pressure, followed by slicing the block into sheets of the desired thickness. Another method consists in dissolving the polymer, with or without plasticizer, in a solvent and then casting films therefrom. For example, when using the interpolyamide derived from 60 parts of hexamethylene diammonium adipate and 40 parts of caprolactam, a suitable solvent for this purpose may be a mixture of a lower alcohol, such as ethanol, and water. The solution may then be spread to even thickness on a smooth surface, the solvent allowed to evaporate, and the resulting film stripped from the smooth surface.

The polyamides, which are used in the practice of this invention, are fiber-forming and may be referred to as superpolyamides. They are generally crystalline rather than resinous. The term "fiber-forming" refers to the property of these polymers of yielding filaments, as by extrusion of the molten polymer, which, upon cold drawing, are formed into fibers which show orientation along the fiber axis by characteristic X-ray diffraction patterns. These polymers are obtained from bifunctional reactants, as for instance, from the reaction of diamines and dicarboxylic acids or amide-forming derivatives of these reactants, or

by the self-polymerization of monoaminomono-carboxylic acids or their amide-forming derivatives. Upon hydrolysis with mineral acids, the polyamides yield monomeric amide-forming reactants. For example, a polyamide derived from a diamide and a dibasic carboxylic acid, on hydrolysis with hydrochloric acid, yields the dibasic carboxylic acid and diamine hydrochloride. Similarly, a polyamide derived from an amino acid yields an amino acid hydrochloride on hydrolysis with hydrochloric acid.

The polyamides used in the practice of this invention contain a plurality of amide (including thioamide) groups as an integral part of the main chain of atoms in the polymers. The average member of carbon atoms in the segments of the chain separating the recurring amide groups is at least two. The recurring amide groups have the structure



where A is oxygen or sulfur and R is hydrogen or a monovalent hydrocarbon radical. Among the several types of these polyamides are the interpolyamides, the ester-amide interpolymers, and the poly-carbamates obtained by reacting equimolecular quantities of a diisocyanate or diisothiocyanate with a bifunctional diol, as for instance decamethylene diisocyanate and decamethylene glycol. The preferred polyamides are those in which the carbon atom in the above defined amide group is attached directly to carbon.

The interpolyamides are especially useful in the practice of this invention since these polymers are more pliable and possess greater compatibility with a variety of plasticizing agents than the higher melting simple polyamides. In addition, the interpolyamides include many polymers soluble in practical solvents. Thus, while simple two-component polyamides are in general soluble only in phenols, strong mineral and organic acids, interpolyamides such as those produced by reacting equal weights of hexamethylene diammonium adipate and decamethylene diammonium sebacate, are found to be readily soluble in mixtures of chloroform and methanol. Among the most desirable of the interpolyamides economically are those derived from diamines, dibasic acids and amino acids. Particularly valuable interpolyamides are those derived from hexamethylene diammonium adipate and 6-aminocaproic acid; from hexamethylene diammonium adipate, 6-aminocaproic acid, and 12-aminostearic acid; from hexamethylene diammonium adipate, hexamethylene diammonium sebacate, and 6-aminocaproic acid; and from hexamethylene diammonium adipate, hexamethylene diammonium azelate and 6-aminocaproic acid. The foregoing reactants can be replaced by amide-forming derivatives thereof; for example, 6-aminocaproic acid can be replaced by caprolactam or 6-aminocapronitrile. The above interpolyamides have good pliability and are, in general, soluble in mixtures of water and lower aliphatic alcohol containing from 5 to 50% of the latter. The interpolyamides from hexamethylene diammonium adipate and 12-aminostearic acid are also very pliable and are for the most part soluble in mixtures of toluene and ethanol or chloroform and methanol.

My invention is described more specifically in the following examples in which parts are by weight.

Example I

One thousand six hundred and thirty parts of the interpolyamide derived from hexamethylene diammonium adipate and caprolactam in the ratio of 60:40, respectively, and having an intrinsic viscosity of 1.29 (defined as in Patent 2,130,948), is placed in a mechanical mixer heated by oil circulated at 275° C. During the melting and mixing operations, the polyamide within the mixer is blanketed with carbon dioxide. After 1.5 hours, at which time the charge will have become sufficiently fluid to permit mixing, the oil temperature is reduced to 250° C. and a dispersion of 16.3 parts of carbon black in 335 parts of a mixture of N-ethyl ortho- and para-toluenesulfonamides is added to the charge in the mixer. During the next 1.5 hours, 755 parts more of N-ethyl ortho- and para-toluenesulfonamide mixture is added, and the mixing is continued for one hour thereafter. The resultant composition is removed from the mixer while in a molten state and is protected from air during cooling with a stream of carbon dioxide gas.

The polyamide composition is then placed on differential speed steel rolls maintained at a temperature of 130° C. and rolled to rough slabs approximately 1/4" thick. Sheets are cut from these slabs to fit in a 9" x 13" chase and are molded into a block by heating for three hours at 137° C. under approximately 213 lbs./sq. in. pressure. After allowing the block thus formed to cool under pressure, it is removed and sliced with a knife into sheets of 0.007, 0.010, 0.018, 0.023, 0.038 and 0.045" thickness.

The sheets described above are cold worked by passing them between smooth faced, even-speed rolls at room temperature. One sheet is rolled 55 per cent in one direction, another sheet is rolled 80 per cent in one direction, and still another sheet is rolled 111 per cent in one direction. Another sheet is rolled in two directions by rolling first 45 per cent in one direction and then 50 per cent in the perpendicular direction. Elongations produced by rolling are expressed in terms of per cent of the original length of the unrolled sheet.

Each of the rolled sheets is then placed in a plate press, one plate being engraved with a pin seal grain pattern and subjected to pressure at a temperature of 85-88° C. The resultant sheets exhibit a pin seal grain of good clarity and possess a leathery feel and drape, whereas similarly treated unrolled sheets are lacking in satisfactory surface grain and drape.

In an entirely analogous manner, white artificial leather is prepared by substituting 218 parts of titanium dioxide for the 16.3 parts of carbon black in the preparation of the polyamide composition in the above example.

Example II

Following the procedure described in Example I, sheets of various thickness are made from a polyamide composition which contains 1556 parts of an interpolyamide of intrinsic viscosity 1.1 derived from equal parts of hexamethylene diammonium adipate and decamethylene diammonium sebacate, 1,041 parts of a mixture of N-ethyl ortho- and para-toluenesulfonamides, and 16 parts of carbon black. The sheets are cold rolled by passing them between smooth faced even-speed rolls at room temperature. A sheet measuring 9" x 13" x 0.020" is rolled in one direction to a sheet measuring 14" x 13" x 0.016" corresponding to an elongation of approximately 55

per cent. Another sheet, measuring 9" x 13" x 0.020" is rolled 65 per cent in one direction and then 25% at right angles thereto to give a sheet measuring 11" x 22.5" x 0.0115".

Well defined patterns are obtained on embossing the cold rolled sheets with a pin seal grain at 77-88° C. in a plate press, while the grain is shallow and indistinct on similarly embossed unrolled sheets of the same polyamide composition. Moreover, the embossed rolled sheets are found to possess much more attractive drape and leather-like feel than the unrolled embossed sheets.

Artificial leather prepared as described in this example is found to be extremely resistant to cracking at low temperatures. For example, a weight may be dropped on a fold in the sheet at temperatures as low as 10° F. without producing any cracks in the sheet. Moreover, the embossed rolled sheets obtained in this example are found to be extremely durable in many leather uses. For example, key holders made therefrom are found to be substantially free from evidences of wear after six months' use, whereas leather key holders subjected to the same wear are scratched and abraded from contact with the keys.

Example III

Following the general procedure described in Example I, sheets (9" x 13") are prepared from a polyamide composition which contains 70 per cent of the interpolyamide derived from equal parts of hexamethylene diammonium adipate and decamethylene diammonium sebacate, 29.3 per cent of a mixture of N-ethyl ortho- and para-toluenesulfonamides, and of 0.7 per cent carbon black. The sheets are cold rolled by passing them through chromium faced rolls under sufficient pressure to cause elongations ranging from 50 to 140 per cent in one direction. In addition some sheets are rolled in a direction at right angles to the original rolling. Thus, one sheet is rolled 80 per cent in one direction and 55 per cent in a perpendicular direction, and another sheet is rolled 30 per cent in one direction and 28 per cent in a perpendicular direction.

The cold rolled sheets are then embossed in a plate press with a pin seal pattern at a temperature of 85-88° C. The resultant sheets possess a leather-like feel, combined with high strength and excellent drape. They are very resistant to failure on continued flexing. This property is tested by upholstering the corners of a conventional theater seat with the sheeting and subjecting the seat corners to repeated flexing, simulating the action of actual use. An embossed sheet which had been rolled 83 per cent in one direction prior to embossing was found to resist 85,000 flexes of the cushion without failure whereas an embossed sheet of the same polyamide composition which was not cold worked developed cracks after 40,000 flexes.

Example IV

Sheets of a polyamide composition containing 75 per cent polyhexamethylene adipamide, 15 per cent of a mixture of N-ethyl ortho- and para-toluenesulfonamides, and 10 per cent diamylphenol are cold rolled, then embossed at approximately 100° C. to yield sheets of artificial leather possessing a well defined grain and leather-like feel.

Example V

A sheet composed of 6 parts of interpolyamide of intrinsic viscosity 0.84 derived from hexamethylene diammonium adipate and decamethylene diammonium sebacate, 4 parts of a mixture of N-ethyl ortho- and para-toluenesulfonamides, and 0.6 part of carbon black is cold rolled 167 per cent in one direction. The cold rolled sheet has a thickness of 0.012 inch. A portion of this sheet is pressed between smooth surfaced plates at about 90° C. As compared with the untreated portion of the sheet, the smooth plated portion has a smoother or more polished appearance, a more leather-like hand, and greater pliability. The greater pliability is evidenced by the fact that approximately 15% less work is required to bend the smooth plated portion of the sheet through a 30° angle, as measured by the Olsen stiffness tester.

Other examples of synthetic linear polyamides which may be used for preparing my new artificial leather are polytetramethylene sebacamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene suberamide, polyhexamethylene sebacamide, polydecamethylene carbamide, poly-p-xylylene sebacamide, poly-p-phenylene sebacamide, the polyamide derived from 3,3'-diaminodipropylether and adipic acid, polymerized 6-aminocaproic acid, polymerized 9-aminononanoic acid, and polymerized 12-aminostearic acid. The invention, as previously indicated, is also applicable to interpolyamides as well as to mixtures of polyamides. In general, only those polyamides which have an intrinsic viscosity of at least 0.4 possess the fiber-forming properties which are found to go hand in hand with the properties of high tensile strength, ability to be cold rolled and embossed to give products of striking similarity in appearance and properties to leather. The preferred products have intrinsic viscosities between 0.6 and 2.0.

Instead of the polyamides mentioned above which are obtainable from bifunctional polyamide-forming reactants as essentially sole reactants, the linear superpolymers obtained by including with the polyamide-forming reactants other bifunctional reactants such as glycols, aminoalcohols, and hydroxy acids may also be used. Although these products contain ester linkages, they can be referred to as polyamides since they contain a plurality of amide linkages and retain many of the desirable properties of the simple polyamides. Examples of modified polyamides of this kind are those derived from diamines, dibasic acids, and glycols; those derived from amino acids, dibasic acids, and glycols; and those derived from dibasic acids and amino alcohols.

In the preparation of the artificial leather of this invention, the polyamides may be modified by the incorporation of suitable plasticizers, pigments, dyes, fillers, resins, antioxidants, cellulose derivatives, etc., for the purpose of securing products possessing the desired color, stiffness, workability, etc. Such modifications of the polyamide are preferably carried out prior to the operation of cold working, but it is also possible to incorporate modifying agents, e. g., plasticizers, with the polyamide during the cold working. If desired, the product can be dyed after the cold working and embossing operations. The polyamides can be dyed with a wide variety of commercial dyes. Among various softening agents

which may be incorporated in the polyamides may be mentioned phenolic compounds, sulfonamides, sulfonamide-formaldehyde resins, and ether esters. Compositions containing between about 5 and 100 per cent of modifying agent based on the polyamide can be used to greatest advantage.

The artificial leather prepared as above described by cold working a sheet of synthetic linear polymer and then compressively impressing the resulting oriented sheet is, among products designed for like purpose, outstanding for its superior strength, leather-like feel and appearance, as well as for its superior durability in service. The artificial leathers heretofore proposed have consisted mostly of fabrics to which a film has been applied, the film itself being incapable of being used as a leather substitute. These products have been lacking in the desired combination of properties found to be characteristic of the cold rolled and embossed films of this invention, namely, excellent response to the process of embossing in obtaining decorative surface effects, and the toughness, resistance to abrasion, drape, and general durability found in leather.

I have found that material for artificial leather applications requiring greater bulk than normally supplied by the self-supported sheets described above and at the same time requiring good pliability, may be readily prepared by cold rolling a textile fabric carrying a polyamide coating until the fabric base has been broken down under the strain applied. The product may be considered a self-supported polyamide sheet, since the originally woven fabric attached to one face has been largely broken down to consist of a plurality of short fibers securely bonded to and supported by the polyamide sheet. The product after embossing is characterized by a high degree of pliability, coupled with good heft and leather-like hand.

The application of a flexible backing to my new artificial leather, although not usually desirable, is not precluded, and in such instances the cold rolled and embossed sheet forming the subject matter of this invention is also designated as self-supporting since a backing or supporting fabric is not essential to the utility of my new product as an artificial leather. It is to be observed that but few synthetic materials have been found capable of being formed into self-supporting sheets which are at all suitable for artificial leather. In the case of those materials previously suggested for such use, the products have been deficient in strength or toughness, and when possessing sufficient strength were brittle or undesirably elastic. While many of such suggested materials may be embossed, the pattern obtained lacks permanence.

A further contribution of my invention to the artificial leather art consists in providing a superior grade of artificial leather which may be supplied in continuous sheets. Thus, the polyamide composition may be extruded in film form, quenched in water, cold rolled and embossed in long sheets. This product offers special advantages to the converter who may pass such sheets through a machine which continuously stamps out the units of his product.

Artificial leather prepared according to my invention is useful in the manufacture of a wide variety of articles such as upholstery covering, patent leather substitutes, saddlery and harness, suspenders, belts, garters, wrist watch bands, bill folds, shoes, luggage, and covers for card tables, baseballs, basketballs, and footballs.

It is to be understood that the mention of

"diamine," "dibasic carboxylic acid," and "amino acid" in the claims includes also amide-forming derivatives thereof.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for making artificial leather which comprises cold working in the solid state and at a temperature below 50° C. to an elongation of 50 to 200 per cent a sheet of synthetic linear polyamide composition, said polyamide having an intrinsic viscosity above 0.4, and then subjecting the sheet to mechanical pressure without materially changing the linear dimensions of the sheet at a temperature above 60° C. but below the melting point of said composition.

2. The process set forth in claim 1 wherein said composition contains pigment and plasticizer in addition to said polyamide.

3. The process set forth in claim 1 wherein said polyamide is an interpolyamide.

4. A process for making artificial leather which comprises cold rolling at a temperature below

50° C. in two substantially mutually perpendicular directions a solid sheet comprising synthetic linear fiber-forming polyamide to a total elongation of 50 to 200 per cent and then embossing the sheet under pressure without materially changing the linear dimensions of the sheet at a temperature above 60° C. but below the melting point of said polyamide.

5. An artificial leather comprising a cold worked and heat pressed sheet of synthetic linear polyamide obtained by the process set forth in claim 1, said artificial leather, as compared to a like polyamide sheet not so cold worked and heat pressed, having a substantially greater resistance to repeated flexing without cracking.

6. An artificial leather comprising a cold worked and heat pressed sheet of synthetic linear interpolyamide obtained by the process set forth in claim 1, said artificial leather, as compared to a like interpolyamide sheet not so cold worked and heat pressed, having a substantially greater resistance to repeated flexing without cracking, and having a more leathery feel and improved draping qualities, said interpolyamide being that obtained from diamine, dibasic carboxylic acid and amino acid.

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