cl. 18

Published Apr. 27, 1943

Serial No. 323,524

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF ARTIFICIAL LEATHER, LINOLEUM, COVERING FABRICS, DRIVING BELTS, PACKING RINGS AND SIMILAR STRUCTURES

Emil Hubert, Dessau-Ziebigk, and Hermann Ludewig, Jessnitz, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 12, 1940

This invention relates to the production of artificial leather, linoleum, covering fabrics, driving belts, packing rings and similar structures.

It has been found that high polymeric resins from polyamide-, polyurea- and polyurethan-forming compounds represent very suitable starting materials for the production of artificial leather, linoleum, covering fabrics, driving belts, packing rings.

Simple polymers, also interpolymers with or without plasticizers and solvents are thoroly kneaded, pressed and calendered in a thermoplastic state for the production of these structures.

It is an object of the present invention to use for the production of the above structures simple polymers consisting of polyamide-, polyurea- and polyurethan-forming compounds.

Another object is to use interpolymers consisting of polyamide-, polyurea- and polyurethan-forming compounds.

These and other objects will appear from the detailed specification following hereinafter.

The resins obtained according to this invention are extremely hard and tenacious and very resistant to water and chemicals. These properties are retained at extremely high as well as at low temperatures and the resins are therefore superior in every respect to all raw materials hitherto employed in the production of artificial leather.

The simple polymers on account of their more hornlike properties need thereby additional plasticizers, whereas the high polymeric mixed condensates consisting of two or several components show per se high flexibility, strength and elasticity which makes them suitable for the production of artificial leather, linoleum, covering fabrics, driving belts, packing rings without additional plasticizers. The polymerization products and interpolymers may be produced from one or several components of the following groups:

1. Amino acids like 6-aminohexane acid, 9-aminononane acid, 11-aminoundecane acid;
2. Lactams of amino acids like ε-caprolactam;
3. Dicarboxylic acids+diamines in the form of their salts or of the single components, for instance ethylenediamine-adipic acid, hexamethylenediamine-adipic acid, octamethylenediamine-sebacic acid, ββ'diaminodiethylsulfide+sebacic acid;
4. Urethancarboxylic acids, for instance urethylan-N-9-pelargonic acid;
5. Diurethan+dicarboxylic acids, for instance octamethylenediurethylan-sebacic acid and adipic acid, tetramethylenediurethan.

Also suitable, especially in connection with the components of groups 1–5 are the following:

6. Diurethans like octamethylene-, tetramethylene-, ethylenediurethylan and -diurethan;
7. Diurethans+diols, for instance components of group 6+glycol or 1,6 hexanediol;
8. Diurethans+diamines, for instance components of group 6+octamethylene-, ethylenediamine;
9. Diurethans+dihalogenhydrocarbons, for instance components of group 6+ethylenebromide, 1,6-dibromohexane;
10. Urethancarboxylic acids+diamines.

The production of artificial leather, linoleum, covering fabrics, driving belts and packing rings is accomplished in a known manner by kneading thoroly the thermoplastic polymerization products, if necessary by additional application of solvents and/or plasticizers and rolling them into skins of suitable thickness. Also filling material and fibers, synthetic and of natural origin, like animalic hair, wool, silk, jute, hemp, cotton, asbestos may be added to the polymerization products. The latter may be applied to one or both sides of the fabric, for example solution of the polymers may be used for impregnating fibers which after drying are pressed and calendered. Fibrous material, fabrics, fiber fleeces or fiber felts may be soaked with solutions of the polymers and interpolymers in glacial acetic acid, formic acid or concentrated sulfuric acid. The polymers may be precipitated on the supporting fabrics by liquid solutions which precipitate the polymer, but dissolve the solvent. By pressing and calendering the evenly impregnated filling materials and fibers, there are obtained according to the working conditions substitutes for leather to be used as artificial leather, linoleum, driving belts, etc. By adding plasticizers, wetting agents, pigments as known for leather compositions, the properties of the products may be varied to a very great extent.

By lacquering the surface of the shaped, leatherlike products with solutions of polymers or interpolymers obtained from the polyamide-, polyurea- and polyurethan-forming compounds and by pressing them with calender rollers having a pattern, the subsitute materials can be shaped according to the various kinds of natural leather. The new artificial leatherlike products are superior to all known similar products on account of their unusual strength and stability. The special properties of the artificial materials make it impossible that portions of the covering fabrics crack or tear off. On account of the excellent dyeing qualities of the polymers and interpolymers the obtained products may be well dyed with acid wool dyes, also after the shaping operation.

In order to lower the price for these structures, it is within the scope of this invention to employ additionally other organic compounds hitherto known for the manufacture of artificial leather, like cellulose esters, high polymeric vinyl compounds like polyvinylchloride and polyacrylic acid esters.

Example I

Even parts of caprolactam and the salt of $\beta\beta'$-diamino-diethylsulfide and adipic acid are heated 16 hours at 180° C. in a steam atmosphere. The high viscous melt is sprayed on a fiber fleece, afterwards kneaded by rollers in a thermoplastic state and rolled out into artificial leather.

Example II

Instead of the interpolyamide of Example I a highly condensed polyamide consisting of 9-aminononane acid and 10 perc. added xylenol is employed.

Example III

A melt of a high polymeric resin obtained by intercondensation 32 hours at 200° C. of ethylene-diamine-adipic acid salt, hexamethylenediamine-sebacic acid salt and $\beta\beta'$diamino-diethylsulfide-adipic acid salt (proportion by weight 1:2:2) is thoroly mixed with asbestos fibers and the mixture worked up into flat structures by spraying and calendering in the usual way. The artificial leather shows great softness and tenacity.

Example IV

Even parts hexamethylenediamine-adipic acid salt, ethylene-diamine-sebacic acid salt, caprolactam, 11-aminoundecane acid are mixed and heated 48 hours at 200° C. in a steam atmosphere. The interpolyamide obtained is dissolved in double the amount of formic acid and a fiber fleece or blotting paper is soaked with this solution. The formic acid is quickly evaporated by heating. When this procedure is repeated a starting material is obtained which can be pressed into highly elastic, tenacious, artificial leather.

Example V

10 parts caprolactam and 17,39 parts adipic acid-hexamethylenediammonium salt are first heated two hours at 200° C. in a nitrogen atmosphere and afterwards four hours at 250° C. The condensation product is pressed into water, cut into pieces and heated together with the same amount methanol and about 8% glycerole 12 hours on a steam bath under a reflux condenser. The highly swollen product yields a highly strong, tenacious artificial leather by pressing it between hot plates. Without further treatment or by rolling and stretching in different directions this product is suitable for driving belts, shoe soles, packing rings, covering fabrics, etc.

EMIL HUBERT.
HERMANN LUDEWIG.