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## MANUFACTURE OF ARTIFICIAL LEATHER

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This invention relates to the manufacture of artificial leather, being more particularly concerned with the manufacture of a product comprising a rubber-impregnated foundation of interfelted cellulose fiber such as that produced on machinery of the paper-making type. In producing artificial leather of this type, it is the practice to form a porous foundation and then to impregnate the foundation with a liquid, rubber-carrying vehicle, such as a so-called rubber solution or an aqueous rubber dispersion such as latex, whereupon the liquid rubber-carrying vehicle is removed from the foundation as by drying. If desired, the rubber-impregnated foundation may then be vulcanized to produce a product of the desired strength and rigidity.

For many purposes, it has been found advantageous to use as the foundation, a fluffy web composed of loosely felted fibers, as such a web is of high porosity and may be readily impregnated with latex, for example, and then dried, and, if desired, vulcanized, to produce a product, which simulates many of the desirable characteristics of natural leather. For instance, the rubber-impregnated product possesses sufficient porosity and flexibility to be used as a raw material for the manufacture of inner soles where these characteristics are of prime importance. Because of the high porosity of the web used as a raw material, after the removal of the liquid rubber-carrying vehicle from the web, considerable of the initial porosity is evidently restored, so that when the rubber-impregnated product contains even as high as 100% or more rubber, based on dry fiber, it is sufficiently porous to be breathed through and to absorb considerable water. Consequently it is unsatisfactory for use in the manufacture of articles, such as mid-soles and outsoles, as in such case it must be quite rigid and must resist absorption of and penetration by water, under the action of which it swells considerably and squeezes out under the pressure of the foot to beyond its normal size, in which condition it sets permanently. If the waterproof qualities of the product are improved by increasing its rubber content, it acquires a distinctly rubbery feel and has even greater flexibility.

I have found that for some articles, such as mid-soles and out-soles, it is highly advantageous to impregnate a porous rubber-impregnated web such as described, with resinous materials preferably the non-brittle, artificial resins such as used in the so-called bakelite varnishes. For instance, we have found that when a dried, latex-impregnated web of porous structure is impregnated with a solution of bakelite varnish and is then dried and, if, desired, cured, the finished product possesses greater rigidity under pressure even while wet, and is more resistant to swelling by the action of water, being comparable to natural leather in these respects. The finished product is also of much higher tensile strength.

While various types of foundations may be used in producing the product of the present invention, it is preferable to employ a fluffy web composed of loosely interfelted cellulose fibers and possessing high porosity. A web of unusually high porosity may be produced by using a substantially unbeaten wood fiber of high alpha cellulose content, say 94% or greater, as a raw material, and forming such fiber into a web on a paper-making machine designed to effect dewatering and drying of the web without the application of the heavy pressures used in ordinary paper-making practice. While other fibers in substantially unbeaten condition, such as sulphite, kraft, or soda pulp, may be employed, a substantially unbeaten wood fiber of high alpha cellulose content is preferred because it is more highly absorptive than the usual unbeaten commercial wood fibers and hence enhances the absorptivity or porosity resulting from the loosely felted, uncompacted condition of the fibers. The dry porous web may be passed through a bath of rubber-carrying vehicle, such as an ammonia-preserved latex of a solids content, of say, about 16%, at which content immersion for about one-half minute to one minute effects a thorough impregnation of the web, whereupon the web may be squeezed until its rubber solids content is about 110%, based on the weight of

dry fiber. In order to prevent migration of the rubber globules to the surface of the web during drying, the ammonia-preserved latex may be treated with the oxide of an amphoteric metal, preferably zinc oxide, as described in application Serial No. 369,267, filed June 7, 1929 by Roger B. Hill, or with alkaline earth metal hydroxides, preferably slaked lime, as described in application Serial No. 373,055, filed June 22, 1929 by Roger B. Hill. When slaked lime is the compound added to the latex to overcome migration tendencies during drying, protective colloids such as soluble soaps or caseinates which are capable of being precipitated by lime as insoluble calcium soaps or caseinates, are preferably added to the latex prior to the addition of the slaked lime in order to overcome coagulating tendencies. Such treatment of the latex prior to its use for the impregnation of the web makes possible the production of a dried rubber-impregnated web of uniformity in respect of rubber distribution therethrough, as troublesome non-rubber constituents of the latex, namely, the proteins and the resins are converted to an insoluble, inert condition. Apparently, setting or coagulation of the rubber by drying is so retarded by the proteins and resins which exist respectively in an ammonia-preserved latex as water-soluble proteinates and alkali resinates, that there is a tendency for rubber particles to migrate to the surface of the impregnated product, where evaporation of water is taking place. The tendency for migration of rubber particles is especially pronounced in the case of highly porous webs of cellulose fiber of the type described, evidently because of the high capillary action taking place during drying to cause such migration.

If desired, a vulcanized latex may be used so that when the latex-impregnated web is subsequently dried, the rubber will be coagulated in the web in vulcanized condition. Or artificial aqueous dispersions of crude or reclaimed rubber may be used in lieu of natural latex. Suitable rubber-compounding materials, vulcanizing agents, and accelerators of vulcanization, may be added to the artificial or natural rubber dispersion so that the dried rubber-impregnated web may be vulcanized, if desired.

After the porous web has been impregnated as hereinbefore described, it is dried. The dried product is porous but the fibers are strongly bonded together by the rubber coagulated therein by drying, so that the initially weak web has undergone a great increase in tensile strength and tear resistance. If not already vulcanized by the use of vulcanized latex, the product may be vulcanized under heat or by treatment with sulphur chloride fumes or with a solution of sulphur chloride in a suitable solvent, as described in application Serial No. 392,480, filed September 13, 1929, by George A. Richter.

The porous rubber-impregnated web may then be passed through a solution of a suitable resinous material, preferably a 10% solution of a bakelite varnish of about 60% solids content in a suitable solvent or thinner. At this concentration, the bakelite solution is thin and easy flowing so that upon immersion for about one-half minute to one minute, the web is thoroughly impregnated with the solution and contains about 20% bakelite solids based on the weight of dry fiber. The varnish-impregnated web may then be air-dried, and when an air-drying bakelite varnish is employed, no heat treatment of the dried product is necessary. If an "intermediate" type of bakelite varnish is used, the dried product should be heated or cured to render the bakelite varnish infusible and insoluble. The heat treatment or curing may be accomplished at a temperature and for a period of time depending upon the flexibility desired in the final product. For instance, curing may be effected as on steam-heated drums, at say 135° C., for about 90 minutes, under which conditions a product eminently suitable for use in the manufacture of soles is produced.

We present herein a table giving certain important characteristics possessed by a rubber-impregnated web containing 110% rubber based on the weight of dry fiber and a similar rubber-impregnated web additionally impregnated with about 20% bakelite solids based on the weight of dry fiber.

| Test | | Rubber-impregnated web | Rubber-impregnated and Bakelite-impregnated web |
|---|---|---|---|
| Tensile strength (lbs. per sq. in.) | With | 923 | 1950 |
| | Across | 650 | 1105 |
| Stretch (%) | With | 17.2 | 4.7 |
| | Across | 28.2 | 10.2 |
| Permanent set (%) | With | 9.4 | 5.6 |
| | Across | 15.6 | 8.6 |
| Tear resistance | With | 238 | 213 |
| | Across | 318 | 282 |

The various tests hereinbefore given were made "with" and "across" the sheet, that is, in the direction of the paper machine and across the paper machine. It is to be noted that impregnation of the rubber impregnated web with bakelite varnish effects a marked increase in the tensile strength of the product and a marked decrease in its stretch and in its so-called "permanent set". The "permanent set" value is obtained by stretching the product and noting the permanent increase in length after recovery is permitted. The tear resistance of the bakelite-varnish impregnated product is lower than that of a product impregnated with rubber alone, but this characteristic is of no particular moment where

the product is intended for such use as in the manufacture of shoe soles.

The original untreated web is preferably made comparatively thin so that its impregnation and drying may be easily effected. Accordingly the impregnated sheet is usually of insufficient thickness for the manufacture of such products as mid-soles or out-soles, it being necessary to bond together two or more sheets. The bonding together of the sheets is preferably effected after impregnation with both the rubber and the bakelite varnish, a comparatively thick or concentrated latex preferably being employed as the adhesive or bonding material. It has been found advantageous to moisten or wet the surfaces of the impregnated sheets to be bonded together before applying the latex and then to superpose the sheets and to unite them under pressure. The multi-ply product may then be dried. Apparently the initial moistening or wetting of the plies promotes penetration of the thick latex into the surface portion of the plies and results in a better interlocking of the plies after the latex is dried. Were the plies bonded together before impregnation with bakelite varnish, the membrane of rubber formed between the plies would interfere with penetration of the varnish throughout the plied product.

By introducing a resinous material into the pores of the web after they have been partially filled with rubber, as hereinbefore described, apparently little combination takes place between the resinous material and the rubber, each of these impregnating materials existing independently in the finished product and imparting desired characteristics thereto, as distinguished from the rubber compound produced when resinous material is incorporated into rubber on compounding rolls or in mixers.

The specific example hereinbefore given deals with the use of bakelite varnish as the resinous material, as this material has been found to give the best results. Any one of a large number of types of bakelite varnishes may be employed depending upon the flexibility desired in the final product. The proportions of rubber and resinous material present in the finished product may vary, but when the product is intended for the manufacture of shoe soles, it should contain a comparatively large amount of rubber and a comparatively small amount of resinous material. Other changes and modifications might be made without departing from the spirit or scope of this invention as defined in the appended claims.

What we claim is:

1. Sheet material comprising a porous foundation of fibrous material impregnated throughout with rubber and with non-brittle, resinous material of the nature of bakelite.

2. Sheet material comprising a porous foundation of interfelted cellulose fiber impregnated throughout with a comparatively large amount of rubber and with a comparatively small amount of non-brittle, resinous material of the nature of bakelite.

3. Sheet material comprising a porous foundation of loosely felted cellulose fiber, the pores of which contain rubber and bakelite varnish.

4. A shoe sole comprising a porous foundation of interfelted cellulose fiber, the pores of which are incompletely filled with rubber and with non-brittle, resinous material of the nature of bakelite.

5. A shoe sole comprising a porous foundation of interfelted cellulose fiber containing about 100% of rubber and about 20% of non-brittle, resinous material of the nature of bakelite based on the weight of dry fiber, uniformly distributed therethrough.

6. A process which comprises impregnating a porous foundation of fibrous material with rubber while preserving considerable of its porosity, and then impregnating said foundation with a non-brittle, resinous material of the nature of bakelite.

7. A process which comprises impregnating a porous foundation of interfelted cellulose fiber with a rubber-carrying liquid vehicle, removing said vehicle, impregnating with a solution of non-brittle, resinous material of the nature of bakelite, and removing the solvent.

8. A process which comprises impregnating a porous foundation of interfelted cellulose fiber with an aqueous dispersion of rubber, drying said foundation, impregnating with a solution of bakelite varnish, and removing the solvent.

9. A process which comprises impregnating a porous foundation of interfelted cellulose fiber with an aqueous dispersion of rubber, drying said foundation, impregnating with a solution of bakelite varnish, removing the solvent, and curing at elevated temperature.

10. A porous, rubberized sheet of interfelted cellulose fibers, the pores of which contain a non-brittle, resinous material of the nature of bakelite.

11. A porous sheet of rubberized interfelted cellulose fibers, the pores of which contain bakelite varnish.

In testimony whereof we have affixed our signatures.

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