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LEATHER FINISH

Donald Edwards Edgar, Philadelphia, and Paul Robinson, Lancaster, Pa., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to leather finishes in general and more particularly to an improved top coating for high luster finishes known as patent leather finishes.

5 This application is a continuation-in-part of our application Serial Number 58,000, filed January 7, 1936.

10 In the manufacture of patent leather according to most processes of the present state of the art, a long sunning treatment is required to dry the composition applied to give the high luster finish and to remove the tack. This is one of the chief disadvantages in the manufacture of the product. Different manufacturers carry out the process according to their own unique procedure 15 which usually involve trade secrets but the two methods which are essentially typical and which involve the sunning treatment are as follows:

20 In one instance, a first or base coating of a mixture of japanners' oil and a pigment is applied and rubbed into the leather with the hands or with a suitable tool. Following this two or three coatings of a clear varnish consisting of a japanners' oil thinned with a suitable hydrocarbon solvent are applied. These coatings are usually 25 dried for a period of from twelve to sixteen hours if necessary at a temperature of from 90° to 100° F. A final coat of japanners' varnish is then flowed on and the leather baked in an oven for about sixteen hours at approximately 160° F. To remove the final tack from the top coat varnish the leather is exposed to sunlight for at least five 30 hours. A possible alternative for sunning is to expose the material to ultra-violet radiating equipment which, however, is also expensive. Even with the sunning treatment or its equivalent, the finish is often still tacky or sticky at slightly elevated temperatures. The japanners' oil is a heavy bodied linseed oil and the japanners' varnish is what is known as a strongly boiled 40 linseed oil. These materials usually contain suitable driers.

45 A second method is to apply to the leather a first or base coating of a pyroxylin composition. This composition consists of pyroxylin and japanners' oil suitably thinned and is applied to the leather with a blunt edged metal knife. Four or five coats of such a mixture are applied, each coating being dried from twelve to sixteen hours at 90° F. After these coatings have been applied and

suitably dried, a final coating of japanners' varnish is applied and must be dried in the manner described above.

Both of these methods, as is evident, are expensive and in the case where sunlight is used is subject to considerable delay in manufacture, depending on weather conditions. Materials made by either of these processes also possess certain inherent defects, namely, the finishes are subject to rapid embrittling and crack readily at reduced 10 temperatures.

15 The disadvantages of the prior practice mentioned above have been overcome to some extent through the use of a synthetic resin of the polyhydric alcohol-polybasic acid type. Synthetic resins in general, however, are not satisfactory in producing patent leather finishes whereas the patent leather product of the present invention which is formulated with the new type of synthetic resin described herein exhibits to a remarkable degree the properties most desired in a patent leather finish and therefore combines the advantage of an improved product with the economy in manufacture pointed out in the previous paragraph. 20

25 This invention has as an object the provision of an improved method of manufacturing high luster leather finishes which does not require sunning or exposure to ultra-violet light. Another object is the provision of a method of manufacturing patent leather having a top coat finish which will more permanently retain its flexibility and consequently eliminate early cracking of the finish as in many of the present types of high luster finishes. A further object is the manufacture of patent leather, the high luster finish of which will not tend to crack in the lasting operation of the use of the leather in the manufacture of shoes. A further object is the preparation of patent leather which possesses improved resistance to cracking at lowered temperatures on being bent. A still further object is the provision of finishes on leather which possess improved properties over material made according to the present state of the art. Other objects will appear hereinafter. 30 35 40 45

These objects are accomplished by the following invention in which the top coating applied in the finishing of the leather is a urea-aldehyde-alcohol resinous composition referred to in more 50

detail below. This coating may be applied as a solution in any suitable solvent or mixture of solvents and may contain in addition other ingredients which enhance the value of the coating.

The urea-formaldehyde-alcohol reaction product used in the present invention is made by the method described in our mentioned prior application. There is reacted in the presence of an acid or other catalyst (mercuric, aluminum, ferric, or stannic chlorides, acid resins, halogens, etc.) ingredients consisting solely or essentially of urea, formaldehyde, and a monohydric aliphatic alcohol. The heating of the reaction product of the urea and formaldehyde with the alcohol is continued in the presence of a hydrocarbon such as benzene or toluene with separation of water of reaction from the condensed hydrocarbon and return of the latter to the reaction mixture until substantially two molecules of water for each molecule of urea are eliminated and a product is obtained which contains an amount of combined monohydric alcohol equivalent from one-half to about one molecule of alcohol for each molecule of urea.

In making these resinous products of urea, formaldehyde and alcohol a mixture containing all the ingredients may be reacted, or the alcohol may be heated, accompanied by the mentioned separation of water, with preformed urea-aldehyde reaction product. With the use of some alcohols it may not be necessary to use in addition a hydrocarbon since the water may be satisfactorily removed by other means, as for instance by the use of silica gel in the separator, or by the use of an auxiliary fractionating column to separate the water from the alcohol before the latter is returned to the reaction vessel. These resins yield upon treatment with zinc chloride and acetic anhydride the acetate of the alcohol. For the purposes of this invention the resins may be used as such or in admixture with other film-forming materials such as raw or treated animal and vegetable oils, natural or synthetic resins, plasticizers, waxes, etc.

The following, in which the parts are by weight, is illustrative of a composition useful in making our improved patent leather finishes:

Urea-aldehyde-alcohol resin.....	32.0
Diethylene glycol ester of sebacic acid.....	24.2
Hydrosolvent.....	18.1
Pentanol.....	14.0
Methyl cellosolve.....	11.0
Nigrosine dye.....	0.5
Orthophosphoric acid.....	0.2

The resin used in the foregoing example was made by reacting under the conditions outlined above a solution of 250 parts by weight para-formaldehyde in 1000 parts normal butyl alcohol with 250 parts urea.

The urea-aldehyde-alcohol resin composition may be either brushed or sprayed on a leather base to which has previously been applied, as is the usual practice, a composition of bodied linseed oil. After a uniform coating had been applied the finish was air dried for approximately one hour to permit the evaporation of the volatile material and the leather then baked for fifteen minutes at 100° C.

The resulting product possessed a high luster, superior to the usual patent leather, was soft and pliable and showed no tendency to cracking on being sharply bent at room temperature. Comparative tests with patent leather made according to the present state of the art as previously

described showed that the material made according to the present invention did not crack when sharply bent at a temperature of -5° F. whereas the present type of material cracked badly at the same temperature when bent around a one-inch mandrel. In a standard leather flexing machine at room temperature regular patent leather cracked after approximately 600 bends, while the patent leather made according to the present invention did not crack until approximately 10,000 bends.

The composition described above may be applied directly to top grain without any conventional base coating having been applied, yielding a product which is satisfactory in every respect. The finish coating may be satisfactorily baked at lower temperatures for a longer period of time, e. g., for two hours at 70° C. or at a higher temperature for a shorter period of time, the particular baking schedule selected depending largely on the available manufacturing facilities.

In place of the diethylene glycol ester of sebacic acid used as the blending and/or softening ingredient in the composition described may be used medium or heavy blown castor oil; glycol sebacate; castor oil modified sebacic acid glyceride; glycol, diethylene glycol, glycerol, etc., esters of organic dibasic acids as such or castor oil modified; dibutyl phthalate; tricresyl phosphate; chlorinated diphenyls, chlorinated naphthalene; natural or synthetic resins, etc. The choice of the particular blending and/or softening agent used will be governed largely by the particular properties desired in the finished product. The resin (solids) plasticizer ratio may range between 10 to 6 and 10 to 10, the ratio 10 to 6 yielding satisfactory results for most purposes.

The amount of dyestuff used may vary within limits which will be apparent to those skilled in the art. The orthophosphoric acid is used to improve the drying and to decrease the drying time of the finish composition and may vary in amount between 0.05 and 0.50% of the total composition. Phosphorous pentoxide may be used in place of the orthophosphoric acid, the amount being within the range as specified. It may be conveniently introduced into the composition in an approximately 10% alcoholic solution. The solids content of composition given above is approximately 65%. This may vary over a range which will be apparent to those skilled in the art and wherever desirable or necessary dilution may be made with hydrocarbon or other suitable solvents. The finish coating may be applied in one or several coatings depending on the solids content of the composition, type of material to be finished, luster desired in the finished product, etc.

If desired pigments may be incorporated in the composition used for the final coating. Such pigmented compositions produce a finished product possessing all the desirable properties of the patent leather previously described. The pigment is preferably dispersed in the blending and/or softening agent by any suitable means such as ball or pebble mill grinding, roller mill grinding, etc., and this dispersed pigment, which may be designated as a mill base incorporated with the urea-aldehyde-alcohol resinous material. In preparing a blue composition, for example, 50 parts by weight of Prussian blue are dispersed in 50 parts by weight of blown castor oil to form the mill base. In preparing the final composition 100 parts by weight of the resin solids dissolved in a suitable solvent mixture is

thoroughly mixed with 100 parts by weight of the mill base.

The following formulae, in which the parts are by weight, are examples of black and green compositions:

Black composition

	Parts
Mill base:	
Carbon black.....	25
Blown castor oil.....	75
Finished composition:	
Mill base.....	66
Urea-aldehyde resin solution (65% solids).....	154

Green composition

	Parts
Mill base:	
Chrome green.....	60.5
Blown castor oil.....	20.0
Hydrocarbon solvent.....	19.5
Finished composition:	
Mill base.....	300.0
Blown castor oil.....	15.0
Resin solution (65% solids).....	351.0
Hydrocarbon solvent.....	202.0

Other pigments may be used either alone or blended to produce desired colors and may be dispersed in blending or softening agents previously described. The phosphoric acid or phosphorous pentoxide may be added to the pigmented compositions as described in the case of the unpigmented compositions. The preparation of suitable compositions with the urea-aldehyde-alcohol resinous composition will be readily apparent to those skilled in the art. The pigmented compositions may be applied in the same manner as the unpigmented compositions previously described.

Either the pigmented or unpigmented compositions may be applied directly to top grain leather without first applying the bodied inseed oil or other composition as a base coating.

It will be seen from the foregoing description that the present invention has several important advantages over the production of patent leather by methods heretofore used. As contrasted with the oil-type finishes formerly used, the present practice eliminates the necessity of sunning since the compositions used herein are hardened by baking. With respect to both the oil-type finishes and the synthetic resin coatings previously proposed, the practice described herein, in addition to producing a satisfactory dry finish free from objectionable tack, yields a product having improved toughness of film which results in a more permanent retention of flexibility in service with less tendency toward the development of cracks. The patent leather finish of this invention shows markedly improved resistance to cracking on being sharply folded at reduced temperatures. The finish described herein is also definitely superior to the previously used finishes, including the synthetic resinous ones, in having markedly less tendency to cracking at reduced temperatures; less tendency to cracking of the finish during the lasting operation in the manufacture of shoes; markedly improved color in white and light colored finishes which is quite important with the present trend toward the use of white and light colored high glaze leathers in shoes, etc. The practice of this invention also produces a film having an elasticity more nearly that of the leather base to which it is applied so that there would be less tendency to cracking of the finish in service at normal temperatures.

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 we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process for manufacturing patent leather which comprises subjecting leather to treatment with a composition comprising japanners' oil, applying over the coating or coatings applied in such treatment a coating comprising the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, and baking to harden said last mentioned coating, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

2. In the manufacture of patent leather products, the steps of applying a pyroxylin-oil undercoat and applying a top coat of the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

3. A step in the manufacture of patent leather which comprises applying a coating of the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, and baking to harden said last mentioned coating, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

4. A patent leather product having a top coat of the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

5. A patent leather product comprising an under coat of dried japanners' oil composition and a top coat of the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

6. A patent leather product comprising a dried film of pyroxylin-oil composition and a top coat of the resinous reaction product of urea, formaldehyde, and an aliphatic monohydric alcohol, said resinous product containing said alcohol in combined form in amount of from about one-half to about one molecule of alcohol for each molecule of urea, said product yielding upon treatment with zinc chloride and acetic anhydride the acetate of said alcohol.

DONALD EDWARDS EDGAR.
PAUL ROBINSON.