

ALIEN PROPERTY CUSTODIAN

PROCESS OF STIFFENING HATS AND THE HATS THUS PRODUCED

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The present invention relates to hats of every kind and it especially relates to a process of stiffening hats.

Felt hats and straw hats or braids consisting of various materials, such as straw, paper, horsehair, or bast, for making hats, furthermore knitted or woven and sewn hats as well as bandeaux are stiffened especially with shellac; glue, gelatine, tragacanth, cherry gum and other similar substances are, however, likewise used for stiffening purposes. Shellac stiffening has proved to be superior, as regards its properties, to such an extent that shellac has nearly exclusively been used for stiffening.

From a chemical and physical point of view shellac is by no means a perfect medium. It is sensitive to heat and already during transport at a high temperature the quality becomes inferior. Bleached shellac is resistant to storing only to a limited extent. Unbleached shellac often possesses an undesirable proper color and even the best-bleached shellac still has a yellow tinge by which pure-white material becomes dyed.

For hat stiffening purposes shellac dissolved in alcohol is used for obtaining stiff hats; for soft hats shellac dissolved in aqueous alkali is used. In order to avoid a bleeding of the dyestuffs, as small a quantity as possible of alkali is used for dissolving the shellac, but the bleeding cannot be entirely avoided. If the felt shows an acid reaction, the shellac readily precipitates and the material is smeared. Moreover, it is necessary to use always several kinds of shellac, i. e. a dark shellac, a shellac of an average color and a bleached shellac of a white color. Dark hats cannot be stiffened with a bleached lacquer and light hats cannot be stiffened with an unbleached lacquer.

In spite of all the afore-named drawbacks it has hitherto been impossible to replace the shellac in a perfect manner by synthetic products. Several synthetically prepared resins containing carboxyl are already known which have been suggested for use as a substitute for shellac, for instance interpolymerization products of maleic anhydride and styrene. In view of too high a content of carboxyl groups these products have, however, the drawback of being soluble again even after having been dried. The material loses its stiffness on dyeing whereas hats stiffened with shellac may be dyed without essentially altering their condition.

Now we have found that resinous interpolymerization products containing at least one ole-

finic compound having no free carboxyl group, and at least one olefinic monocarboxylic acid as components may be used with great advantage for stiffening hats of every kind and are capable of replacing the shellac or other stiffening agents with best success.

As very suitable interpolymerization products there may for instance be named the resins the one component of which is an ester of vinyl alcohol, for instance vinyl acetate, styrene, vinyl-alkyl-ketones, such as vinyl-methyl-ketone, acrylic acid esters, methacrylic acid esters or other polymerizable olefinic compounds without a free carboxyl group, and the other component of which, i. e. the olefinic monocarboxylic acid is acrylic acid, crotonic acid, alpha-vinyl-cinnamic acid or cinnamic acid.

In the afore-named interpolymerization products it is possible to alter to a large extent the number of the carboxyl groups and in consequence thereof the properties of the products so as to adapt them to the desired conditions. An interpolymerization product of vinyl acetate and crotonic acid may serve as example to illustrate the conditions to be seen in each case of an interpolymerization product; the following table shows the composition in percentages of the interpolymerization product and the pH-value of its ammoniacal solution prepared with as small a quantity as possible of ammonia:

| | Per cent | Per cent | Per cent | Per cent | Per cent |
|---------------------------|----------|----------|----------|----------|----------|
| Vinyl acetate..... | 97.5 | 95 | 90 | 70 | 50 |
| Crotonic acid..... | 2.5 | 5 | 10 | 30 | 50 |
| pH-value higher than..... | 10 | 7.5 | 6.5-7 | 5.5 | 4.5-4.8 |

There may be selected a stiffening agent of any desired alkalinity or any desired degree of acidity. In the example given above the mixture suitable for most cases is 90 per cent of vinyl acetate and 10 per cent of crotonic acid. The same or similar is to be observed with other interpolymerization products.

The interpolymerization products are soluble in alcohol and in aqueous alkali. If they have been allowed to dry they are either insoluble or only sparingly soluble so that the material may be stiffened, as if shellac is used, before dyeing it. Like shellac, they are hard in the cold and become plastic when exposed to the action of heat. The stiffened material, therefore, remains capable of being shaped in the heat. In some respects the interpolymerization products are su-

rior to shellac, since they yield entirely colorless impregnations and may be used with the same success for the lightest as well for dark colors. They are resistant to storing for any length of time, insensitive to heat and, after the material has been stiffened, they may be transformed into insoluble salts, for instance into salts of the alkaline-earth metals. The solutions of salts insoluble in water prepared with the aid of organic solvents may likewise be used. Any desired quantity of acid may be added to aqueous alcoholic solutions and to purely alcoholic solutions of the salts of the interpolymerization products or the free acids so that on dyeing not even slight quantities of the dyestuffs are bleeding.

Any desired additions, such as paraffine, artificial resins, insoluble soaps or dyestuffs may be mixed with the stiffening agents used according to the present invention. The mixture with the additions is accelerated by the emulsifying action of the stiffening agents. The simultaneous use of wetting agents may likewise be of advantage. Interpolymerization products having at the same time other valuable properties may be prepared for instance, by introducing by polymerization water-repellent agents such as vinyl stearate, so that during the stiffening operation a water-repellent action is simultaneously produced.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight, if not stated otherwise:

1. Undyed woollen bodies for men's hats are stiffened with an ammoniacal solution of 10 per cent strength of the interpolymerization product of 95 per cent of vinyl acetate and 5 per cent of crotonic acid. After the hat bodies have been squeezed they are steamed, rapidly dried and then dyed. Instead of the ammoniacal solution there may be used solutions in fixed alkalies; in that case the material is suitably acidified after the stiffening operation.

2. Finished men's hats of fur felt are stiffened by applying thereon, by means of a sponge, a solution consisting of 2.8 per cent of the interpolymerization product of 90 parts of vinyl acetate and 10 parts of crotonic acid, 5.6 per cent of acetic acid, 74 per cent of methyl alcohol or ethyl alcohol and 17.6 per cent of water. After the material has been dried it is pressed on the sandbag press.

3. Dyed wool felt bodies for ladies' hats are stiffened with an aqueous solution containing 5 per cent of the interpolymerization product of 90 parts of vinyl acetate and 10 parts of crotonic acid as ammonium salt in the dissolved form. After the bodies have been squeezed they are

immersed into a solution containing 3 per cent of calcium chloride. The material is then again squeezed and dried.

4. Dyed and deacidified woollen bodies in pastel shades are stiffened by means of an alcoholic solution containing an interpolymerization product of 97.5 parts of vinyl acetate and 2.5 parts of crotonic acid as calcium salt in the dissolved form. The bodies are airdried.

5. Dyed fur felt hats for men are stiffened with a solution of 5 per cent strength of the ammonium salt of the interpolymerization product of 70 per cent of vinyl acetate, 20 per cent of vinyl stearate and 10 per cent of crotonic acid. The hats are allowed to dry and have then become water-repellent.

6. Dyed woollen bodies for men's hats are stiffened with a solution of 8.4 per cent strength of the ammonium salt of the interpolymerization product of 75 per cent of styrene and 25 per cent of acrylic acid. The bodies are squeezed in the usual manner and dried.

7. Dyed woollen bodies for men's hats are stiffened with an aqueous solution of 8 per cent strength of the ammonium salt of the interpolymerization product of 65 parts of vinylmethylketone and 35 parts of cinnamic acid. The bodies are then squeezed in the usual manner and dried. There may be operated with the same success with an aqueous solution of 5 per cent strength of the ammonium salt of the interpolymerization product of 40 parts of alpha-vinyl-cinnamic acid and 60 parts of styrene. It is also possible to use an aqueous solution of 7.5 per cent strength of the ammonium salt of the interpolymerization product of 42 parts of methacrylic acid and 56 parts of styrene.

8. Dyed woollen bodies for ladies' hats are stiffened with an aqueous solution containing 5 per cent of the sodium salt of the interpolymerization product of 90 parts of vinyl acetate and 10 parts of crotonic acid. The stiffening operation being done the bodies are slightly dried, acidified in sulfuric acid of 0.5 per cent strength, rinsed and dried.

9. Paper braids for straw hats are stiffened with an ammoniacal solution containing 10 per cent of the interpolymerization product of 90 parts of vinyl acetate and 10 parts of crotonic acid. As soon as the stiffening operation is done the braids are dried and smoothed. The braids thus obtained are then sewn in known manner over a hat frame so as to obtain a straw hat. It is not necessary to further stiffen a hat made of stiffened braids as described above.

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