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PROCESS OF CARROTING FUR AND THE LIKE AND COMPOSITION THEREFOR

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This invention relates to carroting processes for fur and the like, employed to give such fur felting properties, particularly for use in hat manufacture.

In the case of prior carroting processes, it has been the usual practice to brush the carroting solution on the fur while the latter is still on the skins, allow it to dry, then either place the skins in piles or stacks or cut the fur and store the cut fur, and then allow the carroted fur to remain in that stored state for days, weeks or even months, during which time the carroting compound effects a "working in" so that its full effects are secured. That is to say, such processes rely in large part on the continued effect of the carroting after the solution has been applied and dried and during the period that the fur is "aging" or in storage.

For such aging action of the carrot, carroting solutions have heretofore included as active agents non-volatile compounds, such as non-volatile acids, metal catalysts non-volatile salts or non-volatile oxidizers. Thus, in the use of the common nitric acid and mercuric nitrate solution, where the nitric acid is used in relatively low concentration the mercuric nitrate is relied on to prolong and complete the carroting during the aging. When non-volatile, sulphuric acid is employed as the hydrolyzing agent, the acid acts as a factor in completing the carroting effect during aging, and in such case it has been found necessary to prevent destructive action by the acid on the fur during the storage of the latter by the presence of compounds which have an inhibiting effect, such as neutral salts of a strong base and a strong acid.

One objection to the heretofore generally prevalent use of the mercuric nitrate-nitric acid solution is the noxious effect arising from the use of mercury which, as is well known, is deleterious to and endangers the health of the workers, both those performing the carroting and those engaged in the subsequent steps of hat manufacture.

Another objection to carroting processes as heretofore employed, making use of non-volatile carroting agents, has been the fact that they result in deposits on the fur of metal salts or other non-volatile substances which add initially to the weight of the fur, but, due to their water solubility, these substances are removed in the subsequent washing and other processing of the hats. Accordingly, when the carroted fur is weighed to assign a definite weight to the individual hat body preparatory to its formation, a false result is reached since the subsequently formed and processed hat body loses weight in processing and becomes of lesser weight than was intended. Furthermore, this loss in weight cannot be predicted or foreseen since the manual application of the carroting solution in the first instance and the deposit on the fur of the non-volatile, water soluble substances cannot of necessity be uniform for all skins. Fur carroted, therefore, with the use of carroting solutions containing such non-volatile, water-soluble ingredients results in a fur of non-uniform weight, which adds further to the difficulty in securing the finally formed hat bodies of the intended weight.

Furthermore, it is well known that without the aging heretofore referred to, fur carroted by processes heretofore employed is found to have inadequate felting properties, and such prior processes and carroting compositions have been incapable of adequately carroting fur which is required to be used soon after the application of the carroting solution and without aging or storage and which is known as "green" fur.

One object of the present invention is to produce adequate felting properties in the carroted fur, including rapidity in felting, tightness of the felt, and a smooth, firm body in the felted fur.

Another object is to avoid the use of mercury or other metallic compounds harmful to the health of the workers.

Another object of the invention is to secure the intended weight for hats formed from the carroted fur, through the avoidance of the deposit on the fur of metal salts or other non-volatile substances.

Another object is to make use of a carroting solution substantially free from non-volatile carroting agents and of a concentration carefully selected to provide the optimum condition of carroting effectiveness. Due to the volatility of the solution, this permits the continuance of the same ideal or optimum carroting effect during the entire carroting treatment, including both the stage of brushing and the stage of drying. By this means superior felting properties are imparted to the fur since the latter is treated without the necessity of a prolonged stage of aging or storage, which is necessary where non-volatile compounds are employed. In the latter case, during such prolonged stage of drying, the activity and effectiveness of the carroting agents are undergoing a continuing and wide departure from the point of optimum effectiveness, this being accompanied by danger of damage to the fur.

These and other objects of the invention will be best understood from the following description.

I have found that fur may be successfully carroted with adequate felting properties and with increased rapidity in felting, and thereafter be used as "green" fur for felting in hat manufacture without intervening aging or storage, by employing a volatile carroting solution, substantially free from metal salts or other non-volatile carroting agents, and particularly free from mercury and the noxious conditions surrounding its use.

In hat manufacture the effectiveness and commercial availability of any carroting solution is dependent in large measure on the rapidity with which the shrinking can be performed in its several stages after the hat body is formed in the first instance from the carroted fur.

In hat manufacture as now carried on, the shrinking process commonly includes three principal stages—first a so-called "wetting down" or "starting", next a more vigorous shrinking, and, as a last stage, and usually after the partly shrunk bodies have been dyed, shrinking to final size and firmness. Each stage of shrinking is commonly carried out in whole or in part on a machine in which the hat body is subjected to a kneading action and to the simultaneous application of hot water.

The time consumed in each stage of shrinking is highly important, not only because a certain rate of output is commercially essential, but because, with properly carroted fur, a more acceptable felt is produced by relatively rapid shrinking, and, in the third stage of shrinking, if the time of shrinking is prolonged, the dye in the partly shrunk bodies is apt to be deleteriously affected. A certain maximum time period therefore in which the shrinking must be performed in each stage is recognized as essential in the case of any commercially operative or usable carroting process.

In the case of the common mercuric nitrate-nitric acid solution, relatively low acid concentrations and of a relatively narrow range must be employed to bring the shrinking for each of the shrinking stages mentioned within the commercially permissible time. Such time, for example, is exceeded unless the concentration of nitric acid is at least approximately 2½% by weight, but if the acid concentration exceeds approximately 6% such time is again exceeded, the optimum result being reached with a concentration of approximately from 4 to 5%. With concentrations increased above 6%, the time required for shrinking is increased at a rapidly accelerated rate, so that the use of a concentration of nitric acid of even 7 or 8% is inoperative from a practical or commercial standpoint. This is true whether or not the solution is used in the presence of an oxidizer, such as hydrogen peroxide.

I have found that by employing a volatile hydrolyzing acid, such as nitric acid, in high concentration, and a concentration higher than that used or practically usable in the mercuric nitrate-nitric acid solution, and by utilizing in the presence of such high concentration of acid a volatile oxidizer, such as hydrogen peroxide, an effective carroting solution may be had free from mercury and its essential objectionable features and capable of a more rapid shrinking in each of the several stages of shrinking than can be obtained from the usual mercury carrot.

Any volatile acid having a hydrolyzing action may be employed, such as nitric acid, acetic acid, formic acid, hydrofluoric acid in solution, etc. These acids, however, should be employed in relatively high concentrations. For example, in the case of nitric acid (technical acid of approximately 63% concentration), which is preferable for considerations of expense, convenience and availability, concentrations are employed having a wide range of from approximately 11 or 12% to approximately 20% by weight, within which range the shrinking at each of the three stages is effected within the commercially permissible time period.

Using concentrations within the range indicated, an optimum carroted effect may be had which reduces the time required for shrinking at each of the three stages of shrinking to substantially less than the shortest time required for shrinking in the case of mercury carrot. The particular concentration required within this range for producing such optimum effect will depend in each case on the type of fur treated. For example, in the case of fur known as "First Grade Scotch Coney", such optimum effect is reached with concentrations of from 17 to 19% of nitric acid.

A probable explanation of the effectiveness of this carroting solution is as follows:

Animal fiber is an amphoteric substance of colloidal nature having basic and acidic functions which may be brought into action only by means of strong bases or strong acids respectively. At the isoelectric point, or state of electrical neutrality, the amino groups and carboxyl groups of the molecules of these amphoteric substances have interacted to form what may be termed as "inner salt" which, if undisturbed, remains intact, forming double ionized molecules. To split these molecules and bring them into a state of maximum chemical activity appears to be an important function of the carroting treatment.

I have found that the condition of maximum chemical activity for these molecules is reached by the use of an acid having a pH value ranging from 1.4 to 0.8 (acid cresol red as indicator), or by the use of an alkali having a pH value of approximately 11 (La Motte purple as indicator). At all events, under either of these conditions the fur acquires the most desirable carroting properties.

Treatment, however, with an alkali is undesirable due to side reactions and the destruction or impairment of the fur fiber. But, by treatment with an acid having a hydrogen ion concentration represented by a range of pH 1.4 to pH 0.8 (or one corresponding to a concentration of from approximately 11 or 12% to 20% of technical nitric acid at normal or room temperature) and employing a volatile acid in solution free from non-volatile compounds, not only is a pH value furnished in the first instance which is ideal for building up the electrical activity of the fur molecules, but such ideal value is maintained at every stage of the carroting treatment, i. e., the stage of brushing and the stage of drying.

On the other hand, in the case of a solution including non-volatile carroting agents, the pH value of the acid hydrolyzer is constantly undergoing a change during the drying of the fur, and the pH value, if at any time the ideal one, remains so but for a short interval.

If other volatile acids such as those mentioned are employed, the concentration should be such as to have substantially the same hydrogen ion concentration as the concentration of nitric acid above mentioned to give the required hydrolyzing effect in their action on amphoteric substances.

such as proteins. That is to say, a minimum concentration of such acids should be used, which is represented by pH 1.2, which corresponds to a concentration of approximately 12% by weight of nitric acid of approximately 63% technical at normal or room temperature. For example, if acetic acid (technical 56%) is used, it should have a minimum concentration of approximately 44%. If formic acid (technical 90%) is used, it should have a minimum concentration of approximately 38%.

A relatively wide range of concentration may be employed for the oxidizer. In the case of hydrogen peroxide it is preferably used in the order of from 4 to 8% by weight. Hydrogen peroxide is preferably employed as the volatile oxidizer due to its availability, oxidizing effect, and absence of side reactions. Other volatile oxidizers may be employed. Among organic peroxides, for example, there may be used peroxides of the type R—O—O—H such as

$$CH_3—O—O—H;$$

or of the type

$$R—O—O—R$$

such as

$$C_2H_5—O—O—C_2H_5;$$

or hydro-peroxides such as

$$CH_2OH—O—O—CH_3;$$

or peroxides obtained by reaction between aldehydes and hydrogen peroxide in ether. On the other hand, organic peracids may be employed of the type RCO_3H such as CH_3CO_3H.

Where hydrogen peroxide is employed, a small quantity of some stabilizer is preferably used. In the presence of dust and small metal particles which are apt to be deposited on the fur during the processing of the skins prior to carroting, hydrogen peroxide rapidly decomposes, resulting in inadequate and non-uniform oxidation of the fibers. To prevent such decomposition, a minute quantity of some stabilizing substance, such as urea, citric acid, sodium metaphosphate, sodium salicylate, etc., should be employed, these substances being inactive, without carroting effect, and added for the sole purpose of stabilizing the hydrogen peroxide.

The volatile acid and the volatile oxidizer should preferably be selected so that they are incapable of reacting one on the other. For example, it is inadvisable to use such compounds as chloric acid or perchloric acid for oxidizers which produce free chlorine, the latter resulting in chlorination of the natural fibers and the weakening thereof.

A carroting solution prepared as herein described may be brushed on the fur at normal or room temperature and acts promptly following its application to the fur, giving the required carroting effect before it has disappeared through volatilization, leaving no free acids nor oxidizers which must be relied upon to prolong the carroting effect, leaving no other non-volatile, water-soluble substances on the fur, and requiring no storage nor aging of the fur to complete the carroting.

The application of the carroting solution to the animal fibers may be made by brushing or spraying the carroting solution on the fur while the latter is still on the skins, or cut fur may also be carroted.

The invention will be best understood by the following specific examples of carroting solutions which may be prepared according to the general principle of the invention and intended each for application to the animal fibers while still on the skins. In each of the examples, the carroting composition comprises an aqueous solution consisting of 100 parts by weight of the final solution and including in it the following substances, in the proportions specified. The nitric acid is assumed to be technical acid approximately 63% concentration, and the hydrogen peroxide is technical 100% volume (which, for 20 parts by weight yields about 6% of actual hydrogen peroxide by weight).

Example 1

	Parts by weight
Nitric acid	15
Hydrogen peroxide	20

Example 2

Nitric acid	15
Hydrogen peroxide	17
Sodium salicylate	0.05

Example 3

Nitric acid	12
Hydrogen peroxide	17
Urea	0.05
Citric acid	0.05

Example 4

Acetic acid (technical 56%)	80
Hydrogen peroxide	17
Sodium metaphosphate	0.005
Sodium salicylate	0.05

Example 5

Formic acid (technical 90%)	45
Hydrogen peroxide	20
Urea	0.05
Citric acid	0.005

This application is a continuation in part of my prior copending application, Serial No. 212,301, filed June 7, 1938, for Process of carroting fur and the like and composition therefor.

Various changes in and departures from the embodiment of the carroting composition as herein exemplified may be made, all within the scope of the generic invention, it being understood that the matter herein set forth is submitted as illustrative and not in a limiting sense.

I claim:

1. An aqueous carroting solution for treating fur and the like containing as its carroting agent a composition consisting of a volatile hydrolyzing acid selected from the group consisting of nitric, formic and acetic acids, and a volatile oxidizer selected from the group consisting of hydrogen peroxide, organic peroxides and organic peracids, the hydrolyzing acid having a hydrogen ion concentration equivalent at least to that represented by a concentration of 11–12% by weight of nitric acid of approximately 63% technical, and the solution being substantially free from non-volatile carroting agents.

2. An aqueous carroting solution for treating fur and the like containing as its carroting agent a composition consisting of a volatile hydrolyzing acid selected from the group consisting of nitric, formic and acetic acids, and a volatile oxidizer selected from the group consisting of hydrogen peroxide, organic peroxides and organic peracids, the hydrolyzing acid having a hydrogen ion concentration equivalent to that represented by a concentration of between 11 and 20% by weight of nitric acid of approximately 63% technical,

and the solution being substantially free from non-volatile carroting agents.

3. An aqueous carroting solution for treating fur and the like containing as its carroting agent a composition consisting of nitric acid in a concentration of an order represented by from approximately 11 to 20% by weight of technical nitric acid of approximately 63%, and also hydrogen peroxide, said solution being substantially free from non-volatile carroting agents.

4. An aqueous carroting solution for treating fur and the like containing as its carroting agent a composition consisting of nitric acid in a concentration of an order represented by from 17 to 19% by weight of technical nitric acid of approximately 63%, and also hydrogen peroxide, said solution being substantially free from non-volatile carroting agents.

5. The carroting solution defined in claim 2, in which the hydrolyzing acid consists of acetic acid.

6. The carroting solution defined in claim 2, in which the hydrolyzing acid consists of formic acid.

7. The process of carroting fur and the like, which comprises treating the fur with an aqueous carroting solution containing as its carroting agent a composition consisting of a volatile hydrolyzing acid selected from the group consisting of nitric, formic and acetic acids, and a volatile oxidizer selected from the group consisting of hydrogen peroxide, organic peroxides and organic peracids, the hydrolyzing acid having a hydrogen ion concentration equivalent at least to that represented by a concentration of 11–12% by weight of nitric acid of approximately 63% technical, the solution being substantially free from non-volatile carroting agents, and causing the volatilization of the carroting solution on the fur.

8. The process of carroting fur and the like, which comprises treating the fur with an aqueous carroting solution containing as its carroting agent a composition consisting of a volatile hydrolyzing acid selected from the group consisting of nitric, formic and acetic acids, and a volatile oxidizer selected from the group consisting of hydrogen peroxide, organic peroxides and organic peracids, the hydrolyzing agent having a hydrogen ion concentration equivalent to that represented by a concentration of between 11 and 20% by weight of nitric acid of approximately 63% technical, the solution being substantially free from non-volatile carroting agents, and causing the volatilization of the carroting solution on the fur.

9. The process of carroting fur and the like, which comprises treating the fur with an aqueous carroting solution containing as its carroting agent a composition consisting of nitric acid in a concentration of an order represented by approximately 11 to 20% by weight of technical acid of approximately 63%, and also hydrogen peroxide, said solution being substantially free from non-volatile carroting agents, and causing the volatilization of the carroting solution on the fur.

10. The process of carroting fur and the like, which comprises treating the fur with an aqueous carroting solution containing as its carroting agent a composition consisting of nitric acid in a concentration of an order represented by from 17 to 19% by weight of technical nitric acid of approximately 63%, and also hydrogen peroxide, said solution being substantialy free from non-volatile carroting agents, and causing the volatilization of the carroting solution on the fur.

11. The process defined in claim 8, in which the hydrolyzing acid consists of acetic acid.

12. The process defined in claim 8, in which the hydrolyzing acid consists of formic acid.

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