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PROCESS OF CARROTING FUR AND THE LIKE AND COMPOSITION THEREFOR

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15 Claims. (Cl. 8—21)

This invention relates to the treatment of fur and similar animal fibres (herein generically designated as fur), and more especially to give such fur improved felting properties, and said invention further relates to a composition of matter adapted to be employed in such treatment.

In its natural state animal fur has inadequate felting properties and, as is well known, preliminary to the formation of a suitable fur felt to be used in the manufacture of such articles as hats, must be subjected to a chemical treatment ordinarily termed "carroting" to impart thereto the requisite felting properties. The procedure commonly adopted is to brush the carroting solution into the fur while the latter is still on the skin, the latter being then set to one side to allow the fur to dry and the fur being thereafter removed from the skin and made into felt.

The object of the present invention, among other things, is to so improve the carroting treatment and that carroting solution employed in such treatment that, while the fur has imparted to it the property of rapid felting and the capacity of producing a tight, strong felt, certain objectionable features which have been inherent in processes heretofore in use are eliminated in whole or in part, as will be better understood from the following.

The carroting process is dependent on the action of chemical reagents which so act chemically on the surface of the animal fibers that the latter acquire felting properties previously absent, and, when subjected to hot water and pressure, tend to work into a closely interlocked relation with the resultant formation of a compact, tight, firm body of felt.

The process of carroting comprehends not only a cleansing of the animal fibers from fats and other substances, the presence of which interferes with felting, but also chemical reactions of the carroting reagents on the proteids of the fibers.

It is known that a certain carroting effect is produced by the action of strong acids on the fur, such as sulphuric acid, which produce only a hydrolyzing action. The carroting effect of such acids, which is relatively weak when they are used alone, is greatly intensified in the presence of an oxidizing agent. Accordingly it is the generally accepted understanding that the carroting process in its effective form is composed of two principal reactions, a hydrolyzing action by the acid on the animal fibers and an oxidizing action by the oxidizing agent.

The carroting treatment heretofore most commonly employed has been through the application to the fur of a carrot comprising an aqueous solution of mercuric nitrate in nitric acid which, as is well known, is a strong oxidizing agent. In this case the nitric acid acts simultaneously as an acid and an an oxidizing agent, producing a hydrolyzing and oxidizing reaction on the animal fibers, while the mercuric nitrate has a catalytic action on the oxidizing process. At certain concentrations of these two reagents felting properties can usually be imparted to the fur.

This method of carroting, however, has certain material defects and objections, among which are the following.

Unless carried out under carefully regulated conditions, difficult or impossible at all times to meet, the treatment tends to weaken the strength and the felting properties of the animal fibers, and furthermore to so change their structure that they lose in part their ability of fixing dye stuffs, with the result that such treated fibers tend to give off the dyes when washed.

In this process the hydrolyzing and oxidizing actions are effected by the same reagent,—nitric acid,—the oxidizing action of which takes place only at high concentrations. Under high concentrations its hydrolyzing action becomes so effective that it is apt to attack or partially destroy the animal fibers. Accordingly, great care has to be exercised in controlling the strength of the solution so that, on the one hand, it will be of sufficient strength to give the fur adequate felting properties while, on the other hand, it will not be so strong as to impair the quality of the fur.

This difficulty is increased by the fact that, after the solution has been brushed on the fur and the skins are set aside for drying, and as the drying proceeds, the nitric acid becomes stronger and more concentrated and acquires an increasing and greatly intensified oxidizing effect. Such intensified oxidizing effect tends to detrimentally affect the fibers unless carried out under carefully regulated physical drying conditions, within definitely maintained limits of temperature, humidity, etc., which conditions it is difficult or impracticable to strictly regulate.

Another well recognized objection is that carroting through the use of mercuric nitrate is poisonous and dangerous to health in the subsequent shrinking of the felt as well as in the carroting operation. Not only is the application of the solution and the subsequent drying of the skins accompanied by the emission of vapors of lower oxygen compounds of nitrogen which are noxious and dangerous to health, but the use of

mercuric nitrate results in the deposition of mercuric salts on the fibers of the carroted fur. Under the conditions of boiling or steaming to which the fur is subjected during the subsequent felting process, as, for example, in the sizing of formed hat bodies, vapors of mercury and mercuric salts are emitted which long experience has demonstrated are dangerous and highly deleterious to the health of the workers.

A further objection lies in the fact that, on treating white or light colored animal fibers by the mixture of nitric acid and mercuric nitrate, the fibers change color and become yellow or red. This discoloration can be explained by the specific action of nitric acid and of mercuric nitrate on proteids; the latter turn yellow on heating with nitric acid and become red on heating with a solution of mercuric nitrate and nitric acid (Millon's test).

The use of two oxidizing agents in a carroting solution, as, for example, nitric acid and hydrogen peroxide, tends to eliminate the discoloration of white or light colored animal fibers. In such case the hydrogen peroxide oxidizes and destroys the pigments on the fibers formed by the action of nitric acid and mercuric nitrate. The use, however, of two energetic agents, such as nitric acid and hydrogen peroxide, in the same carroting solution tends to produce inordinately strong oxidization of the animal fibers which is difficult to control, with the result that the strength of the fibers as well as their affinity for dye stuffs tends to be detrimentally affected. Moreover, the use of hydrogen peroxide and nitric acid often produces yellow colored fibers on the edges of the skins, the intensity of which discoloration depends upon the drying conditions, such as temperature, humidity, etc., which are again difficult or impracticable to control.

Other carroting compositions have been suggested involving the use of oxidizing agents in an alkaline medium, as, for example, hydrogen peroxide in a sodium hydroxide solution. The hydrolyzing action of alkaline solutions on the animal fibers, however, is very intense and tends to detrimentally affect the strength of the treated fibers, their capacity to take and fix dyes, and also tends to impart a harshness to the "feel" of the finished felt.

Other methods of carroting have been suggested involving the use of sulphuric acid alone or a mixture of sulphuric acid with an oxidizing agent. These methods are free from the poisonous attributes of the mercuric nitrate method and avoid discoloration of white animal fibers but are not sufficiently effective to produce an adequate carroting effect on the fibers unless concentration of the reagents is very high, and high concentration of such reagents as sulphuric acid or hydrogen peroxide acts detrimentally on and affects the strength of the treated fibers. The use of high concentrated sulphuric acid solutions especially tends to destroy the animal fibers in the course of the drying process as the sulphuric acid reaches stages of more intense concentration.

Through our carroting treatment fur may be adequately and satisfactorily carroted, avoiding in whole or in part numerous objections and effects in prior carroting processes.

We have found that by treating the animal fibers with an a cidreagent as a hydrolizer and an oxidizing reagent in an aqueous solution containing a considerable quantity of soluble neutral salts, the fibers may be easily and thoroughly carroted.

As neutral salts we may use any soluble salt of an alkali metal or alkaline earth metal which is formed by a sufficiently strong acid and which has a neutral or an almost neutral reaction. Among such salts, for example, are potassium chloride, sodium sulphate, ammonium sulphate, calcium chloride, bisodium phosphate, etc. A salt of nitric acid, such as potassium, sodium or ammonium nitrate, may be used where resulting discoloration is not important. The term "alkali", as used herein and in the claims, includes the alkali metals (including ammonium) and the alkaline earth metals.

Relatively high concentrations of neutral salts are preferably employed in our carroting composition, and, for reasons hereinafter given, should preferably equal or exceed the concentrations of the acid reagent.

As acids we may use any inorganic or organic acid which produces a sufficient hydrolyzing effect. Of the inorganic acids, we prefer to make use of such acids as hydrochloric, sulphuric, phosphoric or metaphosphoric acids which do not impart any discoloration to the fur. Where the resulting discoloration is not important, nitric acid may be employed.

A hydrolyzer consisting of mixtures of the various acids may be employed to advantage, particularly a mixture of a volatile acid and a non-volatile acid. For example, a mixture of non-volatile sulphuric acid and relatively volatile hydrochloric acid may in some cases be desirable. The hydrolyzing effect of such a mixture is strong in the initial steps of carroting when and immediately after the solution is applied to the fur, but, due to the evaporation of hydrochloric or other volatile acid, diminishes rapidly during the drying stage when the non-volatile acid tends to become more highly concentrated.

Use may also be made of organic acids which are soluble in water and are capable of producing hydrolyzing effects, such as formic, oxalic, acetic and various chloroacetic and sulphonic acids. These acids are relatively weaker in their hydrolyzing action than the inorganic acids mentioned and should be used in greater concentrations than such inorganic acids or should be used in mixtures with the stronger inorganic acids.

As oxidizing agents we may employ such substances as peroxides, persulphates, perchlorates, etc.

We have found that the use of neutral salts in the carroting solution results in a marked improvement in the process of carroting and in the carroted fur treated thereby.

Carroting is ordinarily best effected by reagents which in solution afford a strong and energetic carroting action. This, however, should be maintained within limits which will not cause injury to the fibers. Due to the fact, however, that in the subsequent drying of the skins acid reagents become abnormally concentrated, it is difficult or impossible to avail of such concentrations of acids as are qualified to give the most effective but safe carroting action in solution without at the same time acting destructively on the fibers during the subsequent drying of the fur.

The neutral salts as herein described, however, are found, on the one hand, to strengthen and intensify the carroting action of the solution but, on the other hand, to act reversely, as it were, during the subsequent steps of drying the skins

when the acid reagent becomes abnormally concentrated and to offset or prevent the destructive and damaging action on the fibers which would otherwise result from the then highly concentrated acid, thereby acting first to promote the carroting action and then acting protectively during the final steps of drying the fur.

Although our invention is not restricted by nor dependent on any theory which may be advanced to account for the precise action of the reagents employed in the carroting treatment, the main point being that they accomplish the results herein described, this double or two-fold action of the neutral salts may be explained as follows.

Neutral salts, which are highly ionized and give numerous disassociated ions when placed in aqueous solution, usually exert a strong, increasing effect upon the catalytic activity of the hydrogen ion of an acid. In the presence of neutral salts the catalytic activity of acids is usually much more intense than that of the acids alone acting in the absence of neutral salts. The addition therefore of neutral salts to the carroting composition, as we have found, increases the hydrolyzing effect of the acid or acids employed.

In the relatively weak acid solutions which are used for initially applying the carrot no appreciable reaction takes place between the neutral salts and the acid solution, the sole effect of the neutral salts being to increase activity of the hydrogen ion.

When, however, the fur to which the solution has been applied is being dried, the acid on the fur becomes more and more concentrated as the drying proceeds. Such concentration, however, takes place in the presence of the neutral salts which then combine with the increasingly concentrated acid to form compounds having no appreciable detrimental action on the fibers and none comparable with that of the concentrated acid itself.

It is well known, for example, that such salts as bisodium sulphate or bisodium phosphate in the presence of free acids in concentrated solutions yield acid salts according to the following equations:

$$Na_2SO_4+H_2SO_4=2NaHSO_4$$

$$Na_2HPO_4+H_3PO_4=2NaH_2PO_4$$

These acid salts formed in the later stages of drying have no appreciable detrimental action on the fibers. These reactions, however, take place in relatively concentrated solutions only, but the more concentrated the acid becomes and the greater its capacity to damage the fibers, the more effective becomes the action of the neutral salts in offsetting the effect of the excess acid.

It is also found that in the case of such neutral salts as sodium chloride and calcium chloride, for example, which do not form acid salts with monobasic acids such as hydrochloric or nitric acid, a similar protective action is secured, offsetting the effect of acid concentration. This may be the result of the formation of unstable compounds, as, for example, between hydrochloric acid and sodium chloride, but whatever be the explanation it is found that even in the case of a volatile acid, such as hydrochloric or nitric acid, the neutral salts serve effectively to protect the fibers from detrimental effects which would otherwise result from acid concentration during drying.

We have found that the carroting action and the rapidity with which the carroted fur felts when subsequently put through the felting process, are promoted by employing a mixture of acids for the hydrolyzer or by using for the oxidizer a plurality of oxidizing agents or both.

As acid mixtures we preferably use sulphuric acid with either hydrochloric or phosphoric acid or hydrochloric acid with phosphoric acid.

As combinations of oxidizing agents we may, for example, use hydrogen peroxide with either ammonium persulphate, potassium persulphate, potassium chlorate or potassium perchlorate or potassium chlorate with a persulphate.

This joint action between a plurality of oxidizers is found to give a more thorough and even carroting effect. This we believe to be due to the fact that certain oxidizing agents act more energetically than others on certain fibers or certain portions of the fibers or on certain colors of fibers, while other oxidizing agents, which we may term complementary, act more energetically on the fibers, portions or colors which are relatively resistant to the action of those oxidizing agents of the first class. This complementary action of a plurality of oxidizers accordingly assists in securing a thorough but uniform carroting without detrimental action on the fibers.

It will be observed that the herein described carroting treatment provides a method for carroting fur without danger to the health of the workers, since it is unnecessary to resort to mercury or other substances detrimental to health. If it is desired, however, to employ in addition to the neutral salts a catalytically acting substance, such as mercury, with the aim of further hastening or improving the carroting action, use may be made of such substance while still availing of the principles and advantages underlying this invention. That is to say, while we prefer to avoid the use of mercury or other unhealthy substances, our carroting composition comprehends the employment of an acid, an oxidizing agent and a neutral salt, whether used with or without the addition of further catalytically acting substances, such as a salt of mercury, tungsten, bismuth or other heavy metal.

The application of the carroting solution to the animal fibers may be carried out in the usual manner, which comprises brushing the solution into the fur while the latter is still on the skin. It may, however, be applied to the fur by spraying it on the fur while still on the skin or the fur itself, after having been cut from the skin, may have the carroting solution applied by immersion or otherwise. In the latter case the concentrations of the reagents should be materially reduced as compared to the concentrations used when the solution is applied by brushing or spraying on the fur while still on the skin.

The invention will be better understood by the following specific illustrated examples of various carroting solutions which may be prepared according to the principles of our invention and intended each for application to the animal fibers while still on the skins.

In each of the following examples the carroting composition comprises an aqueous solution having 100 parts by weight of water together with the chemical reagents named, in the proportions named, which proportions are also given in parts by weight.

Example 1

	Parts
Sulphuric acid	6
Hydrochloric acid	2
Hydrogen peroxide	5
Glauber's salt (crystalline bisodium sulphate)	20

Example 2

	Parts
Sulphuric acid	2
Phosphoric acid	7
Hydrogen peroxide	5
Ammonium phosphate	10

Example 3

	Parts
Sulphuric acid	5
Hydrochloric acid	1
Potassium chlorate	3
Hydrogen peroxide	4
Sodium sulphate	15

Example 4

	Parts
Sulphuric acid	5
Hydrochloric acid	1
Potassium persulphate	3
Hydrogen peroxide	4
Ammonium chloride	10

Example 5

	Parts
Sulphuric acid	5
Hydrochloric acid	1
Ammonium persulphate	5
Potassium chlorate	3
Glauber's salt	20

Example 6

	Parts
Sulphuric acid	3
Hydrochloric acid	1
Hydrogen peroxide	4
Ammonium mercuric chloride	3
Glauber's salt	20

Example 7

	Parts
Phosphoric acid	8
Hydrogen peroxide	6
Ammonium mercuric chloride	4
Ammonium sulphate	10

The use of the described treatment not only provides a thoroughly carroted fur capable of producing a fast-shrinking, tight and smooth felt, but also yields certain advantages, among which are the following.

The solution may be quickly and easily prepared. Its preparation and its application may be carried out without the production of noxious and poisonous vapors. Its use need not involve any injury to the health of the workers, and in most of the examples previously given no ingredient is used which can detrimentally affect their health.

The described treatment effects no reduction in the affinity of the animal fibers for dye stuffs but insures a permanency in the dyes.

The described treatment does not discolor the fur fibers but leaves light colored or white carroted fur with its original, natural color unimpaired.

By proper selection of the strength of the acid reagent or reagents in solution, adequate and thorough carroting is had without affecting the strength or otherwise impairing the desirable qualities of the animal fibers. Precautions required to control the carroting effect in the case of the carroting solution produced from nitric acid and mercuric nitrate are not required by the carroting treatment by our process.

Due to the protective action of the neutral salts during the drying process, the drying of the skins and the setting of the carrot may be effected without particular regard to temperatures and other drying conditions, the skins may be stored for long periods of time without deterioration, and drying may be effected either under normal prevailing factory temperatures or under relatively high drying temperatures, thereby shortening the time of drying and materially reducing the time required for the carroting treatment in its entirety.

Various changes in and departures from the embodiments of our carroting composition may be made as the same have been hereinbefore exemplified, all within the scope and principles of our generic invention, and it is understood that the matter hereinbefore set forth is submitted as illustrative and not in a limiting sense.

We claim:

1. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer consisting by weight relative to the water of substantially from 2 to 6% of sulphuric acid and 1 to 2% of hydrochloric acid, an oxidizer consisting by weight of from 4 to 6% of hydrogen peroxide and 2 to 4% of a complementary oxidizing agent of the group consisting of potassium persulphate, ammonium persulphate, potassium chlorate and potassium perchlorate, and further containing bisodium sulphate in an amount approximately equal to or greater than the amount of sulphuric acid.

2. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer consisting of sulphuric acid and a lesser amount of hydrochloric acid, the total acid being of sufficient concentration to produce effective carroting, an oxidizer, and an amount of bisodium sulphate approximately equal to or greater than the amount of sulphuric acid.

3. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer consisting of sulphuric acid and a lesser amount of hydrochloric acid, the total acid being of sufficient concentration to produce effective carroting, an oxidizer, and a substantially soluble neutral salt of a strong acid and an alkali metal present in substantially the same or greater amount than the acid and effective to react with the suphuric acid to form an acid salt during the evaporation of the solution.

4. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer consisting of a plurality of acids at least one of which is volatile and one non-volatile, the total acid being of sufficient concentration to produce effective carroting, an oxidizer, and a soluble substantially neutral salt of a strong acid and an alkali present in amount approximately equal to or greater than the amount of non-volatile acid.

5. As a composition of matter for carroting fur or the like, an aqueous solution containing sulphuric acid, an oxidizer, and bisodium sulphate in an amount approximately equal to or greater than that of the acid.

6. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer of sufficient strength to effect carroting of the fur, an oxidizer, and a soluble substantially neutral salt of a strong polybasic acid and an alkali metal present in approximately equal or greater amount than the acid and having no appreciable chemical reaction with the acid in solution but effective to react with the

acid during the evaporation of the solution to form an acid salt.

7. As a composition of matter for carroting fur or the like, an aqueous carroting solution adapted to be applied to the fur and subsequently dried, said solution containing an acid hydrolyzer, an oxidizer, and a soluble substantially neutral salt of a strong acid and an alkali present in amount substantially equal to or greater than that of the acid and having no appreciable chemical reaction with the acid in solution but effective to act with the acid as an accelecator for the carroting in its initial steps when the solution is first applied and to react with the acid as a retarder for the carroting and to oppose destructive action of the acid on concentration of the latter during the subsequent drying of the fur.

8. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer, a soluble substantially neutral salt of a strong acid and an alkali and having no appreciable chemical reaction with the acid in solution, the salt being present in an amount approximately equal to or greater than that of the acid, and a plurality of complementary oxidizing agents from a group consisting of hydrogen peroxide, potassium persulphate, ammonium persulphate, potassium chlorate and potassium perchlorate.

9. As a composition of matter for carroting fur or the like, an aqueous solution containing an acid hydrolyzer of sufficient concentration to produce effective carroting, a plurality of complementary oxidizing agents, and a soluble substantially neutral salt of a strong acid and an alkali present in amount approximately equal to or greater than that of the acid.

10. The process of preparing fur or the like for felting, which consists in treating the fur with an aqueous carroting solution containing a plurality of hydrolizing acids of sufficient strength to effect a carroting of the fur, at least one of the acids being volatile and one non-volatile, an oxidizer, and a soluble substantially neutral salt of a strong acid and an alkali present in amount approximately equal to or greater than the amount of non-volatile acid having no appreciable chemical reaction with the acid in solution.

11. The process of preparing fur or the like for felting, which consists in applying thereto an aqueous carroting solution and subsequently drying the fur, said solution comprising an acid hydrolyzer of sufficient strength to effect a carroting of the fur, a plurality of complementary oxidizing agents, and a soluble neutral salt of a strong acid and an alkali present in amount approximately equal to or greater than the amount of the acid and having no appreciable chemical reaction with the acid in solution but effective on the drying of the fur to inhibit destructive action by the acid.

12. The process of preparing fur or the like for felting, which consists in hydrolyzing and oxidizing fur by applying thereto an aqueous carroting solution and subsequently drying the fur, said solution containing an acid hydrolyzer of sufficient strength to effect a carroting of the fur, an oxidizer, and a soluble substantially neutral salt of a strong polybasic acid and an alkali metal, said salt being present in amount approximately equal to or greater than the amount of the acid and effective to act with the acid as an accelerator for the carroting in the initial steps when the solution is first applied and to react with the acid as a retarder for the carroting and to oppose destructive action of the acid with the formation of an acid salt on concentration of the acid during the subsequent drying of the fur.

13. The process of preparing fur or the like for felting, which consists in hydrolyzing and oxidizing fur by applying thereto an aqueous carroting solution and subsequently drying the fur, said solution containing an acid hydrolyzer of sufficient strength to effect a carroting of the fur, an oxidizer, and a soluble substantially neutral salt of a strong acid and an alkali, said salt being present in amount approximately equal to or greater than the amount of acid and effective to act with the acid as an accelerator for the carroting in the initial steps when the solution is first applied and to react with the acid as a retarder for the carroting and to oppose destructive action of the acid on concentration of the latter during the subsequent drying of the fur.

14. A process of carroting fur or the like to render it suitable for felting, comprising treating the fur with an aqueous carroting solution and subsequently drying the fur, said solution containing non-discoloring hydrolyzing acid of sufficient concentration to produce effective carroting a soluble non-discoloring neutral salt of an alkali and a strong acid, present in amount approximately equal to or greater than the amount of the hydrolyzing acid and non-reactive therewith in the solution but effective during drying to protect the fur from damage by the acid, and a suitable oxidizing agent.

15. A process of carroting fur or the like to render it suitable for felting, comprising treating with an aqueous carroting solution and subsequently drying the fur, said solution being free from mercuric and other heavy metallic catalytic salts and containing hydrolyzing acid of sufficient concentration to produce effective carroting, a soluble neutral salt of an alkali and a strong acid, present in amount approximately equal to or greater than the amount of the hydrolyzing acid, and a suitable oxidizing agent.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, lines 47 to 49, claim 10, strike out the words "having no appreciable chemical reaction with the acid in solution"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of September, A. D. 1936.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.