CONTINUOUS PROCESS FOR BLEACHING PIGMENTED KERATINOUS FIBERS

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ABSTRACT OF THE DISCLOSURE

Pigmented keratinous fibrous materials are bleached by
passing a web-like belt of the fibrous material successively
through an aqueous mordant solution containing a ferrous
salt, an aqueous bleaching solution containing hydro-
gen peroxide and an aqueous solution of an iron removal
reagent.

This invention relates to a novel continuous process for
bleaching pigmented keratinous fibrous materials with-
out impairing their desirable properties and to such a
continuous process that is particularly adapted for com-
mercial use.

The process involves the continuous bleaching of pig-
mented keratinous fibrous material, such as wool, karakul,
alpaca, cashmere, vicuna, cow and goat hair and the like,
or mixtures thereof to bleach the animal fibers to a light
color by controlled application of a mordant, a bleach
and a stripping bath under controlled conditions of tem-
perature, concentration and time.

All prior methods for bleaching pigmented keratinous
materials, especially dark pigmented wool and hair fibers,
were batch processes requiring long periods during which
constant surveillance of the operation was necessary and
personal judgment regarding adjustments of the system
were required to be made. An example of such a batch
process is the process described in United States Patent
2,914,374, Harris et al., assigned to applicants' assignee.

Principal objects of the present invention are to pro-
vide a novel continuous method for bleaching of pig-
mented keratinous materials which eliminates the need
for personnel surveillance and judgment and to provide
for economical and complete use of chemicals in an
automated commercially feasible system.

It is a further object of the present invention to provide
a system and process which is interchangeably applicable
to the bleaching of animal fibers in the loose condition
or subsequent to fabrication of the fibers into textile webs.

A further object of the present invention is to provide
a process for the continuous bleaching of pigmented
keratinous fibrous materials without impairing the textile
properties or the desirable handle of the treated animal
fibers.

A further object is to provide such a process wherein
pigmented keratinous material may be bleached while
without serious deleterious effect on the quality of the
material being treated.

These and other objects and advantages of the invention
are provided by a continuous process for bleaching pig-
mented keratinous animal fibers which comprises form-
ing the fibrous material to be bleached into a web-like
belt, passing the fibrous belt through an aqueous mordant
solution containing a ferrous salt, maintained at a con-
stant concentration and temperature, passing the mordant
solution treated fibrous belt through an aqueous bleaching
solution maintained at a constant temperature and con-
centration and thereafter passing said fibrous belt through
an aqueous solution of an iron-removal reagent main-
tained at a constant temperature and concentration and
rinsing and drying the fibrous belt.

Throughout the specification and claims, keratinous
fibrous material and fibrous belt are intended to mean
keratinous fibers such as cashmere, vicuna, alpaca, cow
gain, goat hair, and the like in the raw stock state con-
finned into a web either by fabricating the fibers into a
textile by weaving or felting processes or by confining
them between, for example, porous conveyor belts to pre-
vent excessive motion of the fibers with respect to each
other.

The invention will be more particularly described with
reference to the accompanying drawing diagrammatically
illustrating the process of the present invention and ap-
paratus for carrying out said process.

In accordance with the invention, keratinous fibrous
material either in the form of a woven or felted textile
fabric illustrated by roll 10 or loose fibers maintained in
the feed hopper 12 are fed between a pair of porous
conveyor belts 14 and 16. The confined fibrous material
is thoroughly wetted in passing below wetting means 18
connected to a suitable source of wetting liquid which
may contain a wetting agent in addition to water. Follow-
ing the spray wetting, the fibrous material is squeezed by,
for example, roll 20 and cooperating platen 22 and the
fibrous material is passed through a tank 24 containing
an aqueous mordant solution of a ferrous salt containing
sulfuric acid maintained at a temperature of from about
100 to 200° F. The concentration of the aqueous mordant
solution is maintained substantially constant by continu-
ously circulating the solution from a storage source as
indicated by the directional arrows. Further, conven-
tional heating means may be maintained in the tank 24
or at the outlet from the source of mordant solution.

In the mordant step, the pH range of the solution
should be between about 1 and about 3. It has been found
that a pH greater than 3 may result in a bad oxidation of
the ferrous ion at the relatively high temperature of the
bath. As indicated above, the temperature of the solution
is in the range of from about 100 to 200° F, and a particu-
larly useful range is from about 150 to about 170° F. By
maintaining the mordant bath at such a relatively high temperature, the mordant treatment can be
accomplished in a relatively short time, that is, from
about 10 to about 90 minutes although a time period up
to 150 minutes may be used.

The liquor-to-stock ratio of the mordant bath may be
varied substantially. For example, a liquor-to-stock ratio
of 5 to 1 to 100 to 1 or more will provide useful results.

The concentration of the ferrous sulfate may also be
varied substantially and useful results may be obtained
in the range of from about 1 to about 20% as ferrous sulfate
heptahydrate (FeSO₄•7H₂O) based on the weight of the
bath. Further, other ferrous salts may be used in equiv-
alent amounts; for example, ferrous acetate and ferrous
ammonium sulfate have provided satisfactory results.

As the animal fibers leave the bath tank 24, the excess
mordant solution is squeezed therefrom by these belt
26 cooperating with platen 28. Thereafter, the fibers carried
by the endless belts 14 and 16 are passed under spray
head 30 and the fibers are thoroughly rinsed and cooled.
The temperature of the fibers following the rinsing step
should not be greater than, for example, 40 to about 80°
F, in order to minimize oxidation of the ferrous ions.

Following the rinsing step, the belts 14 and 16 carry
the fibers into tank 32 containing the bleaching solution.
The bleaching step comprises the treatment of the fibers
with a solution of hydrogen peroxide containing suitable
buffering materials. It is important that the pH of the
bleach bath be maintained within the range of about 7
to about 9 and preferably in the range of 7.5 to 8.5.
Preferred buffering materials for the bleach bath are
tetra-sodium pyrophosphate and sodium tetraborate used in combination. The amount of hydrogen peroxide in the bleach solution may be varied from about .5 to about 5% calculated as 100% H₂O₂ based on the weight of the bath. Other buffering materials may include sodium carbonate, sodium bicarbonate, sodium oxalate, etc.

The amount of tetra-sodium pyrophosphate may be varied from about .5 to about 5% also based on the weight of the bath while the sodium tetraborate may vary from 0 to 5% based on the weight of the bath and a preferred mixture of buffers is 1 part tetra-sodium pyrophosphate to 2.5 parts of sodium tetraborate. The temperature of the bleaching bath is critical. For best retention of desirable fiber properties, the temperature of the bath should not be permitted to exceed 125° F. while a good working range is from about 100 to about 125° F.

The time required to achieve the desired color reduction in the animal fibers in the bleach tank 32 may range from about 10 to about 90 minutes. The time requirement is determined to a large extent by (1) the initial coloration of the fibers, (2) the concentration of the hydrogen peroxide, and (3) the operating temperature of the bleaching bath. After the fibers have been bleached the required amount in the bleach tank 32, the endless belts 14 and 16 carrying the fibrous material are passed below the squeeze roll 34 which cooperates with the fixed platen 36 to remove excess bleach from the belt. Thereafter the belt is passed below the spray head 38 and the fibers are thoroughly rinsed in a water solution maintained at a temperature of from about 100 to about 150° F. to remove solubilized pigment, soluble iron and residual alkali and hydrogen peroxide.

After the rinsing step, the fibers are carried through tank 40 containing the strip bath, comprising an aqueous solution of an iron removal agent. The strip bath may be maintained at a temperature in the range of from about 125 to about 150° F., at a pH in the range of about 3.5 to about 4.5. Where the iron removal bath contains sodium formaldehyde sulfoxylate, a concentration of from about .2 to about 4.0 on the weight of the bath has been found to provide very satisfactory results. The time employed for thorough removal of any residual iron in the fibers may be in the range of from about 10 to about 40 minutes.

Other iron removal agents may be employed in the continuous process of the invention including, for example, oxalic acid.

Following the stripping step, the fibers are thoroughly rinsed while passing beneath spray heads 42. The final rinsing must be thorough to remove residual chemicals which may affect future processing of the fibers if the chemicals are allowed to remain on the fibers. Following the thorough rinsing, the bleached animal fibers are dried while passing through dryer means 44.

From the foregoing description of an example of the continuous animal fiber bleaching process of the invention, it will be seen that the conditions generally required for a continuous process for bleaching pigmented keratinous animal fibers while retaining good mechanical properties are:

(1) A complete mordanting which may be accomplished with a relatively high concentration of ferrous sulfate heptahydrate maintained at a low pH.
(2) A relatively alkaline peroxide bleach in which the peroxide concentration is maintained substantially constant.
(3) A stripping step to insure complete removal of residual iron from the fibers.

Example 1

The following solutions were prepared:

<table>
<thead>
<tr>
<th>Bath A</th>
<th>Bath B</th>
</tr>
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<tbody>
<tr>
<td>0.05% Triton X 100 in water at 150° F.</td>
<td>2.27% sulfuric acid and 3.1% ferrous sulfate heptahydrate in water at 150° F., pH 1.7</td>
</tr>
</tbody>
</table>

Bath C—1% tetrasodium pyrophosphate, 2.5% sodium tetraborate and 1.25% hydrogen peroxide in water at 115° F., pH 8.3.

Bath D—0.3% sodium formaldehyde sulfoxylate in water adjusted to pH 3.5 with sulfuric acid at 140° F.

Specimens of Black/Brown Awassi carpet wool were arranged on a polypropylene netting (¼ inch square openings) in thin layers, covered with an identical netting to hold the fibers in a fixed position and conveyed through the baths in the following manner:

At any instant the amount of fiber in any bath was such to produce a 24:1 bath/fiber ratio. The fiber-netting assembly was passed through Bath A to wet the fiber, squeezed through rollers at 60 lbs. pressure, then passed slowly through Bath B with an up-and-down motion for a period of 60 minutes during which time the pH was maintained at 1.7, the ferrous sulfate heptahydrate concentration was maintained at 3% and the temperature was maintained at 150° F. After 60 minutes of immersion in Bath B, the assembly passed through squeeze rollers at 60 lbs. pressure. The expressed liquor was returned to Bath B while the assembly proceeded through a forced spray of water at 80° F. for 2 minutes, followed by squeezing through rollers at 60 lbs. pressure, and thence into Bath C which it passed through for 30 minutes. During the 30 minutes the hydrogen peroxide concentration was maintained at 1.25% and the pH maintained between 8.0 and 8.5 with additions of tetrasodium pyrophosphate and borax in the ratio of 1.25. The temperature was controlled at 115° F.

From Bath C the assembly passed through squeeze rolls at 60 lbs. pressure, the expressed liquor being returned to Bath C, through a force spray of water at 125°-150° F., through squeeze rolls at 60 lbs. pressure into Bath D through which it passed in 20 minutes with the temperature maintained at 140° F., pH 3.5 and sodium formaldehyde sulfoxylate concentration at 0.3%.

After 20 minutes the assembly was squeezed at 60 lbs. pressure, force sprayed with water at 150° F., squeezed at 60 lbs, pressure and air dried.

The treated fiber was cream color and uniformly bleached at the end of the processing train. The finished fibers had an ultimate elongation of 30% as compared with 29% for the untreated and a breaking strength of 1.25 grams per denier as compared with 1.27 grams per denier for the untreated fibers.

Example 2

The procedure of Example 1 was repeated except that Black/Brown Aleppo carpet wool was used. The wool was bleached to a creamy white and retained its desirable mechanical properties.

Example 3

The procedure of Example 1 was repeated except that Medium Grey Kandahar carpet wool was used. The wool was bleached to a clear white and retained good mechanical properties.

Example 4

The procedure of Example 1 was repeated with Black/Brown Awassi carpet wool, except the wool was passed through Bath B in 30 minutes with the bath held at 170° F. A bleached product was obtained similar to that produced by the procedure of Example 1.

Example 5

The procedure of Example 1 was repeated with Black/Brown Awassi carpet wool, except that Bath C contained 2.50% hydrogen peroxide, 1.5 tetrasodium pyrophosphate and 3.75% sodium tetraborate. The fiber was passed through the bath at 115° F. for 15 minutes. The fiber produced was a creamy white and had good mechanical properties.
Example 6

Without the aid of the polypropylene netting support a white wool fabric containing a small percentage of highly pigmented fibers was treated as in Example 5 except that Bath B contained 1.0% sulfuric acid and 2.0% ferrous sulfate heptahydrate at pH 2.0. The pigmented fibers were lightened in color to blend with the white wool fibers of the fabric and the hand and tensile properties of the bleached fabric remained unchanged.

Example 7

A specimen of the Black/Brown Awassi carpet wool of Example 1 was treated following the procedure of Example 1 except the ferrous sulfate of Bath B was replaced with an equivalent amount of ferrous acetate and the sodium formaldehyde sulfoxylate of Bath D was replaced with an equivalent amount of oxalic acid.

The bleached color and the breaking strength of the treated fibers were found to be equivalent to the color and breaking strength of the fibers treated in accordance with Example 1.

From the foregoing description of this invention, it will be seen that the continuous process for bleaching pigmented keratinous fibrous materials hereinbefore described may be used with many types of keratinous materials. It will also be recognized that various modifications may be made in form of the apparatus employed in carrying out the process of the invention; for example, the wetting and rinsing steps of the process may be carried out in tanks similar to tanks 24 and 32 and the squeezing or extracting steps may be carried out between pairs of cooperating rolls or by passing the belt or web over a conventional suction box or the like.

It will also be visualized by those skilled in the art that the economic value of dark pigmented keratinous materials such as dark alpaca or karakul is much less than that of material of lighter shades since the lighter shades can find substantially wider use and may be dyed to a greater variety of commercially desirable shades. Further, the amount of such dark materials produced in the world is very large and the darker shades are much less expensive than the lighter ones. For these reasons, the process of the present invention which enables a greater utilization of natural dark pigmented material for the production of light stocks of good quality is of substantial economic advantage to the industry.

We claim:

1. A continuous process for bleaching pigmented keratinous fibers which comprises forming the fibrous material to be bleached into a web-like belt, passing the fibrous belt through a mordant solution consisting essentially of a 1–20% by weight aqueous ferrous salt solution maintained at a temperature of from about 100 to 200°F and at a pH of from about 1 to about 3 for a period of 10 to 150 minutes, passing the mordant solution treated fibrous belt through a bleaching solution consisting essentially of a 0.5–5.0% by weight aqueous alkaline hydrogen peroxide solution maintained at a temperature of from about 100 to about 125°F and at a pH in the range of about 7 to about 9 for a period of from about 10 to 90 minutes, and thereafter passing said fibrous belt through an iron removal solution consisting essentially of a 0.2–4.0% by weight aqueous iron removal reagent solution, said reagent being selected from the group consisting of sodium formaldelyde sulfoxylate and oxalic acid, maintained at a temperature of from about 130 to about 170°F, and rinsing and drying the fibrous belt.

2. A process according to claim 1 wherein the ferrous salt is selected from the group consisting of ferrous sulfate heptahydrate, ferrous acetate and ferrous ammonium sulfate.

3. A continuous process for bleaching pigmented keratinous fibers which comprises forming the fibrous material to be bleached into a web-like belt, passing the fibrous belt through a mordant solution consisting essentially of a 1–20% by weight aqueous ferrous sulfate heptahydrate solution maintained at a temperature of from about 100 to 200°F, and at a pH of from about 1 to about 3 for a period of 10 to 150 minutes, passing the mordant solution treated fibrous belt through a bleaching solution consisting essentially of a 0.5–5.0% by weight aqueous alkaline hydrogen peroxide solution maintained at a temperature of from about 100 to about 125°F, and at a pH in the range of about 7 to about 9 for a period of from about 10 to 90 minutes, and thereafter passing the fibrous belt through an iron removal solution consisting essentially of 0.2–4.0% by weight of an aqueous sodium formaldehyde sulfoxylate solution maintained at a temperature of from about 125 to about 150°F, and at a pH in the range of from about 3.5 to about 4.5 for a period of from about 10 to about 40 minutes, and rinsing and drying the fibrous belt.

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LEON D. ROSDOL, Primary Examiner.
MAYER WEINBLATT, Examiner.