THERMAL SHRINKAGE RESISTANCE OF LEATHER

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Notice: The portion of the term of this patent subsequent to July 16, 1991, has been disclaimed.

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References Cited
UNITED STATES PATENTS
3,775,162 11/1973 Miller 117/142 X
FOREIGN PATENTS OR APPLICATIONS
180,758 6/1922 Great Britain 117/142

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ABSTRACT
Leather having durable resistance to thermal shrinkage, i.e. shrinkage on exposure to high temperature as occasioned by flash fires, is produced by pretreating the leather by immersion in an aqueous solution of tetrapotassium pyrophosphate and thereafter impregnating the pretreated leather with a salt of magnesium. Preferably an ionizable inorganic salt of magnesium, especially the sulfate, is used to impregnate the pretreated leather.

6 Claims, No Drawings
THERMAL SHRINKAGE RESISTANCE OF LEATHER

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 250,208 filed May 4, 1972, now U.S. Pat. No. 3,824,124.

FIELD OF THE INVENTION

The invention herein described was made in the course of, or under, a contract or subcontract thereunder, (or grant) with the Department of the Air Force, United States Government.

This invention relates to methods for increasing the resistance of leather to shrinkage on exposure to heat. More particularly, the invention concerns the treatment, by impregnation, of leather with salts of certain metals whereby the leather has improved resistance to shrinkage on exposure to heat as by flash fires.

BACKGROUND OF THE INVENTION

It is known that gloves, boots, jackets and other articles of apparel are often fabricated of leather and that such articles, especially gloves, tend to shrink excessively when exposed to high temperatures for relatively short periods, as in the case where they are exposed to a flash fire. The shrinkage may be so severe that the use of the hands or other portions of the body protected by glove or other article is seriously impaired. The result is that serious injuries have occurred when the wearer has been exposed to a flash fire.

Many processes for the fireproofing and shrink proofing of leather have been suggested by those skilled in the leather art. For example, U.S. Pat. No. 3,419,344 discloses to a two step treatment of conventional mineral tanned leather whereby the leather is initially treated, "retained," with a phosphonium halide and then the retained leather is subjected to a fatliquoring step with a phosphate ester. The initial retaining is said to impart resistance of the leather to "afterglow" while the second step aids in rendering the leather resistant to combustion. This procedure decreases high temperature shrinkage only slightly and does not significantly extend the use of the leather where high temperature dimensional stability is important. Other methods have not been wholly successful for the reasons that they impart undesirable effects on the hand of the leather or the degree of improvement in resistance to high temperature thermal shrinkage is too small to substantially affect the leather's utility.

Further, it is known (see Doklady Akad. Nauk. S.S.S.R 82:4058 (1952)) that conventional tanning processes do not significantly affect the high temperature (dry collagen) dimensional stability, although the hydrothermal dimensional stability of the tanned leather may be improved.

In application Ser. No. 172,269 of George T. Miller, filed Aug. 16, 1971, now U.S. Pat. No. 3,775,162, and assigned to Hooker Chemical Corporation, it was disclosed that leather could be rendered resistant to shrinkage on exposure to high temperature as occasioned by flash fires by impregnating the leather with a salt of a metal selected from the transition metals of the 4th and 5th periods of the Periodic Table and magnesium. The improvement in thermal shrink resistance however is not fast to washing, it having been ascertained that the metal salts can be leached out of the leather resulting in a reduction or gradual loss of the thermal shrink resistant character.

OBJECTS OF THE INVENTION

It is, therefore, a principal object of this invention to provide leather having a resistance to shrinkage on exposure to high temperatures which is fast to washing. Another object is to devise a process for treating leather to improve its resistance to shrinkage on exposure to high temperatures, which improvement is fast to washing. Other objects will be obvious from the following description of the present invention.

BRIEF SUMMARY OF THE INVENTION

These and other objects of the invention are accomplished by contacting leather preferably after it has been tanned and fat liquored, and which may or may not be finished, with an aqueous solution of tetrapotassium pyrophosphate, and then treating the resulting leather with a solution of a salt of magnesium. Preferably this salt is an ionizable inorganic salt of magnesium and especially magnesium sulfate.

The treatment baths are preferably at ambient temperature, that is, from about 20° to about 30°C in each instance, although higher or lower temperatures, e.g., from about 5° to about 85°C can be used.

Sufficient of the salt solutions should be used so as to impregnate the leather with an amount of salt which is at least 0.5 percent by weight of the leather. Conveniently, sufficient treatment solution is used to provide a solution to dry skin ratio of from about 10 to 1 to about 20 to 1 in parts by weight.

The treated leather thereafter may be dried in a moderate oven or by exposure to air.

In the description which follows glove leather will be used in the specific embodiments. It should be distinctly understood however, that the principles of the invention apply with equal force to other leathers, that is to say that the broad principles of the invention encompass the shrinkproofing of leathers irrespective of their intended use or classification. Thus, the invention applies to the treatment of skins and hides of all animals including cattle, horses, sheep, goats, pigs and the like. It is preferred to treat the leather in the tanned state, especially chrome tanned leather, and preferably after fat liquoring. Although the leather can be treated before or after finishing, it is preferred to treat it before finishing. The leather can be treated before or after fabrication into a useful article. Thus, for example, fabricated gloves can be treated by the present process, or the skin can be treated and then fabricated into a glove or other useful article.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, leather, preferably that which has been subjected to the customary operations which follow the tanning step, is immersed in a dilute aqueous solution of tetrapotassium pyrophosphate for a sufficient time to permit thorough impregnation of the leather with the alkaline salt solution, and thereafter the wet leather is immersed in a solution of a salt of a metal of the above defined group. The leather is worked in the solution until it is thoroughly impregnated with the treating solution. The leather after removal from the solution may be rinsed and dried.
The time of immersion of this solution is not critical in general periods of from 5 minutes to 2 hours or longer being adequate. The concentration of the salt solution for this pretreatment step is not critical. Concentrations of from about 5 to about 20 percent are effective, although more concentrated solutions may be used if desired. The temperature used in this pretreatment step is not critical, temperatures of from about 20° to about 85° centigrade, although it is preferred to pretreat the leather in solutions at temperatures of about 20° to 30° centigrade.

Preferably the leather to be treated, is a chrome tanned leather and especially that which has been fat liquored. At this stage in manufacture, the leather is referred to as "in the crust." The leather may also be treated after subsequent finishing steps such as drying, lacquering, etc.

Following the pretreatment with the tetrapotassium pyrophosphate solution the leather is treated with a water soluble magnesium salt. This metal salt is preferably an aqueous solution, although organic solvent solutions which do not dissolve the fat liquor can be used. Solvents such as alcohol, acetone, methylethyl ketone, and the like can be used. The solvent should be one, or a mixture thereof, in which the metal salt is soluble to the extent of at least one percent by weight.

Sufficient of the solution of the metal salt should be used so that the impregnated leather after treatment will contain at least 0.5 percent of the metal salt by weight. By "metal salt" in this instance is meant the metal compound formed by reaction of the potassium pyrophosphate with the metal salt.

The temperature of the treatment bath may be varied over a wide range, e.g., from about 5° centigrade to about 85° centigrade. Preferably the treatment bath is at a temperature within the range of about 20° to about 30° C. At lower temperatures, the rate of impregnation may be impractically slow whereas at high temperatures, e.g., approaching the boiling temperature of the bath, the leather may undergo shrinkage before the skinkproofing character of the invention has been imparted to the leather.

Conveniently, the treatment solution can be an aqueous solution of the metal salt at a concentration within the range of about five percent by weight and about forty percent by weight. Saturated solutions can be used although such are not necessary and hence are not to be preferred.

The magnesium salts found effective in this invention can contain a wide variety of anions. Suitable anions may be inorganic or organic and include the chlorides, bromides, sulfates, phosphates, carbonates, nitrates, oxyhalides, formates, acetates, propionates, oxalates, carbamates, tartrates, stearetes, oleates, palmitates and the like, as well as mixtures and hydrates thereof. Further, the metal salt can be complexed with complexing agents such as ammonia, quinoline, pyridine, and various amines and the like. Magnesium, in a most preferred embodiment, is used in the form of its sulfate and/or various hydrates.

It is believed that the metal salt reacts with the potassium pyrophosphate in the leather matrix precipitating an insoluble salt which is resistant to leaching. The reaction which is believed to occur may be expressed by the following equation:

\[2\text{MgSO}_4 + \text{K}_2\text{PO}_4 \rightarrow \text{Mg}_3\text{P}_2\text{O}_7 + 2\text{K}_2\text{SO}_4\]

The treatment vessels used for both the pretreatment and impregnation steps can be any vessel in which the leather can be placed in intimate contact with the solution. Open or closed vats preferably provided with means to gently agitate the leather during the treatments should be used. Rotating vessels, e.g., tanning drums, are convenient for these treatments. The treated leather can be washed with cold to warm water or solvent after impregnation and before drying, if desired.

The time of the impregnation step can be varied considerably. The period of treatment in this step should be adequate to permit reasonably thorough penetration of the metal salt solution. As will be evident to those skilled in this art, the porosity of leathers vary over a wide range depending upon the type and pretreatment thereof. Under normal conditions, a chrome tanned cow hide leather can be impregnated at ambient temperature, e.g. 20° to 30° centigrade, in a period of from about 10 minutes to one hour. Longer periods of time can be used, but such are usually without sufficient additional beneficial effects as to warrant the additional effort.

Potassium pyrophosphate has been found to be a more efficient pretreatment agent than the corresponding sodium pyrophosphate. The latter because of its lesser solubility, while effective in reducing the shrinkage of leather in accordance with the process, is substantially less effective than tetrapotassium pyrophosphate, as shown in the examples below.

The following examples will illustrate the present invention. Unless otherwise indicated, all parts and percentages are by weight and temperatures are given in degrees centigrade.

**EXAMPLE 1**
A full chrome tanned caberetta leather skin weighing 436.1 parts was immersed in 6460 parts of water containing 1140 parts of tetrapotassium pyrophosphate at 25°. The leather was gently agitated in the solution for 30 minutes. The skin was removed from the pretreatment bath, permitted to drain for a few minutes and then immersed in a solution containing 3112 parts of magnesium sulfate (\(\text{MgSO}_4 \cdot 7\text{H}_2\text{O}\)) dissolved in 4488 parts of water at 25°, the pH of the solution having been adjusted to 6.0. The leather was gently agitation in the solution for 60 minutes, following which it was washed in running cold water for about 60 minutes. The solution to dry skin ratio, in each of the treatment steps was 17.4/1. Thereafter the washed leather was hung in air and dried by standing for about 16 hours. The dried leather was stretched to make it more supple and then six 4 x 4 inch squares were cut from one side for test purposes.

To test the leather of thermal shrinkage the square sample was suspended by hooks under light tension at the center of a 3 inch diameter hole in a test table. A shutter beneath the sample was opened to allow a 3.0 second exposure to the flame of a Fisher burner having a 1.5 inch diameter top. The flame temperature was about 1,300°. Untreated leather, by this test shrinks about 60 percent. The average area shrinkage of the treated leather of this Example was only 14.4 percent.
EXAMPLE II

To illustrate the surprising superiority of potassium pyrophosphate over sodium pyrophosphate, the following experiment was carried out.

Cabrerra leather samples measuring 1½ x 1½ inches were soaked for 20 minutes at 25° in a 20 percent aqueous solution of tetrasodium pyrophosphate and then for 20 minutes in a 20 percent aqueous solution of magnesium sulfate at 50° and a pH of 6. The impregnated samples were rinsed for 60 minutes in cold water and then air dried. The average area shrinkage of the flamed samples substantially as described in Example I above was 24 percent. This experiment was repeated with the exception that the leather samples after soaking in tetrasodium pyrophosphate were immersed in a 20.6 percent solution of nickel sulfate for 50 minutes at 50° at a pH of 5.5. After being rinsed for 60 minutes in cold water and air drying, the average area shrinkage of the flamed samples was 30 percent.

EXAMPLE III

A full chrome tanned cabrerra leather skin weighing 337.5 parts was immersed in a solution of 570 parts of potassium tetraphyrophosphate dissolved in 3230 parts of water at about 25°. The leather was gently agitated in the solution for 30 minutes. The skin was removed from the pretreatment bath, permitted to drain for a few minutes and then immersed in a solution containing 1556 parts of magnesium sulfate (MgSO₄•7H₂O) dissolved in 2244 parts of water at 25 degrees, the pH of the solution having been adjusted to 6.0. The leather was gently agitated in this salt solution for 60 minutes, following which it was washed in running cold water for about 60 minutes. The solution to dry skin ratio, in each of the treatment steps was 11.25/1. The washed skin was hung in air and dried by standing for about 16 hours.

The dried treated skin was tested for thermal shrinkage as described in Example I above and the average area shrinkage of the leather was only 15.7.

What is claimed is:

1. A process for improving the thermal shrinkage resistance of leather which comprises the steps of treating the leather with an aqueous solution of tetrapotassium pyrophosphate at a temperature of from about 20° to 85° C, and thereafter, treating the resulting leather with a solution of a salt of magnesium at a temperature of from about 5° to 85° C, both of said treatments being carried out for a time sufficient to impregnate the leather with at least 0.5 percent by weight of the reaction product of said magnesium salt and said tetrapotassium pyrophosphate metal salt.

2. The process of claim 1 wherein the leather is chrome tanned leather.

3. The process of claim 1 wherein the magnesium salt is magnesium sulfate.

4. The process of claim 1 wherein the impregnation steps are carried out at a temperature between about 20° and about 30° centigrade.

5. Leather obtained by the process of claim 1.

6. Leather obtained by the process of claim 3.

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