The present invention relates to improvements in the art of tanning hides and skins, and is particularly applicable to the production of white leather.

The tanning of hides and skins and the modern manufacture of leather may be divided generally into two broad classes, namely, those which involve tanning with vegetable tannins and those which employ inorganic or mineral substances as tanning agents. Leather produced by the aid of vegetable tanning agents or tannins, while excellent for many purposes, has a brown color and is not resistant to hot water. On the other hand, mineral tanned leathers have the color which happens to be imparted to them by the particular tanning agent used, and are characterized by resistance to hot water.

Among the most widely used mineral tanning agents are various salts of chromium, which impart a shade of blue to the hides or skins. On the other hand, various salts of aluminum and of zirconium have also been used, these producing a white leather.

Among the organic tanning agents which are different from the vegetable tanning agents is formaldehyde, which, however, does not produce an entirely satisfactory leather when used as the sole tanning agent.

Recently there have been proposed as tanning agents various organic polymers or polymer-producing chemicals with which the hides or skins were impregnated for the purpose of effecting a result analogous to tanning, with the result that the skins were converted into leather. Among those which have been proposed are water-soluble salts of anhydride-vinyl type of copolymers, and also various water-soluble forms of melaminemelamine. It has now been found that a considerable improvement in the production of white leather can be obtained by the simultaneous use of both melamine and formaldehyde, these two materials being used in their free state and not in the form of a condensation product.

Accordingly, one of the objects of the invention is a process of tanning hides and skins which comprises subjecting them to the joint action of melamine and of formaldehyde in an aqueous medium.

A further object of the invention is a process of tanning hides and skins which comprises subjecting them to the joint action of free melamine and of free formaldehyde in a slightly acid reacting aqueous medium.

A further object of the invention is a process of producing leather which comprises immersing skins and hides in an aqueous solution of free formaldehyde and of free melamine for a time sufficient to effect the tanning thereof.

A further object is the production of a melamine-formaldehyde-tanned leather or leather containing the direct reaction-products of both melamine and of formaldehyde on the skin substance.

In the already mentioned proposals for the use of premade condensation products of melamine and formaldehyde, as for example the patent to William Orville Dawson No. 2,316,741, there is employed a condensation product of melamine and formaldehyde which is known as the methylolmelamine, which is produced by boiling 1 mol of melamine with about 3/4 mol of an aqueous 30% formaldehyde, having a pH of about 9.0, for about 20 minutes, followed by cooling, separating and drying the resulting crystals.

These crystals are readily dispersible in hot water. If desired, a methylolmelamine solution used directly as a tanning agent may be prepared by heating the melamine and formaldehyde to produce the condensation product, but omitting the step of separating the product from its mother liquor. In using these compositions Dawson has proposed that the condensation product be applied to skins in a solution of sodium chloride and that eventually a leather would result.

The present inventor, however, has found that the results obtained by this methylolmelamine tanning do not produce a material which has a high enough shrink test, which preferably should be of such a nature that the leather would withstand a short actual boiling with water.

Accordingly, the present discovery involves a procedure in which the melamine and formaldehyde are directly and separately added to the aqueous bath in which the skins or hides are being treated, care being taken to avoid the formation of a condensation product, but rather to allow both the melamine and the formaldehyde simultaneously to react with each other and the skin or hide substance.

In other words, in the present process all of the melamine and all of the formaldehyde is available to react with and thereby tan the skins or hides. It was found that the tanning action in the case of the use of the present invention is gradual and mild, partly because of the limited solubility of the melamine. This is a decided advantage from the standpoint of a smooth grain, as well as of a uniform tannage throughout the entire thickness of the skin or hide. Moreover, the rate of tanning can be more readily con-
trolled. Thus, if fast tanning is desired, a relatively slight increase of the temperature of the tanning liquor will effect this, primarily as a result of the thereby increased solubility of the melamine. It was found that by practicing the present invention, a full 5-minute boiling can be obtained, that is, to say the leather will not shrink upon being immersed in boiling water for 5 minutes. This result is very unusual with tanning agents which yield a white leather, and is superior even to the best white mineral tannage, for which this boiling test is a practical means of determining the tanning action.

The present process is more economical, not only because the total cost of the individual chemicals is lower than that of the premade formaldehyde condensation product, but also because the process can be operated with a higher degree of efficiency. It was found that the entire reaction could be accomplished within a hydrogen-ion concentration range lying between a pH of 5.5 and 4.2, and that there was no need to add formaldehyde to a hydrogen-ion concentration above that equivalent to pH 4. Since the hydrogen-ion concentration range is the correct one to allow of the immediate next operation, which is fat-liquoring, two usual steps in the manufacture of resin-treated leather, namely, acidification and neutralization prior to washing and fat-liquoring, can be eliminated.

It was also found that good tanning could be attained with the use of less formaldehyde than the three mols theoretically required to form trimethylolmelamine. Thus, when 1.5 mols of formaldehyde to 1 mol of melamine were used, which would theoretically yield a mixture consisting mainly of monomethylolmelamine and dimethylolmelamine, a shrink test of 194°F. was obtained. A shrink test of 190°F. is accepted as an adequate one for white leather.

It was also found that the strength of the leather is greater when the tanning is so adjusted that the shrink test falls between 190° and 200°F. than when the leather is so fully tanned as to withstand a 5-minute boiling.

One of the important features of the present invention lies in the fact that it is not necessary to use the conventional neutralizing or depickling agent so as to depickle the skins prior to the tanning, as has formerly been the practice, because, contrary to what would have been expected, it was found that even 50% or more of melamine (on the weight of the wet skins) is used in the present tanning operation, the melamine itself will act as a depickling agent and also as a buffer before there is any significant reaction between the formaldehyde and the melamine and before the tannage effect becomes manifest. Thus, with about 10% of melamine, and omitting sodium acetate, a shrink test of 202°F. was obtained with a 21-hour tanning operation.

The subjoined examples are given for the purposes of illustrating the present invention but are not to be construed as limitations thereon.

**Example I**

This involved a tanning operation employing as the raw material a 50-pound pack of pickled wet weight of pickled skins consisting of 89 bacon rinds, 2 Spanish goat skins, and 2 Paprah sheep skins. The skins were depickled and tanned in a liquor containing 3% of salt, 3% of sodium acetate, 10% of melamine and 20% of Formalin, these per centages being based on the drained, pickled weight of the skins, the leather being taken as 100%. The ratio of liquid to skins was 100%; that is to say, the amount of water was equal in weight to that of the wet skins. All of the chemicals or more of melamine (on the weight of the wet skins) was used in the present tanning operation, the melamine itself will act as a depickling agent and also as a buffer before there is any significant reaction between the formaldehyde and the melamine and before the tannage effect becomes manifest. Thus, with about 10% of melamine, and omitting sodium acetate, a shrink test of 203°F. was obtained with a 21-hour tanning operation.

The subjoined examples are given for the purpuses of illustrating the present invention but are not to be construed as limitations thereon.

**Example II**

This involved the use of a 50-pound pack wet weight of pickled skins consisting of 89 bacon rinds, 2 Spanish goat skins, and 2 Paprah sheep skins. The skins were depickled and tanned in a liquor containing 3% of salt, 3% of sodium acetate, 10% of melamine and 20% of Formalin, these percentages being based on the drained, pickled weight of the skins, the leather being taken as 100%. The ratio of liquid to skins was 100%; that is to say, the amount of water was equal in weight to that of the wet skins. All of the chemicals or more of melamine (on the weight of the wet skins) was used in the present tanning operation, the melamine itself will act as a depickling agent and also as a buffer before there is any significant reaction between the formaldehyde and the melamine and before the tannage effect becomes manifest. Thus, with about 10% of melamine, and omitting sodium acetate, a shrink test of 203°F. was obtained with a 21-hour tanning operation.

The subjoined examples are given for the purposes of illustrating the present invention but are not to be construed as limitations thereon.
Example III

12 pounds (wet weight) of pickled Nigerian goat skins were depickled and tanned in a churn with the ratio of 100% of liquor and with respectively 3% of salt, 5% of sodium acetate, 10% of melamine, and 20% of Formalin (these percentages being on the basis of the wet weight of the skins). All the chemicals and skins were entered in the water separately, but at the same time before running the churn. The melamine was added dry, as in the other examples. After 3 hours running the temperature of the liquor was 72° F. and the pH thereof was 5.2.

The shrink test of the leather was 160° F. After setting overnight and running for 1 hour in the morning, the pH of the liquor dropped to 4.7 and the shrink temperature of the skins averaged 191° F. The tanning action in this case was not quite as complete as when the work had been performed in the drum, undoubtedly because of the lesser amount of mechanical action. The skins were washed, fat-liquored and pigmented. The leather, however, was excellent, just as it had been in connection with Examples I and II.

Some of these skins were then put through the regular process for producing a black suede, using the ordinary developed dye method. The nap was satisfactory, and the color was an excellent deep black, superior, if anything, to that of regular tanned leather, probably because the melamine formaldehyde tannage acts as a mordant for the dye on the protein.

Example IV

25 pounds (wet weight) of pickled pig skin fronts were depickled and treated in 200% water, 3% salt, 5% sodium acetate, 8% melamine and 16% formaldehyde (36-37% actual HCHO), this being done in a drum. The liquor was lengthened (that is to say, a larger amount of water relative to skins was used) because of the lower skin weight. It will be noticed that in this case there was only 1½% solution of salt instead of 3%. After 15 minutes' operation the skins were examined and they were found to be all right even though a lower amount of salt had been used. There was present, however, 5% of sodium acetate. After 6 hours of drumming, the pH of the liquor was 4.9, and the temperature thereof was 80° F. The shrink test on the skins at that time was 185° F. The drum was then allowed to set overnight and run again for 3 hours in the morning, at the end of which time the liquor had a pH of 4.8 and the shrink test of the skins averaged 192° F. These skins were washed, fat-liquored, and pigmented as usual. The finished leather was good.

Example V

100 pounds wet weight of pickled degreased horse shanks were depickled and tanned in 100% of water, entered at 105° F., there also being used 5% of salt, 3% of sodium acetate, 6% of melamine, and 12% of formaldehyde, all entered in the drum together with the melamine, added dry, as usual. After running for 1 hour the pH of the liquor was 4.8 and the temperature 90° F. It was noticed that the liquor was quite clear, indicating that most of the melamine had by this time become dissolved. The drum was then shut down for 1 hour at the end of which the pH was measured and found to be 4.5, while the shrink temperature of the skins averaged 180° F., which is considered very good for such a short time. The drum was then started up again, and run for 1 hour, at the end of which time the pH had dropped to 4.4, the temperature of the liquor now being 95° F., while the shrink temperature of the leather produced averaged 203° F. The drum was then allowed to remain inoperative overnight, but run for one-half hour in the morning. A test then made showed that the pH of the liquor was now 4.3 and the temperature was 83° F. Six samples had an average shrink temperature of 203° F. which was the same as they had been on the previous day after 3 hours of tanning.

This is a good illustration of the marked effect of a slight and practical increase in the temperature of the liquor on the rate of tanning. Since the liquor became clear, as mentioned above, in a much shorter time than in previous examples, this is taken as evidence that a faster tanning was caused primarily by the increased solubility of the melamine at the higher temperature. It will thus be apparent that by controlling the temperature a simple means for controlling the operation is available.

Example VI

50 pounds (wet weight) of degreased pickled horse shanks were depickled by running for one-half hour in 100% of water, 5% salt and 5% sodium acetate. The pH of the liquor was then 4.7. There were then added separately 10% of dry melamine and 10% of Formalin as in the other examples, and the drum was then run for 1 hour and then allowed to set overnight. At the end of that time the pH of the liquor was 5.3, its temperature 80° F. and the shrink temperature of the leather produced 160° F. The drum was then run one-half hour and allowed to set for 3 hours, at the end of which time the shrink temperature of the leather had risen to 170° F. After setting overnight the pH of the liquor was 5.2 and the average shrink temperature of the leather 194° F. The shanks were washed for 15 minutes at 80° F., at the end of which time another shrink test thereon was made and it was found that it was still 194° F. The skins were then horses, shaved, washed, fat-liquored, and pigmented, again horses, and dried by pasting. The shrink temperature was then 198° F. It will be noted that in this example the ratio is 1 mol of melamine to 1½ mols of formaldehyde both on 100% basis. Theoretically this should yield a mixture consisting mainly of monomethyl- and dimethylmelamine and not the trimethylmelamine theoretically predominating in accordance with the previous examples. Nevertheless the tanning was found to be entirely adequate for a high quality white leather.

The present tanning system may also be employed for combination tanning as when using inorganic metal salts or it may be used as a retan. Examples of these procedures are as follows:

Example VII

Melamine to the amount of 1% by the weight of wet skins, that is to say 10 pounds thereof, was added to a 1000-pound pack of bacon rinds during tanning thereof with a combination of basic zirconium sulphate and formaldehyde, after the pH of the liquor was brought to about 4.5. The resulting leather was definitely whiter throughout the factory operations and produced a better base for finishing in spite of the fact...
that only the regular amounts of clay and titanium dioxide were used. The shrink test was also a few degrees higher than normal.

**Example VIII**

A 50-pound (wet weight) pack of chromium tannin hide split was neutralized to a pH of about 4.5, washed, and then retanned with 3% of melamine and 6% of formaldehyde in a 100% liquor for 3 hours of intermediate drumming at 130°F. The resulting leather was processed for black suede and had a better nap, color, and mellowness than the regular leather so made but without this type of retanning.

**Example IX**

A 100-gram piece of Bombay goat skin was de-pickled and tanned overnight with 20% of formaldehyde. The pH was 4.5 to 5 and the shrink test 182°F. The skin, however, due to the absence of the melamine, had the typical empty feel of the regular formaldehyde tannage. 10 grams of solid melamine were then added to the same liquor which was still tanning the same piece of skin, and the tannage continued over another night. By that time the shrink test had risen to 212°F and the skin was full and solid just like the formaldehyde tannage attained when both the chemicals were used simultaneously. This is an excellent example of the effect of the melamine in formaldehyde tannage and is indicative of the fact that both of these reagents, that is to say, the formaldehyde and the melamine, both react with the hide substance as well as with each other to produce the results herein described and claimed.

**Example X**

A 100-gram piece of lightweight kip was de-pickled and tanned in 100% liquor with 5% of salt, 10% of melamine, and 20% of formaldehyde in the absence of any neutralizing agent other than the melamine itself. After standing overnight the pH of the liquor was 4.9 and the shrink test of the skin was 202°F. This indicates that under suitable conditions, melamine itself is adequate as the sole de-pickling agent, and that the tanning reaction is sufficiently slow to avoid local action or polymerization externally of the leather.

From the above experiments it will be evident that in many instances it will not be necessary to use the conventional neutralizing or de-pickling agent on the pickled skins, provided that at least 5% of melamine (on the weight of the skins) is employed, since the melamine itself will act as a de-pickling and buffering agent before there is any significant reaction with the formaldehyde or any tanning takes place.

Thus when using 10% of melamine and omitting the sodium acetate a shrink test of 202°F was obtained in about 21 hours. With 8% of melamine, and again without sodium acetate, the pH of the liquor after 1 hour was 5.3, and after 4½ hours 4.3. At the end of 1 hour the center of the skin was still quite acid, that is below 4, as would be expected, and even at the end of 4½ hours there is still a narrow streak in the center which had a pH below 4. However, after standing overnight the pH of the liquor was 3.18 and the shrink test was 196°F, which is normal for this amount of melamine with the use of a neutralizing agent.

It will be appreciated that the omission of the neutralizing agent simplifies the procedure and makes it less expensive.

The present method of tanning can also be combined with other known tanning methods and while of particular advantage in the manufacture of white and light colored leathers, is also suitable for making colored leathers. No particular theory is advanced to explain the effect of the tanning, but it is evident that both the melamine and the formaldehyde work independently of each other on the hide substance and probably form substances which then react with each other and possibly also with the remaining hide substance to produce the leather. The effects produced are startlingly better than when precondensed methylolmelamine is used. This may be perhaps occasioned by the fact that methylolmelamine, being already a condensation product, has a high molecular weight and therefore its solution does not have the penetrating power of the separate melamine and formaldehyde.

The conditions under which the reagents are used are very much milder than would suggest the formation of condensation products directly between them. Inasmuch as it was not known that free melamine would be effective in conjunction with formaldehyde, much of the present above described excellent tanning action, the reactions and effects obtained in accordance with the present invention are quite unexpected and of a surprising nature, and can unhesitatingly be qualified as being in the nature of a quite unpredictable and unexpected result.

There is considerable latitude in the temperature at which the operations may be accomplished and also the relative weights of liquor of the various types of skins employed. These proportions are, however, well within the skill of those familiar with the tanning art.

Accordingly applicant claims as his invention:

1. Process of tanning which comprises submerging a tannable animal skin for at least three hours in a dilute aqueous solution containing at least about 5% by weight (on the basis of the wet skin) of melamine in suspension together with an amount of dissolved formaldehyde equivalent to at least 1.5 mols of said melamine, the melamine progressively passing into solution as the solution becomes depleted of melamine as the result of the tanning action.

2. Process of tanning which comprises subjecting animal skins to the action of an aqueous solution containing at least about 5% of free melamine on the basis of the wet weight of the skins, as well as more than sufficient free formaldehyde potentially to react with said melamine, both the melamine and the formaldehyde remaining substantially unreacted at the beginning of the tanning process, the latter being carried out for a period of at least three hours, whereby a leather having a shrink test of at least about 190° F. is obtained.

3. The process of claim 2 in which the solution has a hydrogen ion concentration of between about pH 4.0 and pH 5.5 and the time is from about three hours to about 21 hours.

4. Process of tanning which comprises subjecting pickled animal skins to the action of an aqueous solution containing at least about 5% on the basis of the wet weight of the skins of free melamine and more than enough free formaldehyde potentially to react with said melamine, both the formaldehyde and the melamine remaining substantially unreacted at the beginning of the tanning process, most of the free melamine being undissolved and subject to gradual solution as the ensuing tanning action consumes the dissolved melamine, the process being continued for a period of at least three hours, whereby leather
having a shrink test of at least 190°F. is obtained.

5. Process of tanning which comprises subjecting wet pickled animal skins to the action of about an equal weight of water (as based on the weight of said wet skins) containing from about 6% to about 20% by weight of therein dissolved Formalin (of 36-37% actual formaldehyde content) and from about 1% to about 12% by weight of free melamine, at least some of which remains undissolved during the early stages of the ensuing tanning action, the resulting solution having a hydrogen-ion concentration of about pH 4.0 to pH 5.5, the action being continued for a period of from about three hours to about 21 hours, whereby a light-colored leather having a shrink test of at least about 190°F. is obtained.

6. Process of retanning chromium-tanned leather without previous de-tanning which comprises subjecting it for about three hours to an aqueous solution containing about 3% of free melamine and about 6% of free formaldehyde at about 130°F. and at a hydrogen-ion concentration of about pH 4.5, the melamine and formaldehyde being substantially unreacted at the beginning of the retanning process.

WALLACE WINDUS.

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