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TANNING PROTEINACEOUS FIBERS WITH A MIXTURE OF AN ALDEHYDE AND A POLYHYDRIC PHENOL IN A MOLECULAR RATIO OF AT LEAST 2 TO 1

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The present invention relates to the conversion of proteinaceous filaments, particularly those derived primarily from keratin, such, for example, as the hair and wool on animal skins, although the invention is not limited thereto, but may be applied to the hair, wool or other proteinaceous filaments when not attached to a supporting structure.

The present invention is directed primarily to processes which are in effect a species of tannage but depart from accepted principles of tanning by employing both polyhydric phenolic substances and aldehydes simultaneously in a strongly acid-reacting aqueous medium.

In applicant's copending application, Serial No. 669,101, filed May 11, 1946, of which the present application is a continuation-in-part, it already has been broadly proposed to tan tannable protein materials, such as hides, skins, pelts, keratinaceous products, as well as protein artifacts, such as casein filaments, films and the like.

The present invention is to be considered as a further development of the fundamental principles disclosed in said prior application and the extension of the principles thereof to the treatment, particularly, of fur skins and other animal skins, whereby not only the skin portion thereof is tanned, but the keratinous filaments are likewise converted into a condition in which, for example, it will be possible mechanically to straighten such fibers at a fairly high temperature, whereafter the fiber so straightened will not readily revert to the woolly or kinky condition in which they existed upon the normal pelt.

The changes produced in the fibers are far-reaching, and are made evident even by changes in their visual appearance. One of the immediately noticeable effects is the development of color, usually of a reddish, brownish, and sometimes bluish shade, which, upon subsequent dyeing, will advantageously modify the final color obtainable.

A further advantage is that the fibers are rendered more resistant to heat, so that considerably higher temperatures may be employed when finishing them, as by ironing.

The fibers exhibit a marked increase in resistance to the action of alkalies, which is of value in scouring and dyeing.

The fibers are also rendered tougher, i. e. they are more wear-resistant and have a greater tensile strength.

In the case of furs, or imitations thereof, where the fibers (hair or wool) are still attached to the skin, the products show a closer nap, and

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hence give the appearance of a greater hair or wool count. This serves better to cover any blemishes such as ribs, cracks, etc., and permits upgrading of the stock, which is an important commercial advantage. The products also exhibit a greater luster and, in general, a much improved appearance.

The invention is also of great utility in the treatment of protein fabrics as, for example, wool either in the woven condition or in the form of felt and the like. The present process involves the use of certain definite polyhydric phenols in connection with certain aldehydes capable of reacting therewith to form condensation products, but the invention is entirely distinguished from such processes in which already formed condensation products or polymerized condensation products are used as impregnating media. Moreover, the invention is to be sharply distinguished from that type of treatment of proteinaceous material in which even an initial condensation product, such as for instance saligenin (a condensation product of phenol and formaldehyde), is employed, in that the conditions under which the reacting materials are allowed to act upon the raw materials of the present invention are entirely different from the processes of making condensation products.

Thus, in making condensation products, the reacting substances are allowed to react in strong solutions, or even directly upon each other, whereas in the present case, very dilute solutions are employed, the conditions being such that ordinarily condensation products could hardly be expected to form. However, under the conditions hereinafter to be described, the dilute solutions of the potentially reacting materials appear first completely to penetrate the skin, hide and fiber before any significant amount of tannage is effected. The results, therefore, are entirely different from those obtainable with partial reaction products produced elsewhere and then introduced into the hide, skin or fiber.

Thus it is well known that a polyhydric phenol, for example, resorcinol and pyrogallol, will react with an aldehyde, such as formaldehyde, benzaldehyde or furfural, when allowed to act upon each other in fairly concentrated aqueous solutions under which conditions water-insoluble condensation products soon form. The first reaction products, while initially water-soluble, soon become water-insoluble and separate out. Once these reacting materials have reacted with each other to the extent of having become substantially water-insoluble, they thereby lose their

property of acting upon either hides, skins, casein, hair, wool or other proteinaceous material. The most that can be done with them is to dissolve them in an appropriate solvent other than water or perhaps in water by the aid of an alkali to form salts thereof, and then merely to impregnate the proteinaceous material, and then perhaps to complete the further polymerization of the thus introduced condensation products. This, however, leads to quite undesirable results as it will tend to make the proteinaceous material, for example, keratinous filaments, harsh, brittle and stiff. Moreover, the action is purely one of impregnation, and not of tanning.

In contradistinction to the formation of even preliminary condensation products, the present invention proceeds along the lines laid down in the aforementioned copending prior application in that the reacting materials are employed in dilute aqueous solution, the latter having been adjusted to a high degree of acidity, that is to say, a low pH. Under these conditions there apparently takes place a different kind of reaction.

The reactions which will hereinafter be described are made visually evident by a physical change in the appearance of the material undergoing the treatment. This appearance is particularly noticeable when treating, for example, the pelts of various animals having a naturally white hair or wool, such for instance as those of sheep and goats. The color, both of the hide portion as well as of the pelage and the skins, is altered to a deep reddish orange which cannot be removed by washing or bleaching. Moreover, the pelage can subsequently be mechanically straightened as by the use of well known so-called "electrifying" machines, which are provided with means for simultaneously combing and ironing the filaments of the pelage, such as the wool or hair, thereby stretching them and rendering them straight. Moreover, the treatment as hereinafter more fully described will have imparted to the keratinous filaments a very high resistance to heat so that they may be treated during the electrifying operation at far higher temperatures than have hitherto been believed possible, in that prior art teachings have decried the use of high temperatures as it had been believed that at such high temperatures the keratin would be destroyed or burned up or at least singed. By permitting the use of higher temperature, better fiber is obtained by means of the present invention.

Broadly speaking, the detailed treatments which will hereafter be given as examples comprise the treatment of freshly pickled animal skins, preferably while still in the pickling bath, with both a polyhydric phenol, as well as with an aldehyde potentially reactive therewith, such as formaldehyde, furfural and benzaldehyde. It may be mentioned at this point that the aldehydes may be used in admixture with each other to obtain certain special effects.

After treatment, the keratinous filaments(hair or wool) are endowed with an entirely different character from that which is present, for example, in prior art products, such as imitation beaver and the like made from sheep skins in which the keratinous filaments had been treated solely with an aldehyde such as formaldehyde. Thus the fibers exhibit far greater heat-resistance, increased tensile strength, gerater wear-resistance and are of a more silky feel and appearance.

The effect can be still further enhanced by subsequently ironing the hair portions at an elevated temperature, say about 200° F. if wet and about 350°–450° F. if dry, thereby imparting luster to the hair and straightening it out if initially kinky.

Another advantage which resides in the practice of the present invention lies in the fact that the skins are so well tanned in a strongly acid medium due to the unorthodox nature of the process that they are completely resistant to any further acid treatment.

If desired, however, the treated fur or wool may, after tanning, washing and drying, be further treated with formaldehyde and then ironed hot until dry, to produce the characteristic beaver or nutria effect.

If formaldehyde treatment and ironing is to be resorted to, the formaldehyde may be applied by spraying instead of by careful hand swabbing so that no particular care need be taken to avoid getting the strong formaldehyde onto the grain portions of the pelt in order to avoid cracky grain.

Furthermore, in the practice of the present invention, the leather produced by this method of tanning will be characterized by a very desirable mellowness, drape, strength and an adequate stretch, all of which properties are highly desirable in the skins which are to be worked up by furriers into garments. One of the effects of this treatment appears to be a distinct lengthening of the fibers. This is particularly striking in the cases where furfural is the aldehyde which has been used, the fibers in that case having a long, soft and silky appearance.

Among the polyhydric phenols which may be employed are dihydroxy and trihydroxy derivatives of benzene. Particularly useful are resorcinol and pyrogallol.

On the other hand, the aldehydes may be those selected from the group consisting of formaldehyde, polymers of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde and furfural.

It has also been found that the hydrogen-ion concentration of the aqueous medium in which the tanning is effected is a critical one, and that the medium should be strongly acid, for instance, within the range of about pH 0.3 to about pH 3.0.

It has also been ascertained that it is necessary to use more aldehyde than polyhydric phenol, in fact optimum results are obtained when using three or more mols of the aldehyde to each mol of the polyhydric phenol, but even up to six mols of the aldehyde may be used to advantage. There should be at least two mols of aldehyde to each mol of the polyhydric phenol. This is in distinct contrast with the ratios employed in the production of synthetic resins from polyhydric phenols and aldehydes where an excess of the said phenols is usually employed.

The amout of the polyhydric phenol relative to the tannable material treated is about one percent to about ten percent based upon the wet weight of the material, for instance, of well drained pickled skins. The most useful range lies between about 5 percent and about 7.5 percent, depending somewhat upon the type of material treated and the properties desired in the finished product.

It should be pointed out that not all polyhydric phenols are suitable. In fact, careful research has developed the quite unexpected fact that of the dihydric phenols only the metahydroxy derivative of benzene known as resorcinol is effective while on the other hand the ortho derivative, such as catechol, and the para deriva-

tive, such as hydroquinone, yield entirely negative results. Of the trihydroxy derivatives of benzene, only pyrogallol is effective, while gallic acid is entirely ineffective. Further, the monohydric phenols, such as phenol itself, and alpha and beta naphthol, are also ineffective. The aldehydes are preferably selected from the group consisting of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde and furfural. Ketones, however, have been found to be quite ineffective.

Purely for exemplary purposes a number of actual examples will now be given showing the treatment of various types of animal skins as well as wool fabrics. Among these examples are the treatment of lamb or sheep skins in the form known as shearlings, goat skins, muskrat skins, fox skins, and wool fabrics. These examples are not to be considered as being of limiting nature, but merely further to explain the invention and to render its commercial application comprehensible to tanners who, while they might not be skilled in the art of organic chemistry, are nevertheless fully familiar with the art of tanning. Therefore certain preliminary treatments of the skins, such as the fleshing and pickling, will not be described, as these operations are very well known. In accordance with standard practice in tanneries, the weight of the material to be treated, such as skins, pelts and the like, is the wet weight of the material after it has been horsed up and well drained. In many cases the weight may be taken as that of the material after it has been washed and the excess water drained therefrom. The processes are sufficiently flexible so that slight variations produced by this method of weighing will compensate because of the dilution at which the process is carried out. It appears likely that there is an adsorption of the materials from the water of the aqueous medium onto the material being treated, followed by its reaction therewith.

Example 1.—Resorcinol and formaldehyde on shearlings.—This is an example of simultaneous tanning and/or impregnation of different protein fibers, consisting of wool keratin and skin collagen. The raw stock was sheepskins with the wool on. These were put through the customary pretreatment. Fiber treatment and tanning took place in the regular pickle liquor.

The pack consisted of 40 sheepskins weighing 230 pounds. This weight was obtained after fleshing, following scouring. It is not a pickle weight, but is approximately the same. The skins were not removed from the pickle before tanning. The liquor ratio was approximately 10 to 1, that is 10 parts of water to 1 part of skin. The pack was processed in a reel. Weights and percents are based on the 230 pound scoured, fleshed weight.

In the morning 23 pounds (10%) of resorcinol and 46 pounds (20%) of commercial formalin containing 36% by weight of actual formaldehyde were added to the pack in the regular pickle liquor, containing sulfuric acid and salt, and having a pH of 2.0. The paddle was run for about 10 minutes. In the afternoon 2 pounds of concentrated sulfuric acid were added followed by a ten minute paddling. After equilibrium had been reached, the pH of the liquor was 1.5. The pack was not agitated until the next day.

The following morning the pH of the liquor was still 1.5, and the liquor was turbid from the formation of a moderate amount of a white precipitate. The wool and skins still had their unchanged color, but were definitely firmer and their shrink test was 180° F., both of which properties show that tanning had taken place.

The pH was lowered to 1.0 by the addition of 15 pounds of concentrated sulfuric acid, with running. In the afternoon the pH was lowered to 0.5 to 0.6 by the addition of 20 pounds of sulfuric acid in two feeds with brief running, whereafter the skins were paddled for about a minute each hour during the night.

The next morning the pH of the liquor was 0.6, and the shrink test of the skin was 184° F. The skins were fuller than on the previous day. The wool and skins now had a uniform red color, while the liquor contained a red precipitate.

34.5 pounds (15%) of sodium bicarbonate were then added in two separate feeds with brief running. The pH of the liquor was then 1.0. The liquor was drained and the reel refilled with water. A total of 7.5 pounds (3.25%) of sodium bicarbonate were added in four feeds. The liquor pH was then 4.7. The pack was set overnight without further running.

The next morning the liquor pH was 3.0, and the shrink test of the skin was 205° F. The wool and skins were a light brown color. The pH was raised to 4.8 by the addition of 1.2 pounds (0.5%) of sodium bicarbonate.

The liquor was drained, the reel refilled and the skins washed about fifteen minutes. The skins were then hauled, horsed over the weekend, swabbed on the flesh side with a mixture of raw and sulfated neat's-foot oil in water, and hung to dry.

It should be noted that the color stays in the wool and skin and is not removed by washing or subsequent mechanical treatments. It is not due to any precipitate from the liquor. The particular color is characteristic of each aldehyde or phenol used and is good evidence not only of the progress of the reaction but also for chemical combination and firm fixation of the reagents by the skin or pelt.

Example 2.—Resorcinol and furfural on sheepskins.—This example was run by the same procedure as in Example 1, except that furfural was used as the aldehyde in place of formaldehyde. It was run at the same time as Example 1, in an adjacent reel on a pack of the same number of skins and having the same weight, processed by the same preliminary procedure.

The only difference in the procedure was the use of smaller quantities of the polyhydric phenol and aldehyde. These consisted of 11.5 pounds (5%) of resorcinol and 23 pounds (10%) of furfural, the percents being based on the 230 pounds, scoured, fleshed weight of sheepskins with the wool on.

On the first morning, after 24 hours in the tanning liquor, the shrink test of the skin was 168° F. and the skins were firmer than originally, showing that tanning was taking place. The liquor had a light green color and the wool was beginning to show some of this same color. This had been at a pH of 1.5 over the first night.

On the second morning the pH of the liquor was 0.6, as in the case of Example 1. The liquor was a dark green color. The wool and skins were also a dark green color. The shrink test of the skin was 182° F.

After neutralizing and leaving over another night, the shrink test of the skin was 192° F. The wool and skins were dark brown in color.

The color remained the same after draining and washing.

Example 3.—Resorcinol and benzaldehyde on sheepskins.—The test was run on one skin in a small reel. The sheepskin had the regular pretreatment through the pickle and a drained pickle weight was obtained, this being 5 pounds. Percents of chemicals are based on this weight.

The liquor ratio was approximately 12 to 1. The liquor was made up with salt. To the liquor and skin were added 6 ounces (7.5%) of resorcinol and 1 pound (20%) of benzaldehyde. The liquor was acidified with sulfuric acid to a pH of 1.5 and left overnight.

The next morning the pH was 1.5 and the shrink test of the skin 162° F. The pH was lowered to 0.5 with concentrated sulfuric acid and the skin left over another night.

The next morning the pH was 0.5 and the shrink test 172° F. The pH was raised to 4.5 with sodium acetate and sodium bicarbonate and the skin was left over another night.

The next morning the shrink test was 190° F. and the skin felt tanned. The wool and skin had an orange brown color.

The liquor was drained off and the skin washed thoroughly with fresh water. It was hauled, horsed for partial drying, oiled off on flesh and hung to dry. The color of the wool and skin remain the same, indicating that the polymer is firmly fixed in the fibers.

Example 4.—Pyrogallol and formaldehyde on sheepskins.—Two pickled shearlings weighing 10 pounds were treated in a liquor consisting of 15 gallons of water, 11 pounds of salt, 0.5 pound of pyrogallol and 1 pound of formaldehyde. The pH of the liquor when the skins were set was 3.2. This was lowered to 1.3 with sulfuric acid and the skins set overnight.

The next morning the pH was 1.2 and the shrink test 143° F. The pH was lowered to 0.5 and the skins set over another night.

The next morning the pH was 0.8 and the shrink test 160° F. The skins were neutralized to a liquor pH of 4.0 with sodium acetate and ammonium bicarbonate and set three hours. The shrink test was then 176° F.

The skins were washed, hauled and horsed the next day. The shrink test was then 184° F. The wool and skins were tanned and had a black color.

Example 5.—Resorcinol and furfural on goat skins.—Three white haired goat skins were processed with a 170 pound pack of sheepskins (shearlings) in accordance with the regular pretreatment through the pickle. The pack was then tanned with resorcinol and furfural using the same quantities as given in Example 2 and essentially the same procedure as given in detail in Example 1.

The skins were well tanned and had a shrink test of 180° F. after fat liquoring. The hair and skins had the characteristic color of this treatment, namely dark brown.

Example 6.—Resorcinol and formaldehyde on muskrat.—Three muskrat skins having a dry weight of 1 pound were tanned from the pickled condition in a liquor consisting of 0.5 gallon of water, 0.5 pound of salt (sodium chloride), 45 grams of resorcinol and 90 grams of formaldehyde (formalin), in a churn. On the first day the pH was lowered gradually to 0.5 and the skins allowed to remain in the churn without agitation overnight.

The next morning the pH of the liquor was

0.5 and the shrink test of the skins was 190° F. The skins were neutralized with sodium acetate and sodium bicarbonate to a liquor pH of 4.5 at which time the shrink test was 212° F. They were washed, oiled and dried.

The skins were well tanned and mellow. The fur was not obviously changed in color, unlike the results on white haired skins.

Example 7.—Resorcinol and formaldehyde on fox.—A gray fox skin with a dry weight of 2 pounds was tanned from the pickle in a liquor consisting of 0.5 gallon of water, 0.5 pound of salt, 34 grams of resorcinol and 84 grams of formaldehyde, in a churn. The initial pH was 1.8. This was gradualy lowered to 0.5 with continuous running of the churn. The skin was allowed to rest in the liquor overnight without moving.

The next morning the pH of the liquor was 1.2 and the shrink test 170° F. This was again lowered to a pH of 0.5 and run for several hours. The skin was neutralized to a pH of about 4.0, washed, horsed overnight and swabbed with oil and dried.

The skin was well tanned with a shrink test, after oiling, of 186° F. The fur was not noticeably changed in color.

Example 8.—Resorcinol and (1) formaldehyde and (2) furfural on wool fabric.—A white wool blanket was cut into four equal pieces, each with an area of approximately 9.0 square feet. One piece was placed in the tanning liquor with the pack of shearlings covered by Example 1. A second piece was placed in the pack covered by Example 2. A third was run in the conventional chrome alum tanning liquor with a third pack of shearlings. The fourth piece was held as a control. The processed pieces were removed at the end of the procedure with the shearlings. They were, of course, dried without any oiling.

Each piece possessed the characteristic color of the particular tannage, the same as the shearlings. The piece from the furfural treatment was dark brown. The one from the formaldehyde was light brown. The piece from the chrome alum was still white and only slightly changed from the control, although it was less creamy. There was no loss of measurement in any case. The feel was possibly slightly harsher and the experimental pieces felt firmer and fuller than the control.

Example 9.—Resorcinol, formaldehyde and furfural on shearlings.—Two sheepskins with the wool on were tanned in a small reel. The drained, pickled weight was 15 pounds. The pickle liquor from a regular reel, containing salt and acid, was used. They were tanned with 10 ounces (4%) of resorcinol, 7 ounces (3%) of furfural and 10 ounces (4%) of formaldehyde added together to the reel. The pH was 2.0 when set. This was lowered to a pH of 1.5 in the afternoon by the addition of 100 cc. of 85% phosphoric acid.

The next morning the pH was 1.6. The pH was lowered to 1.2 by the addition of a total of 370 cc. of phosphoric acid in two feeds. It was then lowered to a pH of 0.5 by the addition of a total of 750 cc. of concentrated sulfuric acid in several feeds, with the usual short running at the time of each feed.

The next morning the pH was 0.5 and the shrink temperature 160° F. and 176° F. on pieces from the two skins. The pack was neutralized to a pH of 4.5–5.0 with sodium acetate and ammonia. 12 ounces (5%) of formaldehyde was then added and the pack set over another night.

The next morning the pH was 4.2 and the shrink test was a uniform 207° F. The skins were washed, horsed, oiled and dried.

The results were those to be expected, that is, intermediate between formaldehyde alone and furfural alone, as the aldehydes used. The flesh had a lighter brown color than when furfural alone was used. The wool on the finished skin resembled the color of the formaldehyde tannage more than the color of the furfural tannage.

Example 10.—Crotonaldehyde and resorcinol.— One sheep shearling having a drained pickled weight of four pounds was tanned with resorcinol and crotonaldehyde in a churn. The liquor was made up as follows: 15 gallons of water at room temperature, 10 pounds of sodium chloride, 4.75 ounces of resorcinol and 9.5 ounces of crotonaldehyde. After running 10 minutes and resting 2 hours the pH of the liquor was 2.9. This was lowered with sulfuric acid to 1.5 and left over night.

The next morning the pH was 1.5 and the shrink test was 148° F. The color had changed to a light yellow on both the skin and wool. Sulfuric acid was added to a pH of 1.0 with brief running. In the afternoon the pH was lowered to 0.5 and the skin "set" over night.

The next morning the pH was 0.5 and the shrink test 168° F. The color of the skin and wool was a deeper yellow. The liquor and skin were neutralized to a pH of 3.6 with sodium bicarbonate. The shrink test was then 182° F. The color changed to light brown.

Example 11.—Acetaldehyde and resorcinol.— A 100 gram piece of shearling from the skin used in Example 10 was tanned in a quart jar on a shaking machine with acetaldehyde and resorcinol. The liquor was made up as follows: water at room temperature, 1 pint, salt 2 ounces, resorcinol 10 grams and acetaldehyde 12 grams. The steps in the acidification and the amount of time given, were the same as in the above Example No. 10.

On the first morning at a pH of 1.5 the shrink test was 190° F. and the color was about the same. On the second morning at a pH of 0.5 the shrink test was 186° F. The color was a light yellow. Upon neutralizing with sodium acetate to a pH of 3.8 the shrink test was 196° F.

The instrumentalities employed in carrying out the present invention are all well known and fully familiar to those conversant with the tanning and fur-treating arts and hence require neither illustration nor detailed description.

In all of the above examples, a tanned skin with the hair or wool still thereon (except in the case of the wool blanket) was obtained. The hair or wool on the tanned and dried specimens was further converted, in the case of sheep and goat skins, into a fur-like product by the application of formaldehyde, followed by ironing at a high temperature, using a machine provided with a heated rapidly rotating ironing-roller provided with a transverse groove. Such apparatus is well known and widely used in the fur industry for the conversion of kinky haired furs into straight-haired fur imitations. The effects obtainable closely resemble beaver, nutria, and genuine seal. The products obtained were far superior in appearance, feel, apparent hair count and nap than products made without the use of the tannages

hereinabove disclosed. Moreover, the color and permanency were markedly superior, as compared with imitation furs based on so-called "combination dyed" skins.

Therefore, saving for himself the application of the knowledge of those skilled in the art to which this invention pertains and the reasonable use of known equivalents where they may be indicated, applicant claims:

1. Process of tanning untanned but tannable proteinaceous filaments which comprises immersing them at about room temperature in a very dilute aqueous solution of a polyhydroxy phenol from the group consisting of resorcinol and pyrogallol and an aldehyde from the group consisting of formaldehyde, polymers of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, and furfural, the polyhydroxy phenol in the solution not exceeding about 1% by weight and the aldehyde being present in the proportion of at least two moles for each mole of the polyhydroxy phenol, and the hydrogen-ion concentration of the solution being adjusted to and maintained within the range of about from pH 0.3 to pH 3.0.

2. The process as defined in claim 1, in which the molar ratio of the aldehyde to the polyhydroxy phenol exceeds 2 but is not more than 6.

3. The process as defined in claim 1 in which the aldehyde is formaldehyde and the polyhydroxy phenol is resorcinol.

4. The process as defined in claim 1 in which the aldehyde is benzaldehyde and the polyhydroxy phenol is resorcinol.

5. The process as defined in claim 1 in which the aldehyde is furfural and the polyhydroxy phenol is resorcinol.

6. The process as defined in claim 1 in which the proteinaceous filaments are hairs still attached to the skin on which they grew.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,232,620	Stiasny	July 10, 1917
1,395,733	Romer	Nov. 1, 1921
1,912,593	Pollack	June 6, 1933
2,103,138	Becker et al.	Dec. 21, 1937
2,211,645	Calva	Aug. 13, 1940
2,234,138	Kritchevsky	Mar. 4, 1941
2,240,388	Calva	Apr. 29, 1941
2,390,073	Calva	Dec. 4, 1945

FOREIGN PATENTS

Number	Country	Date
4,605	Great Britain	1907
346,197	Germany	Dec. 27, 1921
508,781	Great Britain	June 26, 1939
508,840	Great Britain	June 26, 1939
282,313	Germany	Nov. 19, 1913

OTHER REFERENCES

"Modern Plastics," Aug. 1947, pp. 145, 147, 238, 240, 260–254.

"The Chemistry of Leather Manufacture," by J. A. Wilson, 2d. ed., vol. II, pg. 765, pub. by "The Chemical Catalog Company, Inc.," N. Y. C., 1929.