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TANNING OF LEATHER

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3 Claims. (Cl. 260—124)

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This invention relates in general to the tanning of leather and more particularly to new synthetic tanning agents and to an improved process of tanning leather.

At the present time leather is, in the majority of cases, tanned by either a vegetable tanning process or a chrome tanning process depending upon the type of leather to be produced.

The vegetable tanning process is used principally in the production of heavy leathers such as sole leather. As the rate of diffusion of vegetable tannin into skin is very slow and consequently a long time is required to completely tan heavy leathers with the vegetable tannins, many attempts have been made to speed up this process. One method that has been proposed involves the use of concentrated tanning liquors. However, if hide is put directly into concentrated tanning liquors, the rate of combination of the tannin with the skin protein is very likely to be abnormally great compared to the rate of diffusion of the tannin into the interior of the skin; consequently the outer layers of the hide are drawn or contracted to a greater extent than the inner layers whereby distortion of the outer layers with respect to the inner layers is effected, thus greatly detracting from the appearance and value of the leather.

In order to overcome such difficulties, tanners have found it necessary to adopt a stepwise process when tanning with vegetable tannins. By such a process they treat the skins first with a tan liquor which has already been used to tan a large number of skins and in which, consequently, the ratio of nontannin to tannin is very great. At regular intervals the hides are moved into stronger and fresher tanning liquors until they are completely tanned. In some cases, such as in the tanning of sole leather, months are required to complete the process.

Naturally, such a long drawn out procedure has many disadvantages. Not only must the tanner have a large amount of capital tied up in skins which are in the process of being tanned, but he is also forced to purchase the skins many months before he will be able to sell them as finished leather. Thus with the varying market conditions, a great amount of uncertainty and speculation enters into the tanner's business. Also, in order to maintain a certain output of leather, he must maintain many times the amount of equipment which he would have to have to produce the same amount of leather if the tanning could be accomplished by some shorter and

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simpler method. Because of these and other inherent disadvantages of the aforementioned procedure, the manufacturer's net profit is much less and the cost of the finished leather to the consumer much greater than if a more efficient process were available for producing first-class vegetable tanned leather.

The volume of the collagen fibers in the skin increases as more tannin combines therewith; and in the manufacture of a leather where great solidity is required, such as, for example, in sole leather, it is not sufficient merely to convert all of the collagen into leather; but in order to get the maximum fullness and solidity, the hides after all of the collagen has been converted to leather are treated with very concentrated tanning liquors so that the maximum amount of tannin will be fixed. Thus in such cases the process is even more cumbersome and costly than that as set out hereinabove.

Chrome tanning processes take much less time than vegetable tanning processes, and at the present time most of the world's supply of light leathers is tanned by means of chromium salts. However, in the case of heavy leathers, chrome tannage will not produce the degree of plumpness and fullness which the trade demands. In chrome tanned leathers the individual fibers are usually thin as in dried, raw skin, but in vegetable tanned leathers, the fibers are much larger and in most cases they almost completely fill the interfibrillary spaces, thus giving a very desirable full and plump leather.

In addition to the shorter time required for tanning by the chrome processes, such processes also have the advantage of producing leather possessing a much higher temperature of gelatinization than can be obtained in leather through vegetable tanning. The term "temperature of gelatinization" is used herein to connote that temperature at which the tanned leather shrinks or shrivels when subjected to elevated temperatures. The temperature of gelatinization is a relative measure of the reaction of the tanning agent upon the skin protein causing the latter to withstand or tolerate various degrees of temperature without harm. Leather properly tanned with chromium salts can usually be kept in boiling water for 5 minutes or longer without showing any signs of curling. In other words, the leather has a temperature of gelatinization of 100° C. or higher. However, in the case of vegetable tanned leathers, it is very difficult to obtain a temperature of gelatinization of much over

84° C. to 86° C., and in many cases the resulting value is below 84° C.

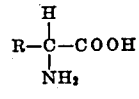
Attempts have been made to combine chrome tannage with vegetable tannage. In such cases the leather is first treated with chrome tanning liquors and then given a surface tannage with vegetable tanning liquors. In some cases and for some purposes leather which has been so treated is tolerably satisfactory, but in many cases and for many purposes it is by no means as satisfactory as straight vegetable tanned leather.

In view of the aforementioned and other various limitations and disadvantages of both chrome and vegetable tanning and combinations thereof, much work has been done in attempting to develop new and improved tanning agents and processes for using the same. One of the pioneers in this field was Stiasny, who presented to the world a new class of materials which he called "syntans." He produced what apparently were condensation products by mixing and heating phenol sulfonic acids with formaldehyde in an acid solution. He obtained water-soluble products which he claimed possessed marked tanning properties. However, the syntans produced by Stiasny and similar products produced by other investigators have had no filling or plumping properties, and when used for tanning give an undesirable thin and empty leather. Moreover, leather produced by the use of such syntans has exhibited a very poor temperature of gelatinization value usually running in the order of about 60° C. to 70° C. as compared to about 80° C. to 86° C. for vegetable tanned leather and 100° C. or over for chrome tanned leather.

To increase the temperature of gelatinization of syntan leather, various investigators have suggested adding chromium salts to the syntans. In some cases chromic salts have been added and in some cases chromate compounds, but when the chromate salts, such as sodium dichromate, are added, they are invariably reduced to the chromic state with concurrent oxidation of the syntan, thus producing quinone groups on the aromatic nuclei and converting the methylenic linkages of the condensation products to carbony groups. In all cases the chromium is apparently present as a positively charged ion, as evidenced by the fact that it may be precipitated with excess strong alkali.

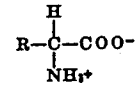
The presence of chromium in the form of a positively charged ion along with carbonyl and ketone groups apparently tends to cause a shrinkage of the surface of the leather which is of course, detrimental to the leather and depreciates the value thereof. It is not definitely known what is responsible for this; however there is a possible explanation for such a result. It is to be understood that the explanation which we advance herein is a theoretical one, but it does seem quite plausible.

As is well known, skin consists principally of protein material which in turn is made up of α-amino acids. The α-amino acids may be designated by the general formula

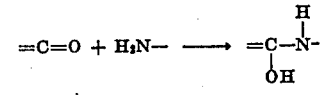


It is known that the hydrogen of the carboxyl group tends to shift over to the amino group, leaving the carboxyl group with a negative charge and giving the amino group a positive

charge, whereby the general formula would then be



As chromium is usually present in tan liquors in the form of a positively charged ion, it apparently combines with the negatively charged carboxyl group. As chromium does form a very stable compound with leather, it seems very likely that it has chemically combined with the protein in some such manner as we have set out. In vegetable tanning liquors, however, the active tanning agents, according to the Procter-Wilson theory, apparently are negatively charged, and thus combine with the positively charged amino groups of the skin protein. It is also known that vegetable tanning agents contain numerous aldehyde and ketone groups, and therefore it is also possible that a chemical combination may be effected between the amino groups of the protein and the aldehyde and carbonyl groups of the vegetable tanning agents in some manner such as, for example,



In any case it does seem apparent that the vegetable tannins combine in some manner with the amino groups of the skin, whereas the chromium in chrome tanning agents probably combines with the carboxyl groups of the skin.

In synthetic tanning agents which have been prepared as noted hereinabove by subjecting sulfonated condensation products of phenolic aromatic compounds to oxidation with hexavalent chromium, there are, as already mentioned, both quinone and carbonyl groups, which may combine with the amino groups of the hide; and positively charged chromium in the trivalent state, which apparently combines with the carboxyl groups of the hide. Since such is the case, it seems possible that this two-fold action tends to draw the different constituent groups of the skin more closely together, thus causing undesirable shriveling and shrinking of the leather.

However, whether our theory is correct or not, it is known that the aforesaid synthetic tanning agents have not functioned satisfactorily in leather tanning processes. The use of the syntan brings about the undesirable result of shrinking the leather.

Since leather having a relatively high temperature of gelatinization can be produced and such a leather is highly desirable, there is a great demand for a tanning agent which may be used to treat leather so that the finished leather will not only have the high temperature of gelatinization of chrome tanned leather, but also the excellent fullness and solidity of vegetable tanned leather without having the undesired qualities of leather tanned by either method or by any of the various hitherto known synthetic tanning agents.

There is also a great demand for a process whereby the time required for the tanning of leather by vegetable tanning processes may be materially decreased. As aforementioned, in most cases from two to three months are required to complete the usual vegetable tanning of heavy leathers, whereby the processing costs remain exceedingly high.

It is the object of this invention to obviate

the foregoing and other disadvantages inherent in the tanning of leather.

It is also the object of this invention to provide new and improved synthetic tanning agents.

A further object of the invention is to provide improved synthetic tanning agents, which will produce leather which is plump and soft and which has a desirable color and a high temperature of gelatinization.

Another object of the invention is to provide synthetic tanning agents which may be used to pretan leather, and which when so used will materially lessen the time required to thereafter thoroughly vegetable tan said leather.

An additional object of the invention is to provide an improved process of tanning leather whereby the time required is materially decreased.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has now been found that the foregoing and other objects of the invention can be accomplished by treating a sulfonated lignin compound with a compound containing hexavalent chromium, in such a manner that the chromium or the major part thereof will be reduced to trivalent chromium, but so regulating the conditions and quantities of materials that instead of chromium being present in the finished product in the form of a positively charged ion, it will be present in a negatively charged complex ion; and by using tanning agents so produced in a manner as set out hereinafter.

According to Werner's coordination theory, as set out in his book Neure Anschauungen auf dem Gebiete der Anorganischen Chemie, certain atoms tend to draw to themselves, in the form of surrounding shells and by forces other than primary valence, a number of other atoms or coordinated groups. The central atom with its coordinated groups constitutes a nucleus outside of which are located the atoms or radicals which are held to the rest of the molecule by primary valence forces. The coordination number of an element indicates the number of groups which an atom can hold in this surrounding shell. Chromium happens to be one of the metals whose atoms have this power to combine with other atoms, not only by means of their recognized primary valence forces, but also by means of these so-called auxiliary valences. The majority of metals, including chromium, have a coordination number of six.

This property of certain elements to form such complex ions containing coordinately bound atoms or groups may be illustrated by structural formulae of three different forms of chromic chloride. The α form of chromic chloride is a violet salt of the formula $CrCl_3.6H_2O$. All of its chlorine atoms are precipitated from solution by the addition of silver nitrate, and according to Werner's theory its structural formula is:

$$\left[\begin{matrix}H_2O & & H_2O\\ H_2O & Cr & H_2O\\ H_2O & & H_2O\end{matrix}\right]^{+++} 3Cl^-$$

The water molecules are thus coordinately bound to the chromium atom while all three of the chlorine atoms are combined with the chromium nucleus by means of primary valence forces, and in this state they are readily precipitatable by silver ions.

The β form of chromic chloride is a green salt of the formula $CrCl_3.5H_2O$. Only two-thirds of its chlorine is precipitated from solution by

silver nitrate, which indicates that only two of the chloride atoms are bound to the chromium nucleus by primary valence forces and that the third is now contained within the nucleus. Thus the formula would be:

$$\left[\begin{matrix}H_2O & & H_2O\\ H_2O & Cr & H_2O\\ H_2O & & Cl\end{matrix}\right]^{++} 2Cl^-$$

When the one chloride ion penetrates into the nucleus it displaces one of the water molecules; and as the chloride ion is negatively charged, it neutralizes one of the three positive charges on the nucleus. When it does this, the chloride ion ceases to be an ion any longer, but now forms part of the complex which constitutes the nucleus, and it is incapable of being precipitated by silver ion.

In the γ form of chromic chloride, two chloride ions have penetrated into the nucleus thus displacing two of the coordinately bound water molecules to give the formula $CrCl_3.4H_2O$, which may be depicted structurally as follows:

$$\left[\begin{matrix}H_2O & & H_2O\\ H_2O & Cr & Cl\\ H_2O & & Cl\end{matrix}\right]^{+} Cl^-$$

The two chloride ions have neutralized two of the three positive charges on the nucleus and thus ceased to be ions any longer and have become a part of the nucleus. The nucleus now has only one positive charge, and only one chloride ion is left capable of precipitation by silver nitrate.

By suitably varying the conditions, it is possible to replace all of the coordinately bound water molecules with chloride ions and thus obtain a nucleus having three negative charges. Thus, for example, it is possible to obtain a chromium compound such as sodium hexachlorochromiate whose structural formula would be:

$$\left[\begin{matrix}Cl & & Cl\\ Cl & Cr & Cl\\ Cl & & Cl\end{matrix}\right]^{\equiv} 3Na^+$$

Thus the chromium is now present in a negatively charged complexion, and all of the chlorine atoms are attached to the central chromium atom by nonionized links.

The chlorides of chromium have been used here merely to illustrate Werner's theory. Chloride ions are not the only ions that may so penetrate into the nucleus; a great many other atoms or radicals will also penetrate into the nucleus and become bound by nonionized links. In fact even molecules may do this as we have already seen in the case of the hydrated chromic chlorides where molecules of water are contained in the nucleus. When charged ions or radicals penetrate into the nucleus, they either increase the positive charge or decrease the negative charge, or decrease the positive charge or increase the negative charge of the nucleus depending upon whether the nucleus is originally positively or negatively charged and whether the ion or radical penetrating into the nucleus is positively or negatively charged respectively.

We have found that by treating sulfonated lignin compounds with hexavalent chromium in such a manner that the sulfonated compound will be partially oxidized, and the hexavalent chromium reduced to trivalent chromium, and negatively charged complex chromium ions formed instead of positively charged chromium ions as is usually the case, very efficient tanning agents

result which when used to tan hides will produce a very desirable leather. Furthermore, if hides are given a pretan with such tanning agents, they may then be treated immediately with concentrated tanning liquors, whereby vegetable tanned leather of very high quality is produced. By such a process vegetable tanned heavy leather may now be produced in from 10 to 12 days. Moreover, the leather resulting from this process is far superior to that produced in from 60 to 90 days by the ordinary known vegetable tanning methods. In addition to the shorter length of time required for the tanning and the leather having all the desirable qualities of the usual vegetable tanned leather, the leather also possesses many of the highly desirable qualities of chrome tanned leather, e. g. a high temperature of gelatinization.

In preparing the synthetic tanning agents of our invention, various sulfonated lignin compounds may be used; thus the lignin sulfonic acids themselves or their alkali metal salts may be treated with hexavalent chromium compounds in the production of the tanning agents of the invention. Also the lignin sulfonic acids or the salts thereof may be reacted with formaldehyde, much the same as aromatic compounds are reacted with formaldehyde for the purpose of forming condensation products, and the resulting products then treated with hexavalent chromium-containing compounds, if so desired.

Any suitable hexavalent chromium-containing compound may be used to treat the sulfonated lignin compounds, although, of course, the more convenient forms, such as sodium dichromate and potassium dichromate, are highly preferred. In order to produce the synthetic tanning agents of our invention, it is very important that the conditions under which they are prepared be carefully controlled, and that the proper proportions of materials be used.

We are aware of German Patent No. 664,086, and its disclosure dealing with the treatment of sulfite cellulose waste liquors with chromate or bichromate in such a manner that nontanning fillers in the sulfite cellulose waste liquors serve to convert the hexavalent chromium to trivalent chromium with concurrent oxidation of the nontanning fillers. In the process disclosed in this patent, the sulfite liquors are used just as they are obtained from the cellulose boiloff, rather than in a somewhat concentrated form. Such waste liquors contain only a small percentage of total solids. In regard to the actual content of total solids of such liquors, it is stated in "The Manufacture of Pulp and Paper," volume 3, 3rd edition, section 4, p. 95, that "the solids represent only 11 to 12 percent of the total liquor." Therefore, in the single example which is given in the patent, the patentees have used approximately three parts of sodium bichromate for every two parts of solids in the waste sulfite liquor. Such an amount of chromate is entirely too much to produce the products which we obtain by our invention. The patentees say that their final product is completely free of chromate ion and has exchanged its original brown color for the green of the trivalent chromium which indicates that the chromium is present as the positively charged trivalent ion. Solutions of our products are usually of a reddish brown color.

We prepared products according to the process set out in the one example given in the German patent and found that the chromium

was in fact present as the positively charged ion since when an excess of caustic alkali was added to solutions of the products, a precipitate of chromium hydroxide was obtained. When an excess of caustic alkali is added to solutions of the products produced from the solids in waste sulfite liquor according to our invention, no precipitate of chromium hydroxide is obtained.

We have found that in order to obtain the desired chromiate ions, much less dichromate must be used than is used in the aforesaid German patent. In determining the amount of dichromate to use in treating the solids obtained from waste sulfite liquors, it has been found to be more convenient to calculate the amounts on a percentage basis rather than to attempt to use a mole basis. In order to obtain the desired products, we have found it best not to use over about 20% of sodium dichromate on the basis of the total solids in the waste sulfite liquors, and we prefer to use about 12% to 14% of dichromate based on the total solids in the liquors. However, even smaller amounts of dichromate may be used, if desired.

Before treating the waste sulfite liquors with the dichromate, they are acidified with a suitable mineral acid, sulfuric acid being preferred, preferably using from 30% to 35% or more of acid on the basis of the total solids in the waste liquors, although amounts as low as 20% may be used. When carrying out the dichromate treatment it is preferred that the waste sulfite liquors contain 50% or more water. The upper limit of the amount of water in the sulfite liquors will depend of course on how concentrated it is desired to have the final product. If desired, the waste sulfite liquor solids may be obtained in the dried form and used in producing the products of our invention. In such a case it will be necessary to add water to the dried solids before treating them with the dichromate.

In neutralizing the excess sulfuric acid, care must be taken to add the alkali slowly and with stirring in order to prevent the formation of lumpy particles in the mass. It is preferred to use from a 15% to a 30% NaOH solution to neutralize the excess acid, although other bases may be used if so desired. Enough alkali is added so that a 2% aqueous solution of the end product will have a pH between about 3 and 6.

The products of our invention may be used in the tanning of leather just as other tanning agents are used. They are particularly applicable, however, to the pretanning of heavy leather, such as sole leather. Leather pretreated in this manner may then be vegetable tanned in from 10 to 12 days whereas ordinarily several months would be required to give the heavy leathers a complete vegetable tannage. To obtain an optimum penetration of the syntans into the hides, the pH of the tanning liquor should preferably be between about 4 and about 5. Also it is preferred that the concentration of the tanning liquor when the leather is tanned in drums be such that it contains at least 6% of syntan solids. The presence of neutral mineral salts, such as sodium chloride, sodium sulfate, potassium sulfate, etc. will also assist the penetration of the syntans into the hides. In the case of sodium chloride a concentration of 0.5% (based on the weight of the tanning liquor solution) has given very good results; however even smaller amounts will materially aid the penetration of the syntans. The pH of the tanning

liquors should not be much less than 3, nor much greater than 5.

Because of the availability and relative inexpensiveness of waste sulfite liquors, our products produced by treating waste sulfite liquors form the preferred embodiment of our invention. Either the waste sulfite liquors as such, or the commercially available concentrated liquors containing about 50% water may be used. Also, if desired, the dried solids of the liquors may be used in which case they are dissolved in water before being used. It is immaterial whether the lignin sulfonic acids in the liquors are present in the free acid form or as alkali metal salts, as either form may be employed in accordance with our invention.

For a fuller understanding the nature and objects of the invention, reference should be had to the following examples which are given merely to further illustrate the invention and are not to be construed in a limiting sense, all parts given being by weight.

Example I

Waste sulfite liquors containing about 50% water were acidified with sulfuric acid, and then treated with a solution of sodium dichromate (about 10% $Na_2Cr_2O_7$ on the weight of the sulfite liquor). The addition of the dichromate was made slowly while cooling. The mixture was allowed to stand overnight at room temperature, and then the mineral acid was neutralized with caustic soda and the product adjusted to a suitable pH. This product was used to tan raw kid skin. The leather produced was well filled and had a temperature of gelatinization of over 100° C.

Example II

50 parts of dried solids obtained from waste sulfite liquors were mixed with 400 parts of water and 25 parts of sulfuric acid and treated much the same as the waste sulfite liquors in Example I with 9 parts of sodium dichromate in a 50% solution. The product was neutralized with soda and adjusted to the desired pH.

10 parts by weight on the total solids basis of this product were added to 100 parts of water, and the resulting tanning liquor used to tan 100 parts of pickled kid stock by drumming at room temperature for six days. The leather was then removed, washed, fat-liquored and dried. A very good quality leather having a temperature of gelatinization of over 100° C. was obtained.

Example III

A tanning agent was prepared from dried solids obtained from waste sulfite liquors as in Example II except that 20 parts of formalin (37% formaldehyde) were added to the waste sulfite liquors and the mixture was allowed to stand over night before the treatment with dichromate.

Pickled kid skin was tanned with the resulting product as in Example II and equally good results were obtained.

Example IV

400 parts of concentrated waste sulfite liquors containing about 50% water were acidified with 60 parts of sulfuric acid and then treated with 49 parts of a 50% solution of $Na_2Cr_2O_7.2H_2O$. The dichromate was added at about room temperature and the mixture then warmed to about 60° C. for one hour after which it was neutralized with 30° Bé. sodium hydroxide. Leather tanned with this product had a firm feel, tight grain, was medium brown in color, and had a temperature of gelatinization of about 98° C.

Example V

40 lbs. of one of the synthetic tanning agents of the invention were made up to 17.5 gallons with water and adjusted to the proper pH. The resulting tanning liquor and 145 lbs. of hides were placed in a drum and run for six hours. The wheel was then stopped for two hours, and then turned on for one-half hour every two hours for twenty-four hours. (Constant running creates too much heat.) After this pretanning the hides were vegetable tanned in the usual manner. Much less time was required to completely vegetable tan the leather than in the case of hides not pre-tanned with one of the synthetic tanning agents of the invention.

Example VI

Excellent leather may be produced by the following procedure in which the leather is first pretanned with one of our synthetic tanning agents and then given a vegetable tanning. Much less time is required to complete the process than with the usual vegetable tanning methods.

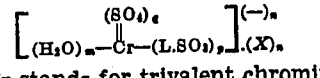
Use a slow running drum about six to eight R. P. M. Place in this drum a short liquor consisting of one pound of solution for each pound of bated stock. This solution should be so made up that it contains 10% of syntan solids based on bated stock weight. The stock should be run in this solution for 24 hours using a procedure such that the mill is run thirty minutes each two and one-half hour period, after which the solution should be drained from the mill. Next use a long vegetable tan liquor made up of a tail rocker liquor and run intermittently for 24 hours. Then run tail liquor to sewer.

The semi-tanned hides are then run until struck through in a short vegetable tan liquor having an 85° barometer strength, using for this solution a blend of tan materials similar to that used in layaways or extract wheels. This run should be intermittent as in the previous steps, after which the hides can be wrung and are then ready for the usual extracting, tempering, bleaching, loading and finishing procedure.

From the above examples and description, it can readily be seen that we have produced novel synthetic tanning agents. These syntans apparently contain chromium in the form of a negatively charged ion or chromiate. They apparently react with the skin collagen to form leather in much the same way as vegetable tanning agents. Not only do they have the desirable features of vegetable tanning agents, but also those of chrome tanning agents, and thus they are well adapted to tanning various types of leather. In addition they are excellent pretanning agents, and heavy leather which has been pretanned with them may be given a complete vegetable tannage in from ten to twelve days, whereas several months would ordinarily be required for usual vegetable tanning.

The exact chemical structure of the tanning agents or the exact mechanism by which they are formed has as yet not been definitely determined. However, we believe that negatively charged constituent groups or possibly a whole molecule of sulfonated material bearing a negative charge penetrates into the chromium nucleus, thus giving it a negative charge as a result of which the chromium will not be precipitated when excess alkali is added to the product. However, it is pos-

sible that the negative charge may not be due entirely to the sulfonated aromatic compounds or the condensation products thereof, since the reaction is carried out in the presence of a mineral acid, preferably sulfuric acid, and acidic radicals may thus penetrate into the chromium nucleus and contribute to producing the negative charge thereon. Furthermore, the charge on the nucleus may vary from a minus one to a minus three, since one or two molecules of water may be within the nucleus. Thus when the reaction is carried out in the presence of sulfuric acid and a monovalent base such as sodium hydroxide is used to neutralize the reaction mass, the syntans have the following general formula:



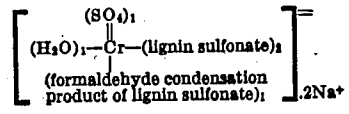
wherein Cr stands for trivalent chromium, L.SO$_3$ represents lignin sulfonate or a formaldehyde condensation product thereof, m represents a whole number of 0 through 2, n represents a whole number of 1 through 3, q stands for a whole number of 0 through 2, p represents a whole number of 1 through 6, and X represents a positive mono-valent salt-forming element or group. A covalency of 6 for the chromium atom will obviously call for the following algebraic relations between m, p, q and n:

$$m+2q+p=6$$

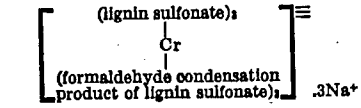
$$n=2q+p-3$$

Whenever p is more than 1, L.SO$_3$ may represent both lignin sulfonates and formaldehyde condensation products thereof. It will be noticed that in every case the complex ion has a negative charge of at least one, and that there is always at least one L.SO$_3$ group in each complex ion. From inspection of the general formula, it will be seen that there may be either one or two SO$_4$ groups in the complex ion or there may be none at all; likewise with the water molecules. Of course, if some mineral acid other than sulfuric acid, e. g. hydrochloric acid, is used in the process, the SO$_4$ groups in the general formula may be replaced by other acidic groups or ions, e. g. chloride ions, Since, however, waste sulfite liquors contain sodium sulfate, there may be sulfate groups in the complex chromiate ion even when sulfuric acid is not used in the reaction. If lignin sulfonate, part of which has been condensed with formaldehyde, is reacted according to the process of our invention with sodium dichromate in the

presence of sulfuric acid and the reaction mass neutralized with a sodium alkaline agent, such as sodium hydroxide, synthetic tanning agents may be obtained having a formula such as one of the following:



or



Of course, there are many variations of the general formulae given above which may be formed.

Large and complex molecules may thus be built up and give the syntans the filling properties which are desired. It is also known that under certain conditions two or more chromium nuclei containing coordinately bound atoms or molecules may unite and thus form still larger compounds. This is known as "olification" and it is very possible that such may be taking place in the formation of our tanning agents and may partly be the reason for their desirable filling properties.

Since certain changes in carrying out the above process and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described our invention, what we desire to secure by Letters Patent, is:

1. A process of producing novel chromiates having tanning properties which comprises reacting a water-soluble dichromate with lignin sulfonic acid, the quantity of dichromate used being not more than 20% based on the weight of the solids in the lignin sulfonic acid.

2. A process of producing novel chromiates having tanning properties which comprises reacting a water-soluble dichromate with lignin sulfonic acid, the quantity of dichromate used being within the range of 12% to 14% based on the weight of the solids in the lignin sulfonic acid.

3. The product of the process of claim 1.

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