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I hereby recommend that the thesis prepared under my supervision by ROBERT M. LOLLAR

entitled A STUDY OF THE MECHANISM OF THE DE-CHROMING OF CHROME TANNED LEATHER

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

Approved by: Jesse D. Lokey

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A Study of the Mechanism of the De-Chroming of Chrome Tanned Leather

A dissertation submitted to the

Graduate School

of the University of Cincinnati

in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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An investigation of the mechanism of de-chroming may seem a rather antithetical study in the leather industry; however, such an investigation does have many applications to leather chemistry which are very interesting. First, the fact that chrome tanned leather can be de-chromed is the basis of the utilization of scrap or damaged leather as a source of glue stock. Moreover, a study of de-chroming would be of interest since it would represent an extreme accentuation of the type of effects which will be encountered whenever any of the solutions which come into contact with the leather after tanning are too drastic. This information will be applicable to explain the effects of over-neutralization, or to explain the undesirable results encountered whenever a drastic electrolytic solution is in contact with leather in a leather finish or polish. Finally it is possible that a knowledge of the mechanism of de-tannage would give us some confirmatory evidence as to the nature of chrome tanning. Attempts to elucidate the mechanism of chrome tanning have, for the most part, followed the uptake of chrome by the hide substance; however, since the mechanism of chrome tanning is not yet completely explained, any information which a study of de-chroming might yield would be very worthwhile.

A preliminary report has previously been submitted upon this investigation (3). In it, germane de-chroming literature was discussed; moreover, the methods employed in this investigation were reported in detail, and the de-chroming

action of phosphate solutions was discussed. The general procedure followed in this present study is the same as that already reported; consequently no detailed discussion of the methods involved will be presented here, those interested being referred to the first article for more specific information as to the methods employed.

However, a brief review of the general methods employed will serve to eliminate confusion. The leather used was a commercially tanned chrome "in the blue," which was prepared for use by washing it free of excess chrome liquor, drying it at room temperatures, allowing it to age for a period of at least one month, and then grinding the leather in a Wiley mill. Ten grams of this ground leather was then placed into a Wilson-Kern extractor for treatment; five liters of the solution being tested were allowed to flow over this leather at such a rate that approximately seven hours were required to complete the test. A comparison of the analysis of the original leather and of the treated leather demonstrated the de-tanning action of the solution under consideration. The leather used in this work varied somewhat in analysis from skin to skin, but Table I presents a representative set of data.

The previous studies in de-chroming have treated the leather by a method which we shall hereafter refer to as the soaking method. In this method, the leather is placed into contact with a given volume of the solution under consideration and allowed to remain in contact during the duration of

TABLE I.

An Average Analysis of the Chrome Tanned Calf Skins in the "Blue" used in these Experiments

	Per Cent Air Dried Basis	Grams per 100 Gm. of Hide Substance
Chrome expressed as Cr_2O_3	3.77	5.05
Hide Substance (% N_2 times 5.62)	75.2	----
Total Sulfate expressed as SO_3	3.47	4.69
Neutral Sulfate expressed as SO_3	0.56	0.74
Chrome-Bound Acid Sulfate expressed as SO_3	2.32	3.09
Protein-Bound Acid Sulfate expressed as SO_3	0.59	0.86
Basicity of the Chrome Complex	61.1	
pH of the leather - 2.75		

the test. In a few of these studies, the de-chroming solutions were poured off at intervals and replaced by fresh solutions. But, none of them used the continuous extraction method by which these data were secured, and there is an essential difference between these two methods of treatment. In the continuous extraction method which we have employed in this study, the leather is treated with a continually replenished solution of the de-chroming agent, and the products of the de-chroming reactions are removed continuously from contact with the leather. In contrast, in the treatment by soaking, a limited volume of de-chroming solution which contains increasing quantities of the chrome removal products remains in contact with the leather throughout the duration of the de-chroming period. This accrual in the reaction products might well exert an inhibiting effect upon the de-chroming. Consequently, when studying de-chroming, one should be able to acquire a clearer picture of the mechanism of de-chroming where the added variable of the increase in the products of the de-chroming reaction is not a factor. The greater part of the data to be presented here was secured by the extraction method; however, certain data will demonstrate the validity of the belief that the de-chroming by soaking and by continuous extraction differs.

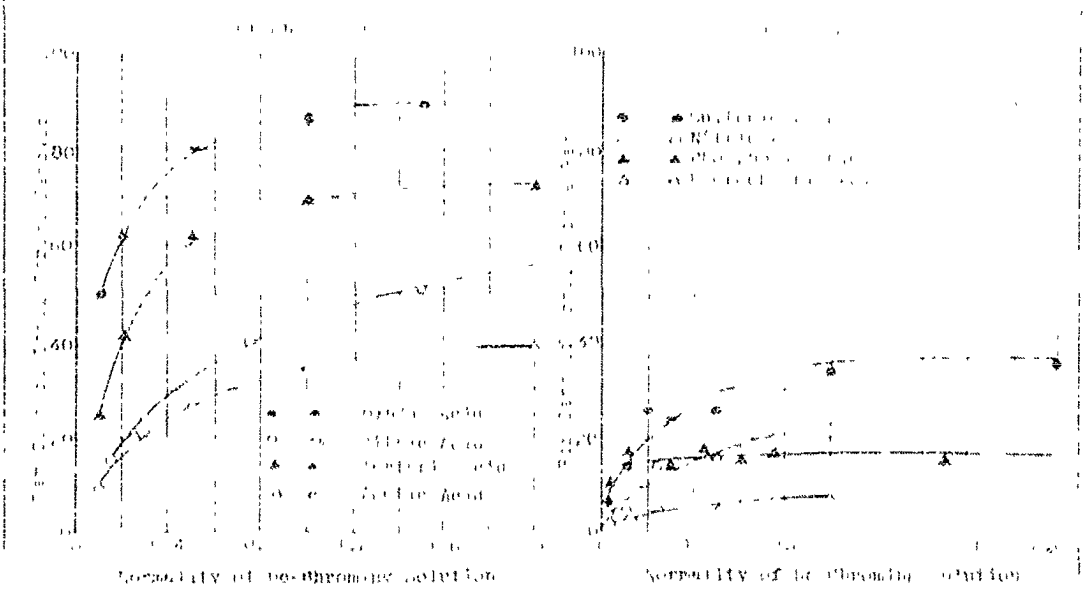
It must not be inferred that the de-chroming figures presented here present an absolute value for the amount of de-chroming under all conditions, even though the extraction

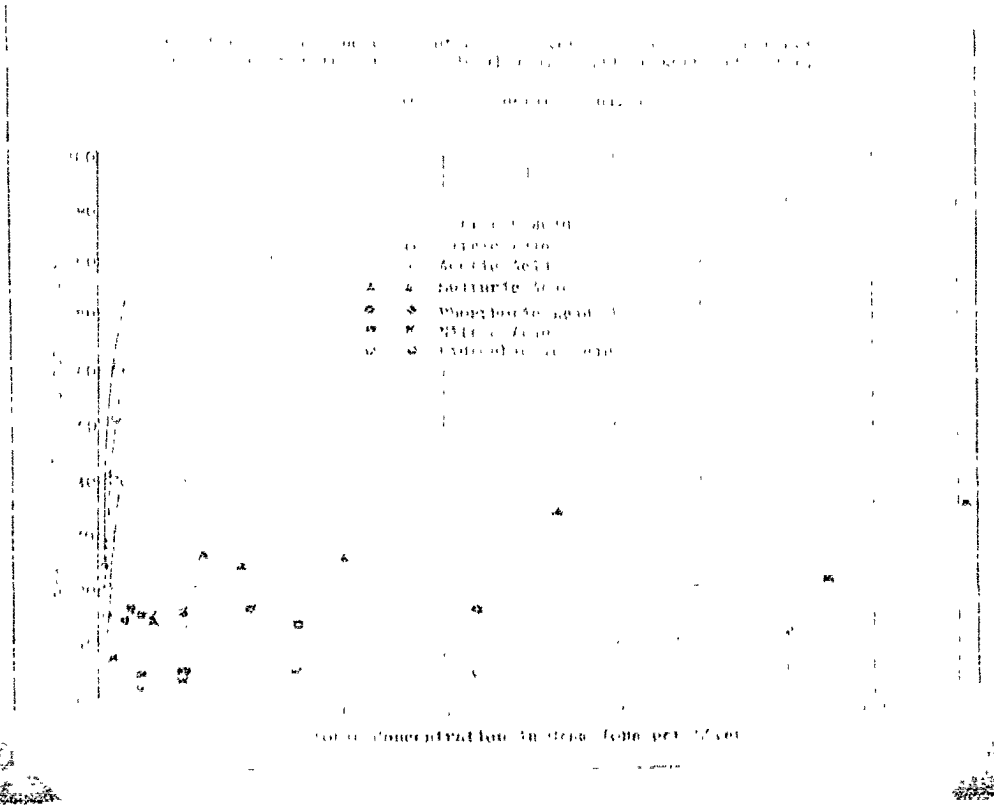
method is used. Obviously, if the leather, the rate of solution flow, the total solution volume, or any other similar germane factors were varied, de-chroming would vary. The data are comparable only to data secured as outlined as far as absolute values of the extent of de-chroming are concerned. A comparison of the effect of various materials will bear a direct relationship to the information secured under any conditions, except when the method of treatment introduces new variables as is the case in de-chroming by soaking.

The Action of Acids

The de-chroming action of acids has been a subject of considerable interest. The earliest de-chroming experiments were performed with organic acids and salts thereof. If we picture the deposition of the chrome salts in, on, and around the fibers of the leather as being due to the removal of acid from the chrome liquor by the protein of the skin or hide, so that an insoluble chrome compound is formed, it is easy to realize that added acid could easily re-dissolve the chrome compound unless some change has occurred in it after precipitation. Consequently, it is not surprising that de-chroming in acid solutions has attracted so much interest.

Proctor and Wilson (6) postulated that de-chroming occurred with hydroxy acids and their salts. It has since been found that other acids de-chrome; in general, organic





acids are vigorous de-chroming agents, but inorganic acids can also remove chromium. Simoncini (7) has compared the action of certain acids, employing the soaking method. This current study has extended this work, using the continuous extraction method so that a comparison of the results secured by the two methods can be made.

Table II and Figures I and II present the de-chroming data secured by the use of the various acids indicated. Sulfate removal was not determined in every case, but Table III gives results which show the course of sulfate removal. In Table II, it might be noted that the chrome removal data by boric acid are preceded by a + sign. This indicates that the chrome analysis after treatment was greater than it was before treatment; obviously, however, it does not represent an actual increase in chrome content of the leather. In fact, these results are merely an expression of the accuracy of the methods employed. In the first paper of this series (3) it was postulated that the possible error was five per cent in the chrome removal figures. Here, where no de-chroming has occurred, we have a much closer agreement.

From these results, we see that the organic acids are much more effective de-chroming agents than the inorganic acids. In Figure I, it would seem that acetic acid is an exception. However, when the chrome removal figures are plotted against the ionic concentration of the de-chroming solution, as in Figure II, it is evident that acetic acid

The De-Chroming Action of Acids.

Concentration Molar	Concentration Normal	Concentration Ionic	Per Cent Removal
Oxalic Acid			
0.03	0.06	0.022	----
0.05	0.10		49.8
0.10	0.20		61.6
0.25	0.50		80.0
0.50	1.0		86.5
0.75	1.5		89.4
Tartaric Acid			
0.05	0.10	0.0066	24.4
0.10	0.20	0.010	40.8
0.25	0.50	0.016	61.5
0.50	1.0	0.021	69.0
1.0	2.0	0.029	71.8
Citric Acid			
0.05	0.15	0.0063	14.8
0.10	0.30	0.009	23.7
0.25	0.75	0.013	40.0
0.50	1.5	0.018	50.7
1.0	3.0	0.027	61.5
Sulfuric Acid			
0.01	0.02	0.016	7.2
0.05	0.10	0.065	13.5
0.10	0.20	0.121	25.9
0.15	0.30	0.166	23.2
0.25	0.50	0.283	24.9
0.50	1.0	0.536	33.5
1.0	2.0	1.014	35.1
Acetic Acid			
0.10	0.10	0.0045	9.7
0.25	0.25	0.007	20.1
0.50	0.50	0.011	26.9
1.0	1.0	0.015	33.9
2.0	2.0	0.021	38.9
Nitric Acid			
0.05	0.05	0.049	4.2
0.10	0.10	0.096	4.8
0.25	0.25	0.229	13.6
0.50	0.50	0.439	15.8
1.0	1.0	0.848	21.1
Phosphoric Acid			
0.01	0.03	0.006	10.0
0.035	0.10	0.016	16.8
0.10	0.30	0.028	13.3
0.15	0.45	0.037	17.1
0.20	0.60	0.0[illegible]	14.6
0.25	0.75	0.054	16.1
0.50	1.5	0.095	14.5
1.0	3.0	0.175	15.9
Hydrochloric Acid			
0.05	0.05	0.048	2.1
0.10	0.10	0.095	3.2
0.25	0.25	0.227	4.9
0.50	0.50	0.438	3.8
1.0	1.0	0.796	6.5
Boric Acid			
0.05	0.15		+1.0
0.10	0.30	0.0[illegible]8	+0.8
0.15	0.45		+2.5
0.20	0.60		+3.8
0.25	0.75		+1.8
0.50	1.5		+3.2
0.80	2.4	$0.0_4 24$	----

(Ionic concentration in moles per liter, assuming primary ionization except for sulfuric acid, where ionization into $2H^+$ and $SO_4^=$ is assumed.)

is similar to the other organic acids in its chrome removal. Complete ionization data for most of these acids are presented by Wilson (14); however, for oxalic acid and for boric acid, we have insufficient data. Oxalic acid is a strong acid, being just below nitric, hydrochloric, and sulfuric acids in activity. Consequently, though oxalic acid seems particularly active in de-chroming from the standpoint of concentration expressed in terms of normality, when considered ionically, it is definitely more effective than the inorganic acids, but not more active than the other organic acids. Boric acid will be noted to be almost unionized, and this fact will be shown to be a factor in its lack of de-chroming.

What is the explanation of this de-chroming by acids? As a working hypothesis, let us assume that we have within the leather an insoluble two-thirds basic chrome sulfate. This would be in agreement with the chrome theory, as well as the analysis of the leather used. The tanning compound within the leather would then approximate the formula:

$$\left[(H_2O)_4 \, Cr \, (OH)_2 \right]_2 \, SO_4$$

This chrome compound has been isolated by Werner (13) as a definite, basic, crystalline, water insoluble salt. Of course, it need not be assumed that the chrome compound within the leather is as simple in composition as this formula would indicate. All of the phenomena of the aging of

leather would indicate that the chrome compound within the leather is much more complex as a result of such changes as olation, oxolation, and penetration of other groups into the complex.

The chrome compound in the leather is not totally resistant to the action of solutions which wet the leather. Thus, Wilson and Lines (15) have shown that all of the sulfate in chrome tanned leather can be removed by running water when the leather is washed for a period of two months. Yet, during the washing the total chrome oxide content was unchanged; of course, the nature of the chrome compound within the leather was changed as a result of this removal of the sulfate. Preliminary to the present study, 10 grams of leather in a Wilson-Kern extractor were treated with 100 liters of distilled water over a period of five days. This treatment removed 90 per cent of the total sulfate in the leather, without any appreciable loss in total chrome oxide content. Thus, though water exerts a sufficient solvent action upon the chrome compound within the leather to remove the sulfate of the compound, it will not remove the chromium itself. Consequently, the action of the de-chroming agents must be fundamentally different from the action of water alone.

To do this, the de-chroming agent would have to enter into the chrome complex, reverse the changes of aging, and replace such groups as the sulfate, water, or hydroxyl which

are bound to the chrome. The sulfate, as we have shown, is rather easily removed, since water is able to accomplish this. The water groups, bound to the chrome atom, are also readily removed; moreover, hydroxyl groups may be affected, although with somewhat greater difficulty. Let us consider the ways in which these changes could occur.

First, the sulfate group is removed as we note from the sulfate removal data. In this action, either the de-chroming agent or the water itself could be active. Then, with the acid de-chroming agents, the acid ion could react with the hydroxyl group:

$$H^+ + \left[\begin{matrix}HO- \\ HO-\end{matrix} Cr\ (\ H_2O\ )_4\right]^+ \longrightarrow \left[HO-\ Cr\ (\ H_2O_5)\right]^{++}$$

Thus, the insoluble two-thirds basic chrome sulfate would be converted into the soluble one-third basic chrome compound. However, if these changes were the only ones involved, the effect of all of the acids on an ionic basis should be the same. Obviously therefore there is some special effect of the negative ion of the de-chroming acid.

It has long been known that many groups, either ionic or neutral, can be co-ordinated to chromium. Furthermore, there is a distinct difference in the stability of the co-ordination union. The order of decreasing stability of this union is hydroxyl, tartrate, oxalate, acetate, formate, sulfate, nitrate, water, and chloride. Furthermore, the same series is in the order of decreasing ability of the

group to penetrate into the chrome complex nucleus; also, it is a decreasing series when considering de-olation activity. It might seem that de-olation reaction by the acids is too slow to permit it to be significant in de-chroming. But, it must be remembered that we have very dilute solutions with respect to the chrome salts, and this fact alone favors de-olation. Furthermore, the establishment of any of these stable complexes lessens the tendency of the chrome salts to olate. The net result is, therefore, a greater tendency to de-olate.

Whenever any of the very stable chrome complexes are formed such as the oxalato chrome complexes, the tendency of the chrome to co-ordinate with other groups is greatly decreased. This would therefore make any other groups co-ordinately bound to the chromium much easier to remove. Furthermore, if the chrome complex is bound to the hide substance by any co-ordinate linkage, this union would be greatly weakened whenever the very stable chrome compounds are formed.

It will be noted that this series of decreasing stability of the chrome complexes is also the order of decreasing activity of acids in de-chroming. It is easy to explain this agreement. The active de-chroming agents are active penetrators of the chrome complex; and, having penetrated, they actively promote the de-olation of the complexes, thus making them easier to affect further. Furthermore, the active penetrating agents form very stable compounds so that the insol-

uble two-thirds basic chromium sulfate can not be re-formed. The net result is the transformation of the insoluble chrome sulfate complex in the leather into other chrome complexes of entirely different properties.

One striking difference in the properties of these other chrome complexes is their solubility and stability in the presence of alkaline materials. With chrome sulfate solutions it is possible, by the removal of acid or the addition of alkali, to discern a very appreciable range where the precipitation of the insoluble two-thirds basic chrome sulfate occurs. It is upon this fact that chrome tanning with chrome sulfate solutions rests. Whenever we have other ions present, and particularly these which tend to penetrate into the nucleus of the chrome complex, this precipitation is not so pronounced. Thus, Stiasny and Szego (10) have found that chrome sulfate solutions treated with sodium oxalate will eventually lose all sensitivity to alkalis and lose the ability to tan. This does not imply that there are no oxalato compounds precipitable by the addition of alkali or valuable in tanning. In fact, in low oxalato concentrations, the chrome fixation actually increased over the amount fixed from untreated chrome liquor. But, these results of Stiasny and Szego do demonstrate that it is possible to form alkali-insensitive, non-tanning chrome oxalato salts.

Stiasny (8) has explained the action of oxalic acid

as follows:

$$\underset{\text{Insoluble}}{\left[(H_2O)_4Cr(OH)_2\right]}_2 SO_4 + 2\,H_2Ox \longrightarrow \underset{\text{Soluble}}{\left[(H_2O)_4CrOx\right]}_2 SO_4 + 4\,H_2O$$

The oxalato group would not very readily displace the hydroxyl group directly, but there are two ways in which this could occur. First, there is a mass action effect; that is, where there is an excess of the oxalate ion, they will displace even the more firmly held hydroxyl group. Also, the seeming displacement of a hydroxyl group by an oxalato group could be due to an acid ion reaction with a hydroxyl group to form water which the oxalate ion then displaces, giving the net effect of a hydroxyl group being replaced by an oxalato group. Di-oxalato salts are also known and of course these complex nuclei are negatively charged:

$$\left[(H_2O)_2 Cr (Ox)_2 \right] H$$

It is also possible to displace the last two water molecules and form:

$$\left[Cr (Ox)_3\right] H_3$$

The mono-oxalato salts may be precipitated by alkalis under the proper conditions, while the di- and the tri-oxalato salts have an infinite precipitation figure. So, there is an adequate explanation of the solubilizing effect of oxalic acid upon chrome salts in leather.

Merry (5) in studying the de-chroming action of oxalic

acid has found that only two-thirds of the chrome is readily removed by oxalic acid. He postulates that this might represent evidence to indicate two different types of chrome binding in the leather. Merry evidently soaked his samples with the oxalic acid solutions. We have also tested the de-chroming action of oxalic acid by the soaking method, and did find that only 70 per cent of the total chrome was removed by a 0.10 M. solution, even though the samples were soaked for weeks. But, this need not indicate a difference in the state of chrome combination. Where the products of the de-chroming reaction are left in contact with the leather as they are in the de-chroming by soaking, they could easily exert the inhibitory action shown in this study. Furthermore, as Cameron, McLaughlin, and Adams (1) have shown, the swelling of the hide substance by the acid as the chrome is removed exerts an inhibiting action upon further chrome removal.

It will be observed that the extraction method utilized in this study has removed 90 per cent of the total chrome without any evidence of cessation in chrome removal. It will be remembered that a seven hour treatment with 5 liters of solution was arbitrarily selected as the standard in this work. To determine whether the remainder of the chrome could be removed, this treatment was extended upon certain samples. With oxalic acid the chrome content of the leather was reduced to about 0.1 per cent Cr_2O_3 by allowing 7 liters of a 0.10 M. solution to flow over the leather in eleven hours. Excessive

swelling occurred during the last three hours which retarded the flow of the oxalic acid and the chrome removal. But, it will be observed that the chrome has been almost completely removed. So, these data would not indicate any difference in the binding of any portion of the chrome in the leather.

It is not necessary to discuss the action of all the other organic acids in as great detail since their action is essentially the same as that of oxalic acid. There are many complex compounds of chromium which are discussed by Werner (12) and by Weinland (11). Werner (13) has however made an interesting study of the action of acetic acid upon chrome salts which is very illustrative. He has established the following reaction for the solubilization of precipitated two-thirds basic chrome sulfate by acetic acid:

Insoluble

$$\left[Cr\begin{pmatrix}OH\\OH_2\end{pmatrix}_4\right]_2 SO_4 + 6\ HAc \longrightarrow \underset{\text{Moderately Soluble}}{2\left[Cr(OH_2)_6\right]Ac_3} + H_2SO_4$$

$$\left[Cr(OH_2)_6\right]Ac_3 \xrightleftharpoons{H_2O} \left[Cr\begin{pmatrix}OH\\OH_2\end{pmatrix}_4\right]Ac + 2HAc$$

The first reaction product, though appreciably soluble, could be precipitated out of solution in the presence of other salts such as sodium acetate. The hydrolytic reaction yields a complex which is much easier to precipitate. In the presence of sodium sulfate, the hydrolytic product gives a new precipitate of insoluble two-thirds basic chrome sulfate, while in the presence of mineral acids the hexaquo salt of the mineral acid is formed. These secondary reactions may well explain the

difference in chrome removal which will be demonstrated later when de-tanning by soaking and by extraction is compared. In soaking, where the de-chroming solutions are not changed, secondary reactions occur which result in the re-precipitation of the chrome within the leather. Thus, though the nature of the chrome complex upon the fibers is changed, there would be a cessation in the actual chrome removal. By the extraction method as employed in this study, the solubilized chrome does not remain in contact with the leather, so that secondary effects can not re-precipitate the chrome.

The relative inactivity of the inorganic acids is very evident when the chrome removal as a function of the ionic concentration of the treating solution is considered. Sulfuric acid will be noted to be the most active de-chroming agent of all of the inorganic acids considered. It of course exerts the action of all acids, titration of unolated hydroxyl groups of the complex, and reversal of olation. The net result of such action is the conversion of the insoluble two-thirds basic chrome sulfate into the soluble normal sulfate.

In an earlier report upon this subject (3), it was reported that the action of phosphoric acid was nearly independent of the molar concentration of the solution. This is adequately explained upon examination of the chrome removal data based upon the ionic concentration. The ionization of phosphoric acid is such that the actual ionic concentration does not change appreciably with the solution strengths used, so it is not surprising that the de-chroming

should not vary appreciably.

Nitric and hydrochloric acids do not remove chrome very rapidly. However, this is not surprising when one remembers the series for the stability of chrome complexes. These ions form less stable complexes than sulfate and penetrate very slowly. In fact, nitrate ions do not penetrate into the chrome complex. In other words, the sulfate complex is more stable than the other two types of complexes, and it is only by exerting a mass action effect or a pure acid effect that they can de-chrome. Boric acid is almost completely un-ionized, and the penetration of the borate ion is low, so that boric acid solutions do not solublize the chrome.

However, Table III shows that boric acid is displacing the total sulfate of the leather. Since in the most concentrated solution it removed two-thirds of the total sulfate, yet only one-third of the sulfate is neutral and protein-bound sulfate, it is evident that boric acid is able to remove chrome-bound sulfate and change the chrome complex even though it does not solubilize it so that it is removed from the leather. This sulfate removal is too great to be due to the water alone, so the boric acid must be responsible.

It will be noted that the organic acids, except acetic, quickly displace all of the sulfate. Thus, even in the very dilute solutions of oxalic, tartaric, and citric acids, the

TABLE III

Total Sulfate Removal from Chrome Tanned Leather by Acids

Wilson-Kern Extraction Method

Concentration of De-Chroming Solution		Per Cent of Total Sulfate Removed
Molar	Normal	
Oxalic Acid		
0.05	0.10	98.2
0.10	0.20	100.0
Tartaric Acid		
0.10	0.20	71.2
0.25	0.50	88.4
0.50	1.0	100.0
Citric Acid		
0.05	0.15	78.8
0.10	0.30	88.4
0.25	0.75	100.0
Acetic Acid		
0.10	0.10	14.3
0.25	0.25	24.2
0.50	0.50	25.9
1.0	1.0	34.6
Nitric Acid		
0.05	0.05	57.2
0.10	0.10	76.3
0.25	0.25	85.6
0.50	0.50	95.0
1.0	1.0	100.0
Hydrochloric Acid		
0.05	0.05	40.6
0.10	0.10	56.8
0.25	0.25	64.8
0.50	0.50	70.7
1.0	1.0	70.7
Boric Acid		
0.05	0.15	9.3
0.10	0.30	30.9
0.25	0.75	45.0
0.50	1.5	67.5

chrome sulfate is destroyed long before the chrome itself is solubilized and removed. The first chrome salts which are formed by these acids are not sufficiently soluble to be readily removed. But, when there is an excess of these acids present, more soluble chrome salts are formed which are readily washed out of the leather. This is to be expected from the known action of these acids upon chrome liquors and upon the precipitated two-thirds basic chrome sulfate.

With acetic acid a somewhat different effect is noted. Here, sulfate removal is very low. Yet, when the chrome-bound acid sulfate was determined, it was found to be removed more rapidly than the total sulfate. This can readily be explained on the basis of the chrome removal reactions postulated earlier. Acetic acid, in de-chroming, forms sulfuric acid which becomes protein-bound acid sulfate. So the first sulfate to disappear is the chrome-bound acid sulfate. This is shown by the data for 1.0 M. acetic acid, where only one-fourth of the total sulfate is removed, yet 42.9 per cent of the chrome-bound sulfate is removed. The protein-bound acid sulfate is 112 per cent of the protein-bound acid sulfate in the leather before treatment.

This is the same effect that was noted with phosphoric acid, as reported earlier (3). It is therefore quite probable that phosphoric acid is also forming sulfuric acid which becomes protein-bound acid sulfate. With both phos-

phoric and acetic acids, the greater persistence of the protein-bound acid sulfate is thus explainable.

Nitric, hydrochloric, and boric acid have displayed less activity in removal of sulfate than the other acids, especially the organic, have; but they are still active sulfate removal agents. In fact, upon the basis of its very slight ionization, boric acid is a very active sulfate remover. Nitic acid is the most completely ionized of these acids, and it is the most active in sulfate removal; hydrochloric acid which is somewhat less active as an acid is also less active as a sulfate remover.

The nitrate ions do not penetrate the chrome complex so that the total removal of the sulfate by nitric acid might indicate that the chrome-bound acid sulfate was ionically-bound and not complex-bound. But, complex-bound sulfate could diffuse out of the complex and become ionically-bound sulfate. This would then give the effect of nitric acid displacing the chrome bound sulfate in the complex, without the nitrate ion ever penetrating into the complex.

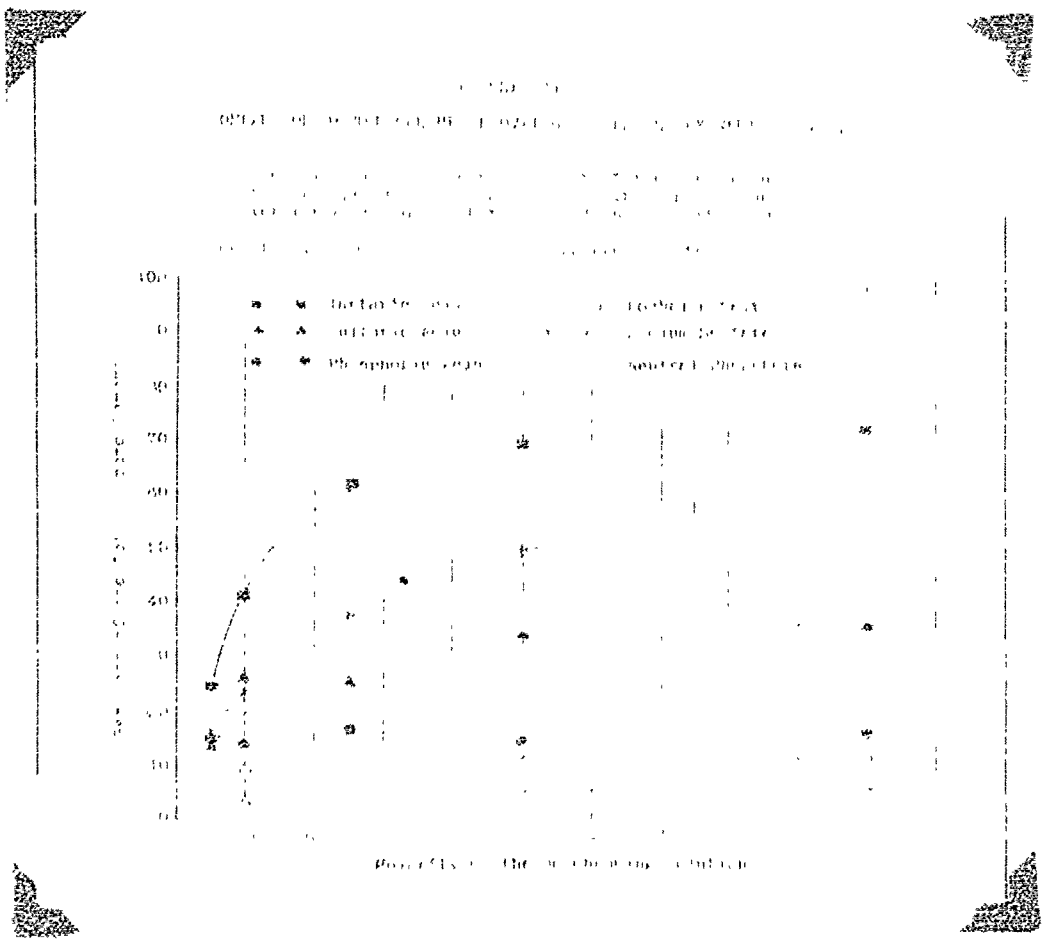
The Action of Salts

It has been postulated that acids de-chrome because they form soluble chrome complexes which are more stable than the insoluble two-thirds basic chrome sulfate. To do this, they act as acids to reverse the changes which

have occurred as a result of aging. The negative ions also act as penetrating agents to form new complexes which are soluble and stable.

If we consider the salts of these same acids, it will be evident that the same negative ions will still be present to act as penetrating agents. In fact, we might have a greater ionic concentration from the salt solutions of the same concentration as the acid solutions, since salts are postulated to be completely ionized while acids are not. But, we would not have the acid to start the chain of the de-chroming reactions. So, though de-chroming would still be expected, it might very well be less. There is however a factor in favor of salts as de-chroming agents; since they do not swell the leather as the acids do, there is no inhibitory action due to swelling when salts are used to dechrome.

In a previous report (3), it was shown that monosodium orthophosphate is less effective in de-chroming than is orthophosphoric acid. Thus, as anticipated, the lowering of the hydrogen ion concentration decreased the de-chroming action. However, there was still a high concentration of acid ions in this acid salt solution, and it was desired to check the effect of several approximately neutral salt solutions to see if this was a general condition. From the very active organic acids, tartaric acid was selected and a study made of the effect of its neutral sodium potassium salt commonly



known as Rochelle salt. The effect of neutralization of sulfuric acid was also rather extensively studied. Also, a mixture of mono-sodium and di-sodium ortho phosphate was used to approximate neutrality with phosphate ions. Table IV and Figure III present these results.

Rochelle salt is less active in chrome removal than is tartaric acid, although the decrease is not as pronounced as it is with sulfuric acid. This is not surprising since it was postulated that the penetrating action of the negative ion upon the chrome complex is an important cause of chrome removal. With both salts, one would not have the acid to actively reverse the changes of aging. But, with tartrates, the negative ion is very active, and there is no swelling, so that chrome removal is high though no acid ion is present. With sulfuric acid, however, only the acid is of value since the sulfate ion has very little effect upon the co-ordinately bound hydroxyl group unless there was a large excess of the sulfate ions. So, sodium sulfate is a very poor de-chroming agent. The phosphate ion will be noted to behave more like an organic ion than like the sulfate ion, since the neutral phosphate solution acts much like phosphoric acid. In other words, the phosphate ion is a rather effective penetrating agent, so that it overcomes the loss in activity due to the removal of the hydrogen ions.

The effect of decreasing the acidity of solutions whose major action is due to their acid nature is shown by results

TABLE IV

A Comparison of the Chrome Removal by Acids and by Neutral Salts

Wilson-Kern Extraction Method

Molar Concentration	Per Cent of Total Chrome Removed					
	Tartaric Acid	Rochelle Salt	Sulfuric Acid	Sodium Sulfate	Phosphoric Acid	Neutral Phosphate
0.05	24.4	14.8	13.5	----	14.5	1.0
0.10	40.8	22.9	25.9	2.4	13.3	8.7
0.25	61.5	37.1	24.9	----	16.1	11.1
0.50	69.0	49.4	33.5	4.0	14.5	10.9
0.75	----	57.8	----	----	----	----
1.0	71.8	----	35.1	4.9	15.9	11.0

of de-chroming with 0.50 M. sulfate solutions of decreasing acidity. 0.50 M. sulfuric acid removed 33.5 per cent of the total Cr_2O_3. Under the same conditions, the half neutralized salt, sodium acid sulfate removed only 16.8 per cent of the total chrome, while 0.50 M. neutral sodium sulfate removed only 4 per cent of the total chrome. Here we have a very excellent demonstration of the effect of the acid ion concentration, since the only change in these solutions is the replacement of the active acid ions to form more neutral solutions.

The effect of salts of the other acids was not as extensively studied. Sodium oxalate has long been known to de-chrome, and sodium citrate is likewise effective. With sodium acetate, a marked decrease in de-chroming occurred, since it was necessary to have an excess of the acetate ions to remove chrome with the neutralized acid. Thus, a 3.0 M. sodium acetate solution removed only one-sixth of the total chrome. Sodium chloride likewise was very ineffective in chrome removal, since a 3.0 M. solution removed only 2.5 per cent of the total chrome, although it did remove 90 per cent of the total sulfate.

In general, therefore, the salts were less effective than the acids containing the same ions. With organic and other active penetrating ions, the effect of the removal of the acid ions was not especially noticeable. However, with some of the acids, particularly inorganic acids like

sulfuric or hydrochloric, removal of the acid ions almost entirely eliminated the de-chroming action, even though the chrome salt in the leather was changed, as the sulfate data showed. Salts were also noted to be more effective in those cases where a large part of the chrome had been removed and the acid produced excessive swelling which retarded the removal of the chrome. But, this is a physical rather than a chemical effect. Of course, salts will remove the chrome more completely when conditions like those discussed by Hemmings, Lamb, and Lamb (2) prevail. They found that the ammonium salt of the chrome oxalato compound was more soluble than the chrome oxalato compound itself, so that chrome removal was more complete with ammonium oxalate than with oxalic acid. But, even though oxalic acid left chromium in the leather, it was not the original chrome sulfate, but a chrome oxalato compound of low solubility. The controlling factors in its formation were still the penetration of the negative ion and the action of the acid ion.

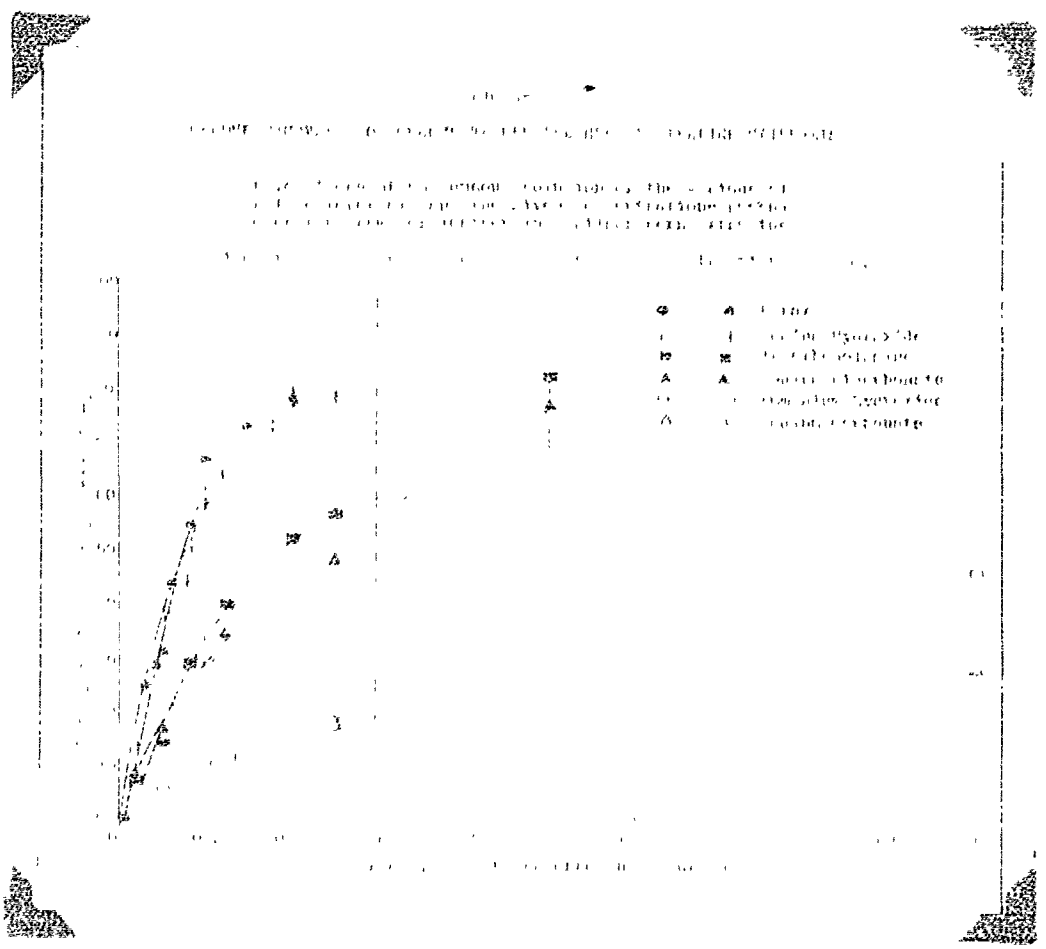
The Action of Certain Alkaline Materials

This section will discuss the action of sodium bicarbonate, certain borates, sodium carbonate, ammonium hydroxide, triethanolamine, and sodium hydroxide. Table V and Figure IV present these data. The explanation of the action of certain of these materials is quite different from that

TABLE V.

The De-Chroming Action of Alkaline Materials.

Concentration Molar	Concentration Normal	Per Cent Removal
Sodium Bicarbonate		
.05	0.05	8.3
.10	0.10	16.4
.25	0.25	35.0
.50	0.50	48.5
.0	1.0	76.7
Borax		
.01	0.02	0.0
.03	0.06	24.8
.04	0.08	28.7
.05	0.10	31.0
.06	0.12	44.0
.08	0.16	54.8
.10	0.20	66.6
.15	0.30	73.0
.20	0.40	77.8
Sodium Carbonate		
0.10	0.20	10.7
0.25	0.50	18.0
0.50	1.0	17.7
1.0	2.0	28.4
1.5	3.0	30.9
Triethanolamine		
0.05	0.05	7.7
0.10	0.10	14.2
0.15	0.15	29.0
0.25	0.25	40.0
0.40	0.40	51.8
0.50	0.50	56.2
1.0	1.0	82.2
Sodium Hydroxide		
0.01	0.01	0.0
0.05	0.05	13.5
0.10	0.10	38.6
0.12	0.12	44.3
0.15	0.15	50.8
0.20	0.20	59.4
0.25	0.25	65.3
0.30	0.30	77.1
0.35	0.35	73.1
0.40	0.40	79.0
0.50	0.50	78.6
Ammonium Hydroxide		
0.10	0.10	5.5
0.25	0.25	11.0
0.50	0.50	17.9
1.0	1.0	51.3
2.0	2.0	46.2



which has been previously postulated, so that a complete discussion of the results will be necessary.

The results with sodium bicarbonate and sodium carbonate are rather difficult to interpret, in view of the de-chroming action of sodium hydroxide. But, these results have been subjected to very careful check, and in every case the more acid bicarbonate was always more effective than the carbonate solution.

Stiasny (9) has presented evidence to indicate that carbonato chrome complexes exist. He considers the effect of making a chrome liquor basic with sodium carbonate, and establishes the following reaction:

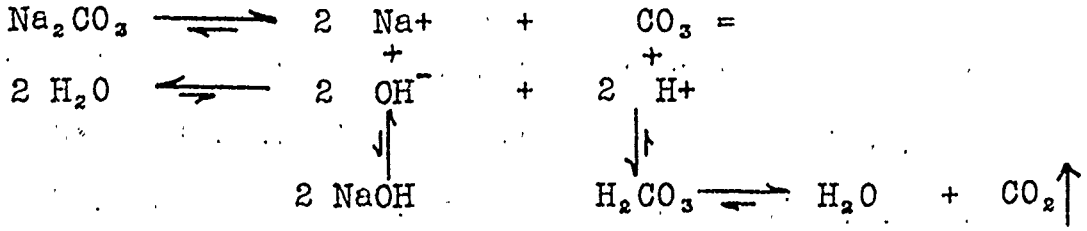
$$2\ CrX_3 + 2\ Na_2CO_3 + H_2O \longrightarrow \left[\begin{matrix} Cr\langle OH \\ Cr\langle CO_3 \\ Cr\langle OH \end{matrix}\right] X_2 + 4\ NaX + CO_2$$

This leads to a compound which olates very readily, but does not form the insoluble two-thirds basic chrome sulfate when further sodium carbonate is added. Finally, a very highly olated, stable product precipitates. This carbonato complex given above loses its carbonate slowly to form the insoluble two-thirds basic chrome salt.

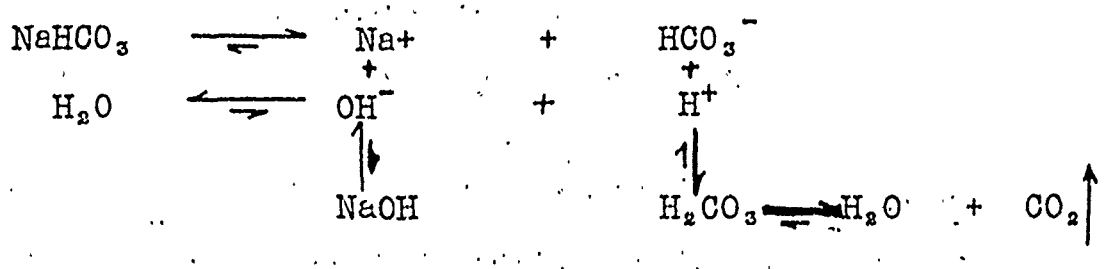
One action of sodium carbonate in de-chroming could therefore be the formation of the above salt since it is more soluble than the basic chrome sulfate in the leather. But, as more and more sodium carbonate is added, the compound polymerizes to form an insoluble, highly olated chrome

salt again, so that increased treatment does not encourage more complete chrome removal. Sodium bicarbonate gives as a primary ionization product an univalent ion, so that if this ion penetrated into the chrome complex it could not form these bridges between two chromiums so that olation would not be encouraged. The net results would be that a smaller, more soluble chrome compound would be formed, and the chrome removal would be more complete with sodium bicarbonate.

Both sodium bicarbonate and sodium carbonate hydrolyze. As is shown by its higher pH, sodium carbonate hydrolyzes to give a more alkaline equilibrium:



On the other hand, the hydrolysis of sodium bicarbonate gives:



Now a more alkaline condition favors olation of the chrome complexes, so that entrance of other groups and formation of small water soluble complexes is discouraged.

Sodium carbonate, producing the more alkaline solution would therefore not tend to encourage solubilization as much as the more acid bicarbonate.

There is also a physical effect which explains the lower de-chroming with sodium carbonate. Sodium carbonate produces a more alkaline solution, so that its solutions produce a greater alkaline swell in the leather, and consequently a greater retardation of the diffusion of the chromium compounds out of the leather even after they are solubilized. All of these chemical and physical effects work to the same end, a greater de-chroming by the more acid sodium bicarbonate than is produced with sodium carbonate.

The very vigorous de-chroming action of borax is rather unexpected in view of the fact that boric acid did not de-chrome. However, it should be remembered that boric acid is almost entirely un-ionized. Borax, in contrast, is more completely ionized, and furthermore, it hydrolyzes:

$$Na_2B_4O_7 + 3\ H_2O \rightleftharpoons 2\ NaBO_2 + 2\ H_3BO_3$$

$$NaBO_2^{\cdot\cdot} + 2\ H_2O \rightleftharpoons NaOH + H_3BO_3$$

The first reaction occurs in concentrated solutions, while in very dilute solutions the hydrolysis is more complete, including the second reaction. Consequently, one might conceive that de-chroming by borax is due entirely to its alkaline nature, and not to its borate ions. This possi-

bility seems even more likely when the sodium hydroxide and the borax curves for de-chroming are compared. To check this possibility, a sample was treated with sodium metaborate. This is more alkaline than borax as one would expect from its one to one ratio of NaOH to H_3BO_3, in contrast to the one to two ratio for borax. Now, if the de-chroming action of the borates is due entirely to their alkaline nature, sodium metaborate should be more effective than is borax. However, a 0.25 M. sodium metaborate solution removed only 18 per cent of the total chrome under conditions where a 0.25 M. borax solution removed approximately 70 per cent of the total chrome. In the sodium metaborate solution, hydrolysis has resulted in most of the borate ions being bound in the un-ionized boric acid, and the solution is primarily a very weak alkaline solution. So, it is not surprising that it is not a vigorous de-chroming agent. Borax, on the other hand, due to the equilibria between the hydrolytic and ionic reactions, furnishes a better supply of borate ions so that they can penetrate and cause de-chroming.

This does not imply that a portion of the de-chroming by borax is not due to its alkalinity. Borate ions are not particularly good penetrating agents, so that they are not especially active in chrome removal; on the other hand, de-chroming by sodium hydroxide demonstrates that hydroxyl ions are good de-chroming agents. Borax represents a reservoir of hydroxyl ions available for de-chroming without

being accompanied by extreme fiber swelling due to the strong alkali. It is therefore probable that de-chroming by borax is a combination of a specific borate ion effect along with a buffered alkaline action.

Sodium perborate was also used as a de-chroming agent. Almost as soon as the leather was wetted with a 0.10 M. solution of this salt, the blue color of the leather was changed to yellow. In about four hours of extracting with 2.5 liters of this solution, the chrome was quantitatively removed, leaving an unswollen hide substance. Since this salt in an aqueous solution gives off nascent oxygen, it is a very effective oxidizing agent. Consequently, it converts the hexavalent chrome salt in the leather to the yellow, soluble trivalent chrome salt. This is by far the most active de-chroming agent of those considered in this study.

The de-chroming action of sodium hydroxide might seem contrary to its known precipitating power upon chrome liquors. Whenever sodium hydroxide is added to chrome sulfate liquors, the chrome compound in the liquors becomes more and more basic, precipitation of the chrome occurs, and one finally obtains the chrome in the form of the insoluble hydrated $Cr(OH)_3$. However, chromium is an amphoteric metal, so that its hydroxide can act as an acid in the present of high concentrations of alkalis. The final result is the solubilization of the gel, as Mellor (4) shows:

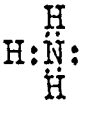
$$Cr(OH)_3 + NaOH \xrightarrow{-H_2O} Cr(OH)_2ONa \xrightarrow{-H_2O} NaCrO_2$$

Soluble — Sodium Chromite

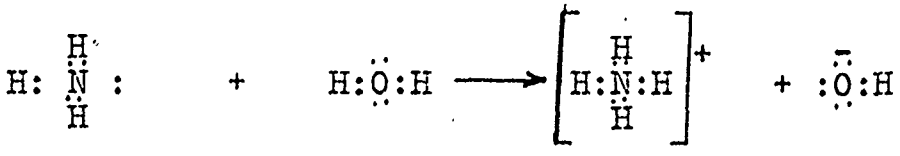
This progressive conversion of the insoluble two-thirds basic chrome sulfate in the leather into the chrome hydroxide gel and finally to its soluble chromite state would adequately explain the action of sodium hydroxide in de-chroming.

Other alkaline materials should have somewhat the same effect. It is this action which is referred to earlier as the alkaline action of the other basic de-chroming agents. Ammonium hydroxide will also de-chrome, although the data show that it is not as effective as sodium hydroxide. However, ammonium hydroxide is a very weak alkali. If these data were plotted upon an ionic basis they would indicate a more vigorous de-chroming agent than is sodium hydroxide. This is possible since many ammine chrome compounds are known (11) (12), so that both the negative and the positive ions could be active in de-chroming with ammonium hydroxide.

The homologous organic ammonium compounds are often much stronger bases when in aqueous solution. Ammonia electronically could be pictured as:



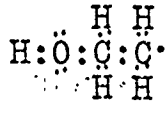
By virtue of its unshared pair of electrons, it can coordinate a hydrogen atom to become the ammonium ion:



The hydrogen atoms of the ammonia can be replaced by another group which needs an electron. Thus, we have compounds of the type NR_3 which act in the same way that ammonia does in forming alkaline solutions. One of these compounds is triethanolamine which is:

$$(HOCH_2CH_2)_3N$$

That this is electronically the same as ammonia is shown by the fact that the net electronic picture of the R group is the same as that of hydrogen:



(Note the unshared electron.)

It thus desires to share another electron, which the nitrogen atom can provide in the same way that it shares an electron with hydrogen in ammonia. The resultant amine still has the pair of unused electrons from the nitrogen, so that it can co-ordinate a hydrogen atom to form an ammonium hydroxide type of basic solution.

Since triethanolamine is a stronger base than ammonium hydroxide, it should exert a more vigorous de-chroming action than ammonium hydroxide. This is borne out by the de-chroming figures which show that it is much more effective than ammon-

ium hydroxide, but that it is not as effective as sodium hydroxide. There was evidence that the positive portion of the compound was active in de-chroming, since the partially de-chromed samples were a peculiar purple blue color, while sodium hydroxide produced a greenish yellow cast to the partially de-chromed leather. Triethanolamine could easily become co-ordinated to chromium due to its pair of unshared electrons.

In the concentrated triethanolamine solutions where the chrome removal was high, extreme difficulty was encountered due to the swelling of the partially de-chromed leather which inhibited further swelling. It should not be inferred that any of the highest chrome removal figures actually represent a maximum in chrome removal beyond which further chrome removal can not occur readily due to the fact that a portion of the chrome is more firmly held. The inhibiting action to diffusion resulting from the swelling of the partially de-chromed leather slows up further de-chroming and gives a false impression that a maximum has been reached. In other cases, as with borax, the limited solubility of the de-chroming material prevents the use of more concentrated solutions to attain complete removal of all of the chrome. In every case where a given volume of a de-chroming solution removed only a portion of the chrome, more could be removed by further treatment with more of the same solution. As swelling progressed, removal sometimes became slow, but all

of the chrome could finally be removed if treatment was continued long enough and if swelling was controlled.

Sulfate removal data for these alkaline de-chroming agents do not require numerical figures. Analysis showed that the total sulfate was completely removed by the most dilute solutions of all of these materials. Sulfate removal thus preceded the removal of the chrome considerably.

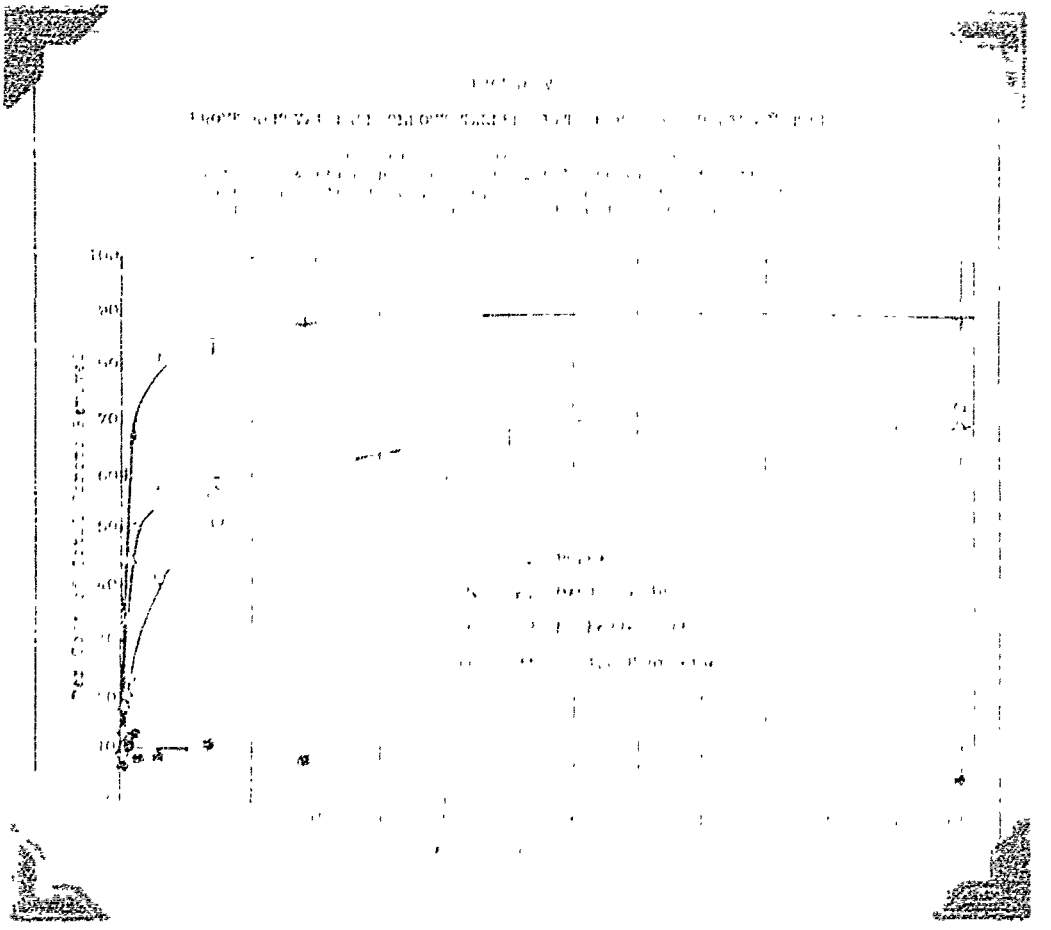
Comparison of the De-Chroming by Extraction and by Soaking

Earlier de-chroming studies have been conducted by a method which we have agreed to refer to as soaking. In this method, the leather is placed in a suitable container and the de-chroming solution poured onto it. The sample may then be agitated or allowed to stand without agitation, but the essential fact is that the leather is left in contact with a definite, limited amount of the dechroming solution. In the extraction method used in this study, the leather is placed in a Wilson-Kern extractor and treated with a continually replenished solution of the de-chroming agent, at the same time removing the products resulting from the destruction of the chrome tannage. There is an essential difference in the two methods due to the fact that the chrome removal products build up in the soaking method, and therefore may exert an inhibitory action to further de-chroming. Table VI and Figure V will demonstrate the validity of this assumption when the data are compared to the earlier data.

TABLE VI.

De-Chroming by Soaking

Time	Per Cent Removal			
	Borax	Rochelle Salt	Oxalic Acid	Sodium Hydroxide
1 hr.	36.0	8.7	9.2	6.3
3 hrs.	----	11.5	17.2	----
8 hrs.	57.9	19.8	33.7	11.9
16 hrs.	66.9	22.2	44.5	12.9
1 day	67.6	27.6	50.0	7.2
3 days	82.0	41.5	57.8	8.0
7 days	83.5	51.2	56.9	10.3
14 days	87.3	----	----	7.6
65 days	89.1	73.3	69.3	3.7



It will be noted at once that the soaking method is much slower in its chrome removal than the extraction method. These soaking tests were conducted so that the ratio of the volume of the de-chroming solution to the weight of the leather was the same as the instantaneous solution volume-leather weight ratio in the Wilson-Kern extraction method. Of course, the total volume of the de-chroming solution flowing over the leather in the extraction method was much greater than the volume with which the leather was soaked in the soaking method; moreover, it might seem that this fact would invalidate any comparisons between the two methods. However, it must be remembered that only the de-chroming material in contact with the leather at a given instant can be of any value in de-chroming. Much of the de-chroming material flows over the leather without any de-chroming action when the extraction method is used. The greater volume is a necessity to maintain a continually fresh solution of the de-chroming material, uncontaminated by large amounts of chrome removal products. Moreover in the soaking method, an excess of the de-chroming reagent was present so that there was unutilized de-chroming material at the end of the test to prevent any cessation in chrome removal due to lack of de-chroming material. Consequently, for the same time of contact and the same solution concentration in both methods, a comparison can be made. In all of these experiments of de-chroming by soaking, a 0.10 M. concentration was used. In the Wilson-Kern extraction

method, the time of contact was approximately seven hours, and a comparison of the de-chroming data presented earlier in this paper can be made with the de-chroming by soaking in this same period. This comparison will show that de-chroming by soaking is definitely slower than that by extraction.

It will be noted that with borax, Rochelle salt, and oxalic acid, chrome removal is still increasing after two months of soaking. Of course, the rate of removal has decreased due to the swelling of the leather. Furthermore, this decrease in rate of removal is partially caused by the build-up of the chrome removal products, as is shown by the fact that the rate of chrome removal increases when the contaminated solution is replaced by a fresh solution. Furthermore, if the swelling of the partially de-chromed leather is reduced, the remaining chrome rapidly diffuses out of the leather. Thus, as Cameron, McLaughlin, and Adams (1) have previously shown, it was found that chrome removal was readily made complete by replacing the oxalic acid solutions by sodium oxalate solutions to decrease the swell.

With sodium hydroxide chrome removal starts as would be expected, but then seems to decrease. Swelling is very pronounced in this solution so that diffusion is very slow. Also, the chrome has been changed by contact with the highly alkaline solution over the long period of time. But, due to the fact the chrome removal products remain in contact with the leather, the chrome, though changed, is not solubilized so that it can

be removed from the leather. With the extraction process, the solubilized chrome is rapidly removed from the leather, so that it is possible to de-chrome with sodium hydroxide, despite the alkaline swell.

Summary

It has been shown that it is possible to de-chrome aged chrome tanned calf skins in the "blue" with a great variety of materials. With acid de-chroming agents, organic acids are more effective than inorganic acids. However, any acid which ionizes to give an appreciable ion concentration will de-chrome, either due to its acid reaction or penetration of the negative ion into the chrome complex to form stable, soluble compounds with the chromium. Variations in this latter factor are important in determining the difference in the activity of the different acids. Salts of these same acids also de-chrome. With some salts, whose negative ions are poor penetrating agents, and therefore poor de-chroming agents, there is little de-chroming action. With other salts, and particularly the organic salts, whose negative ion is very active in de-chroming, there is little difference in the de-chroming by acids and salts. De-chroming is also very pronounced upon the alkaline side, borax, sodium bicarbonate, sodium hydroxide, and triethanolamine being very active de-chroming agents. These alkaline materials exert a variety of de-chroming actions. First, they form soluble chrome salts

by penetration as the acids did. Also, they solubilize the chrome by converting the chrome sulfate in the leather into chrome hydroxide and finally into the soluble chromite stage. Finally, alkaline oxidizing agents are quite effective since they readily oxidize the chromium to soluble hexavalent compounds, sodium perborate furnishing an excellent example of this.

These data have been secured by the treatment of the leather in a Wilson-Kern extractor, with continual replenishment of the de-chroming solution and continual removal of the solubilized chrome. It has been established that the removal of the solubilized chrome is significant since it prevents the inhibitory action which the solubilized chrome has upon further de-chroming. By this method there is no evidence that there is any difference in the firmness with which different portions of the chrome are bound to the hide substance. Swelling may reduce the rate of chrome removal when the chrome is partially removed, and it is that fact which explains the seeming break in chrome removal appearing in some studies.

These data were secured with leather ground in a Wiley mill. A later report will show that de-chroming occurs just as completely, though more slowly, upon un-ground leather. Thus, though a greater fiber area is exposed in the ground leather it controls only the rate of removal. The essential factor in chrome removal is the formation of soluble compounds

out of the insoluble chrome compound in the leather. Whenever soluble products can be formed, chrome removal will continue till all of the chrome is removed from the leather.

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