

USE OF REACTIVE CHROME-COMPLEXES

FOR THE TANNING OF LEATHER

by

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INDEX

I. Summary	1
II. Introduction	2
A. Composition of hides	2
B. Normal tanning procedure	2
C. Proposed mechanisms of tanning	4
D. Properties of Volan	5
E. Coating of leather	7
F. Object	7
III. Procedure	9
A. Tanning	9
B. Coating	10
Figure 1	11
Figure 2	12
IV. Results	13
Table 1	14
Table 2	15
Table 3	15
Table 4	16
Figure 3	17
Figure 4	18
Figure 5	19
Figure 6	20
V. Discussion of Results	21
A. Tanning	21
B. Discussion of Error	23
C. Coating	24
VI. Conclusions	27
VII. Recommendations	28
VIII. Appendix	29
A. Details of procedure for tanning	29
B. Details of procedure for coation	30
C. Sample calculations	32
D. Literature Citations	33

I. SUMMARY

Many thermoplastic materials such vinyl resins, polystyrene and the methacrylates, have been used to coat leather. These substances, are however, normally non-adherent to leather; it was believed that adhesion might possibly be improved by tanning the hide with organic chrome complexes containing vinyl groups which can copolymerize with resin forming compounds.

By the use of Volan(methacrylate chromic chloride) as a tanning liquor, good leather was obtained. It compared favorably with conventional chrome sulfate leather in respect to shrinkage temperature, chrome fixation and flexibility.

Leather samples tanned with Volan were treated with styrene in emulsion and bulk form to allow polymerization. It appeared that no styrene copolymerized with the methacrylate, because all the styrene deposited in the leather could be extracted with benzene. There was, however, evidence of good adhesion between the polystyrene and the leather.

It is believed that oxygen inactivated the methacrylate, therefore inhibiting copolymerization with styrene. For future work, it is recommended that the leather either be dried in an inert gas such nitrogen or be placed immediately after tannage, without drying, into an emulsion of styrene for polymerization.

II. INTRODUCTION

A. COMPOSITION OF HIDES

Raw skins are composed of different kinds of protein matter varying from skin to skin and in different parts of the same skin. Collagen is the most abundant of these proteins and is of greatest importance to the tanner since it is the basis for leather.

B. NORMAL TANNING PROCEDURE

Conversion of skins into leather involves the removal of some of the proteins by action of alkalies, enzymes, or bacteria and the interaction of the remainder with tanning materials, oils, soaps or other materials. The steps commonly employed by the leather industry are listed below.

1. Curing-- the treatment of fresh skins with rock salt on the flesh side to prevent bacterial decay. This leaves the skins in a hard, stiff condition.
2. Soaking-- the continuous washing of cured skins with water until the salt is washed out and the skins become soft.
3. Liming-- the treatment of skins with lime solution to solubilize the epidermis layer of skin to facilitate the removal of flesh and hair. Liming also swells the skin fibres to the proper degree so as to insure good quality leather. After liming, the skins must be thoroughly washed.

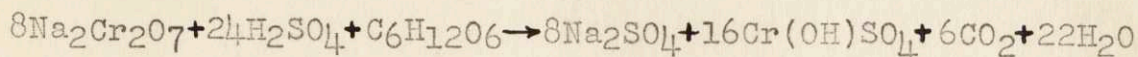
4. Bating-- the treatment of skins, after liming, with proteolytic enzymes to convert skin to a soft, flaccid condition and to solubilize some of the interfibillar skin substance. The skins, after treatment, are left in a condition which upon tannage gives a fine, tough grained, light weight leather.

5. Pickling-- the treatment of skins with a solution of salt and acid(usually sodium chloride in sulfuric acid). Pickling conditions the skins for tannage by providing better absorption of tanning liquors. The skins, during pickling, are brought to a pH of about 1.5. When skins are acidic, in the presence of salt, they do not swell and are not susceptible to bacterial action; hence, pickled skins may be kept for a long time without putrefying.

6. Tanning--the deposition, on the fibre surfaces of the skin, a substance which destroys the sensitivity of hide to water, heat, and putrefaction. The tanning process can be carried out with various kinds of materials such as aldehydes, alums, or the more common tanning agents which are vegetable tannins or mineral tanning agents such as aluminum, iron, or chromium salts. During tanning, a masking agent which is usually sodium chloride, is added to the tanning liquor to prevent the skin from swelling in the acidic solution and inhibiting chrome fixation.

After tanning, the leather must be neutralized with a suitable alkali like borax, sodium carbonate, or sodium bicarbonate.

In the leather industry, chrome leather is tanned almost exclusively by the one bath process. The process is carried out by first preparing a chrome liquor from sodium dichromate, sulfuric acid and glucose as a reducing agent.

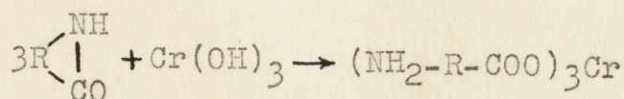


The basic chromium sulfate is the effective tanning agent. This liquor is allowed to age for about one week. Pickled skins are then placed in large wooden drums containing the liquor and the tanning process is carried out with constant rotation of the drum. Normal tanning procedure requires from 5 to 12 hours.

C. PROPOSED MECHANISMS OF CHROME TANNING

The mechanisms of chrome tanning are not thoroughly understood. Three different theories of the mechanism of chrome tanning have been proposed by leather experts.

1. Collagen, acting as an acid, and chromium hydroxide form the very stable salt chromium collagenate.



2. Negatively charged chromiates present in chrome liquors combine with positively charged collagen.

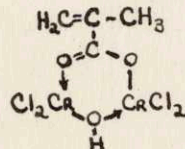
3. Each of the six coordinative positions about the central chromium atom may be occupied by protein groups (-NH₂-, -NH-, or -CO-) uniting the central chromium atom to collagen

by six bonds. It is possible to have nine bonds between chromium atoms and protein by the entry of six negative protein groups into the nucleus, which would give the nucleus three negative charges, permitting further combination with three basic protein groups.

D. VOLAN AND ITS PROPERTIES

In this investigation, the principal of the one bath process was used with Volan(methacrylate chromic chloride) as the tanning agent.

The structure of Volan is:



It is a dark green alcoholic liquid(28-30% solids in isopropanol), sp. gr. 1.0263 at room temperature, boiling point 180.3°F, and a molecular weight of 347.89. It is miscible with water in all proportions and undergoes no apparent deterioration when stabilized with isopropanol. The complex is precipitated when subjected to a pH of about 6.0. Precipitation is also accelerated by anions such as sulfate, chromate, and phosphate at as low a pH as 4.0. Once precipitation has started, the solution is no longer effective as a tanning agent.

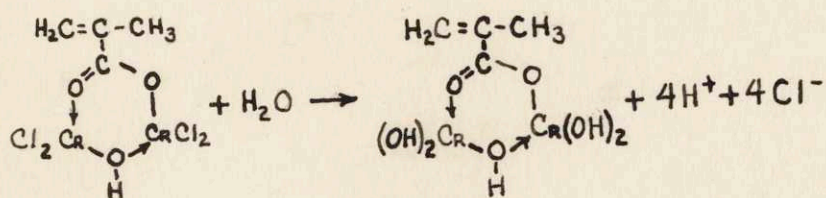
The diluted complex is unstable in strong mineral acids and should never be subjected to a pH of less than 2.0 for any length of time. It is also adversely affected by free halogens

or strong oxidizing agents.

Adsorption of the complex on a surface is inhibited by materials which tend to form complexes with chromium such as organic acids, with the exception of formic, amine compounds and cyanides. Addition of alkaline materials such as sodium hydroxide, sodium carbonate, or even sodium acetate tends to cause local precipitation of insoluble basic complexes.

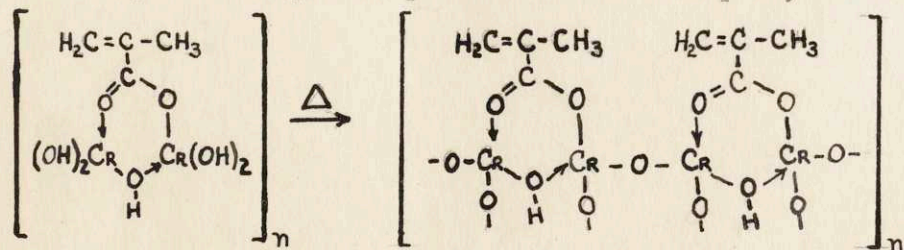
The complex may be buffered without precipitation by a solution containing 16.5% urea and 5% sodium formate adjusted to a pH of 6.0 with formic acid.³

Upon dilution or raising of pH of Volan, hydrolysis takes place with the formation of a basic complex.



This is a favorable property for tanning. Chrome complexes which are free of hydroxyl groups or which do not, on hydrolysis, form complexes containing hydroxyl groups, have no tanning properties.⁴

On standing, a slow dehydration takes place with the formation of Cr-O-Cr linkages.⁵ This process is accelerated by heat or by raising the pH with for example, sodium formate.



7

If polymerization does not proceed too far, the polymer remains soluble and is a suitable tanning agent. Tanning power of a chromium complex increases with the size of the molecule until a certain limit is reached. In the case of Volan, if polymerization proceeds too far, the polymer becomes insoluble.

When Volan is applied to negatively charged surfaces such as protein substance, the complex chromium cation is strongly adsorbed.

E. COATING OF LEATHER

Leather coated with resins such as polystyrene has practical uses where a strong, water proof, chemically inert material is desired, which has the appearance of leather.

Normally, resins such as polystyrene do not adhere to leather. When proper tannage is attained by the use of reactive chrome complexes such as Volan, the leather fibres are coated with a film which can react with a wide variety of unsaturated resin forming materials such as vinyl and allyl compounds. This is due to the existence of the active methacrylate group $\text{CH}_2=\underset{|}{\text{C}}-\text{CH}_3$ present in the chrome complex. Theoretically, the treated leather can combine with any compound that reacts with a double bond.

F. OBJECT

The purpose of this investigation was to determine the

8

feasibility of using a chrome complex containing a polymerizable organic group as a tanning agent, to determine optimum conditions for tannage, and to investigate conditions for polymerization, within the leather, of reactive resins.

III. PROCEDURE

A. TANNING

In this investigation, calf skin and split cowhide were tanned using Volan with sodium chloride and sodium formate used as masking agents. Several runs were also made with chromium sulfate so that Volan tanned leather could be compared with ordinary chrome tanned leather.

All tanning runs were made over 24 hour periods to insure the best possible tannage throughout the hide. The only two variables used in this investigation were chrome concentration of the tanning liquor and the pH of the liquor. Runs were made at pH's of 4.0 ± 0.5 and 3.0 ± 0.5 using sodium formate as masking agent while the chrome concentration was varied from 1.15 to 44.5 mg Cr_2O_3 /ml liquor at equilibrium. With sodium chloride as masking agent, runs were made at a constant pH of 3.0 ± 0.5 while the chrome concentration was varied from 8.55 to 43.1 mg Cr_2O_3 /ml liquor at equilibrium. Runs were made with Volan which had the isopropanol boiled off.

The analysis for chromium was carried out by the oxidation of chromium in a sample of Volan liquor to the +6 state, reduction to the +3 state with potassium iodide and then titration of the liberated iodine with standard thio-sulfate. The volume of tanning liquor was measured accurately

during preparation of the liquor. Chrome fixation in the hide was determined by the difference of the products of the chrome concentration and volume before and after tannage. It is expressed, in this report, in terms of mg Cr₂O₃/mg dry skin.

All tanning was done in glass bottles which were placed in a shaker. After tannage, the samples were washed, neutralized, washed again and then dried.

The shrinkage temperature of the leather was determined by placing a small sample in an apparatus especially constructed for this purpose(fig. 1) and heating the water until the leather shrank.

B. COATING

The best tanned leather samples were coated with styrene. Coating was done by emulsion polymerization with benzoyl peroxide and ammonium persulfate as catalysts. Polymerization under high pressure(2000-4000psi) and temperature(120°C) was also used, with benzoyl peroxide as a catalyst.

Coated leather was tested for water proofness in the apparatus for measuring the permeability of leather to water (fig. 2).

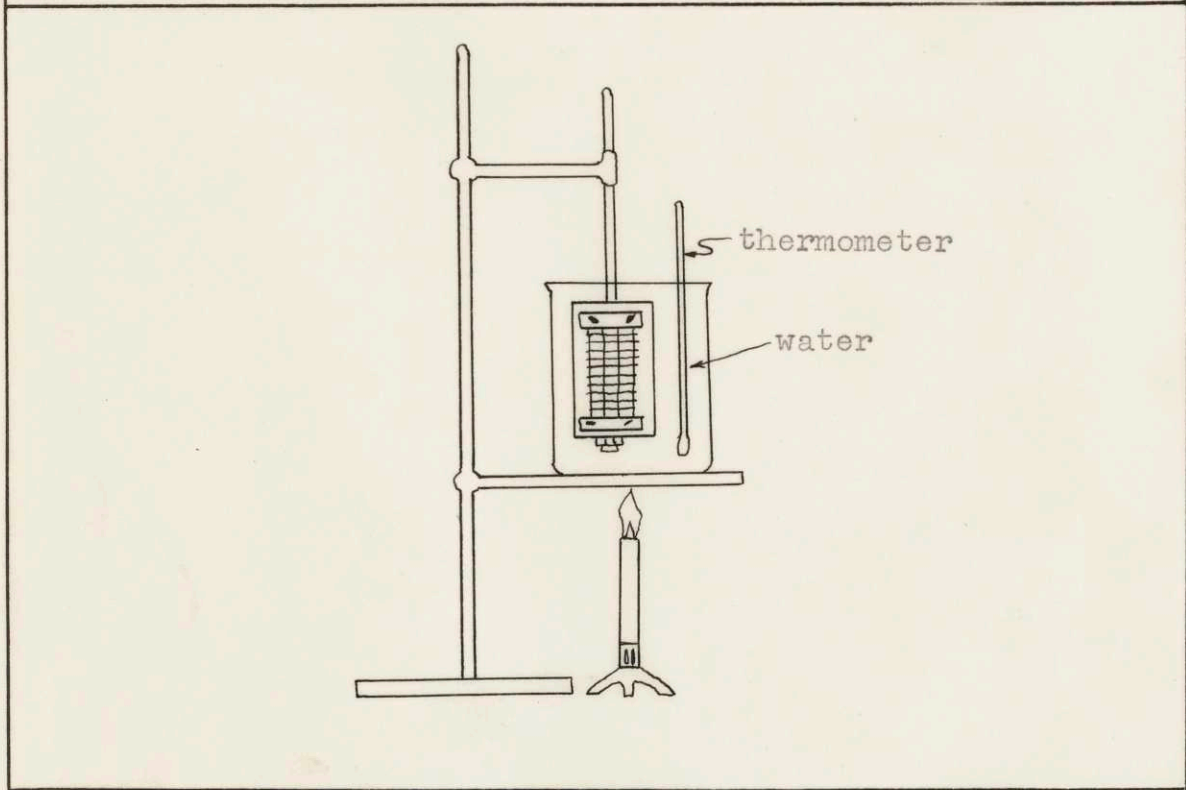
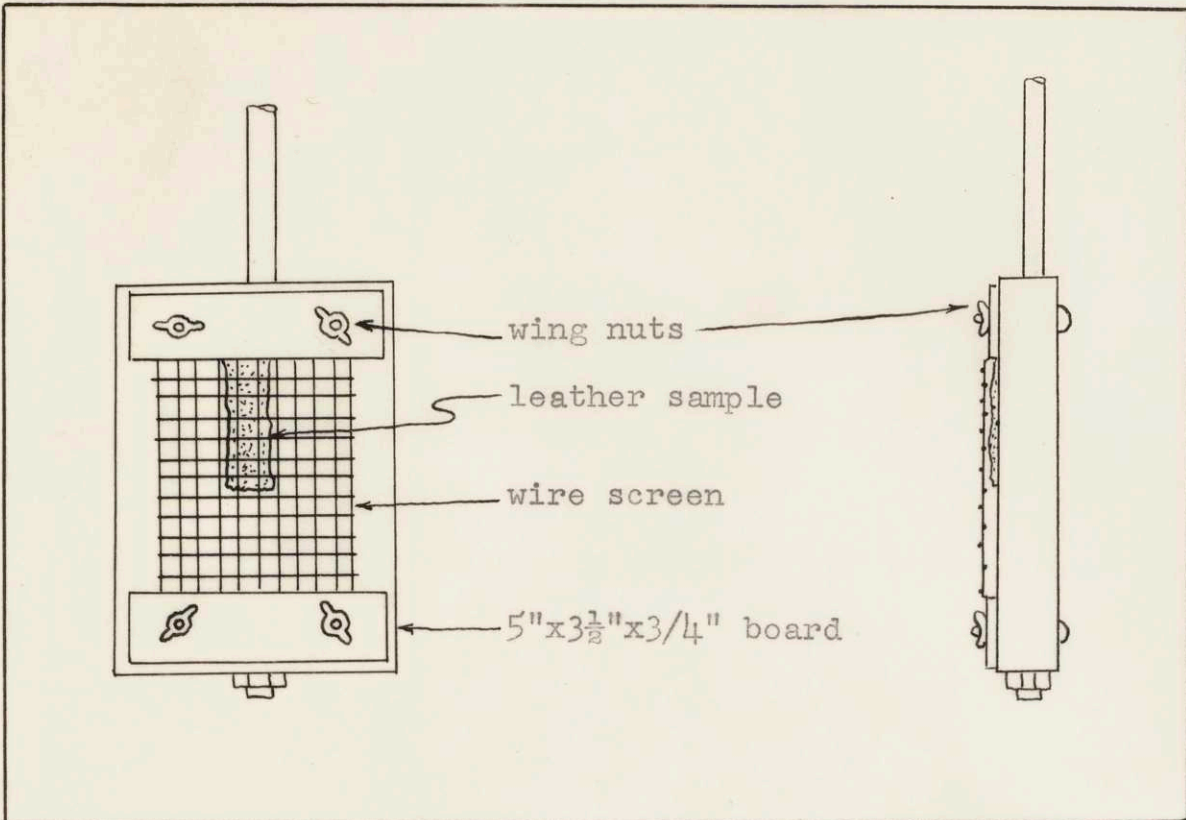


FIGURE 1

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APPARATUS TO MEASURE
SHRINKAGE TEMPERATURE

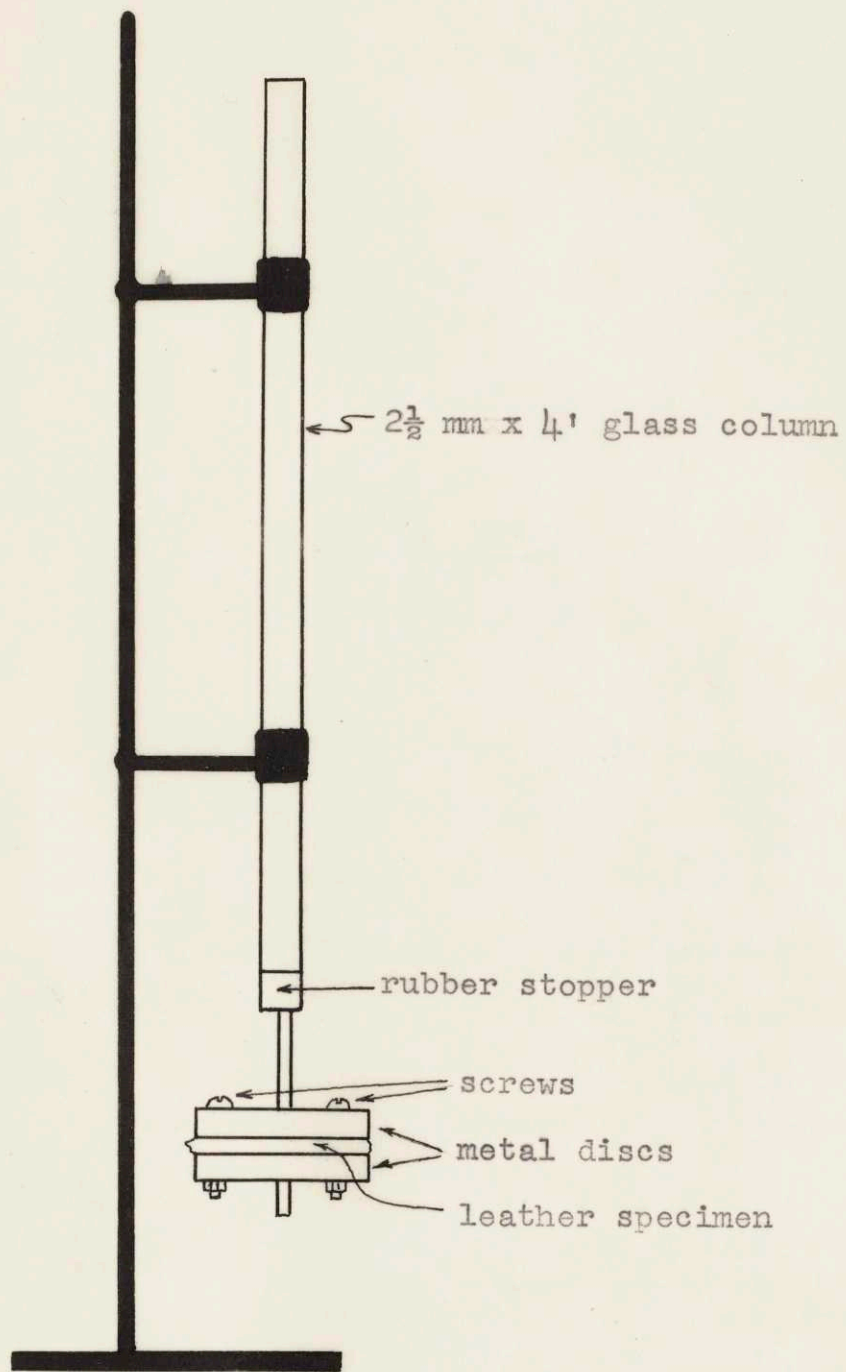


FIGURE 2

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APPARATUS TO MEASURE
PERMEABILITY OF LEATHER
TO WATER

IV. RESULTS

The results of this investigation are presented in tables 1, 2, 3 and 4 and in figures 3, 4, 5 and 6. These show the effect of different masking agents, pH and chrome concentration upon the chrome fixation in hides.

Leather tanned with Volan compared favorably with chromium sulfate tanned leather in respect to chrome fixation, shrinkage temperature and flexibility. The best leather was obtained by tanning with a Volan liquor which had the isopropanol distilled off.

Leather which was tanned with Volan and treated with styrene was less flexible than the untreated leather; had a glossy surface, in contrast to the untreated leather, which had a dull surface; and changed, upon treatment, from a grey to a green color.

Leather treated with styrene was water proof while the untreated leather was not.

TABLE 1

LEATHER TANNED WITH DISTILLED VOLAN

Sodium Formate Masking
pH 4.0±0.5

<u>Sample No.</u>	<u>Conc.*</u>	<u>% Sodium Formate</u>	<u>mg Cr₂O₃ fixed**</u>
1	2.07	10	0.0215
2	2.94	10	0.0241
3	7.02	10	0.0301
4	11.43	10	0.0396
5	15.20	10	0.0456
6	19.00	10	0.0533
7	24.10	10	0.0609
8	25.80	10	0.0583
9	32.10	10	0.0644
10	35.90	10	0.0968
11	41.50	10	0.120
12	44.50	10	0.128

*
mg Cr₂O₃/ml tanning liquor at equilibrium**
mg Cr₂O₃/mg dry skin

TABLE 2
LEATHER TANNED WITH VOLAN
Sodium Formate Masking
pH 4.0±0.5

<u>Sample No.</u>	<u>Conc.</u> *	<u>% Sodium Formate</u>	<u>mg Cr₂O₃ fixed</u> **
1	1.15	10	0.0064
2	7.50	10	0.0163
3	10.85	10	0.0439
4	14.80	10	0.0331
5	29.70	10	0.0668
6	42.80	10	0.0864

TABLE 3
LEATHER TANNED WITH VOLAN
Sodium Chloride Masking
pH 3

<u>Sample No.</u>	<u>Conc.</u> *	<u>% Sodium Chloride</u>	<u>mg Cr₂O₃ fixed</u> **
1	3.74	6	0.0065
2	8.55	6	0.0198
3	12.25	6	0.0390
4	43.10	2	0.0810

* mg Cr₂O₃/ ml tanning liquor at equilibrium

** mg Cr₂O₃/mg dry skin

TABLE 4

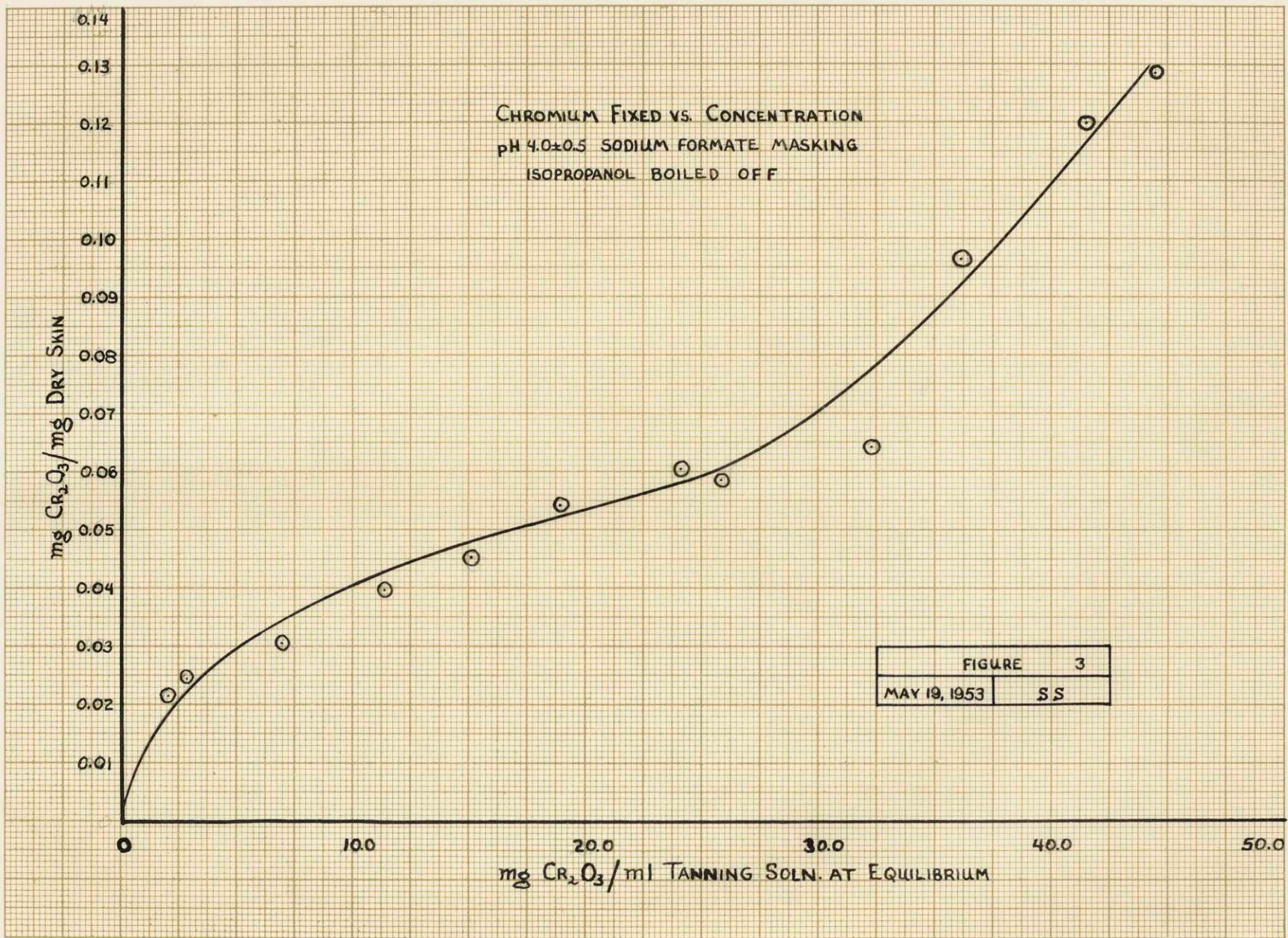
LEATHER TANNED WITH VOLAN

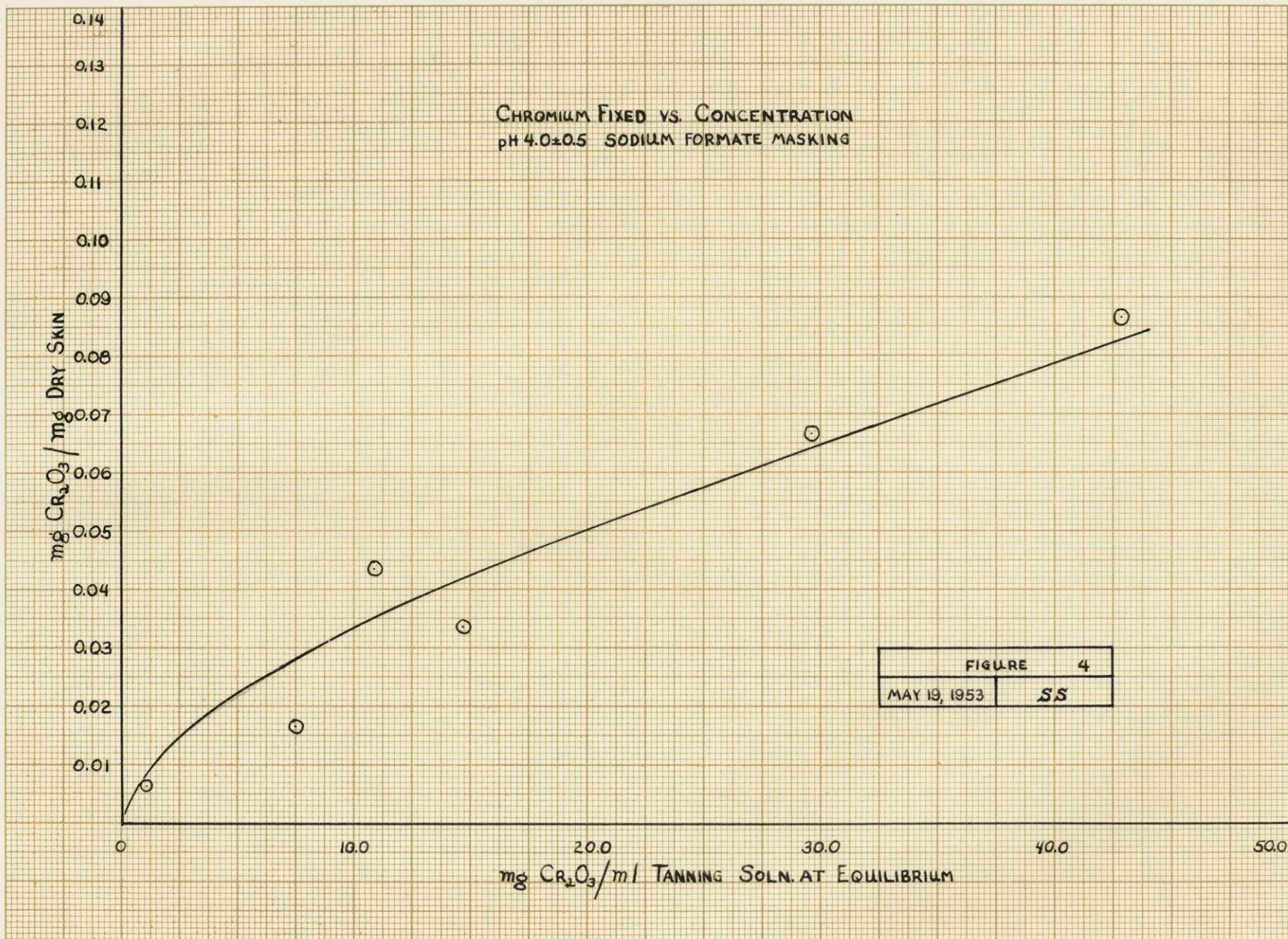
Sodium Formate Masking
pH 3

<u>Sample No.</u>	<u>Conc.</u> [*]	<u>% Sodium Formate</u>	<u>mg Cr₂O₃ fixed</u> ^{**}
1	1.15	8	0.0060
2	3.56	4	0.0099
3	5.26	6	0.0226
4	7.14	5	0.0098
5	8.69	6	0.0020
6	24.10	5	0.0187
7	44.10	2	0.0284

* mg Cr₂O₃/ml tanning liquor at equilibrium

** mg Cr₂O₃/mg dry skin





CHROMIUM FIXED VS. CONCENTRATION
pH 3 SODIUM CHLORIDE MASKING

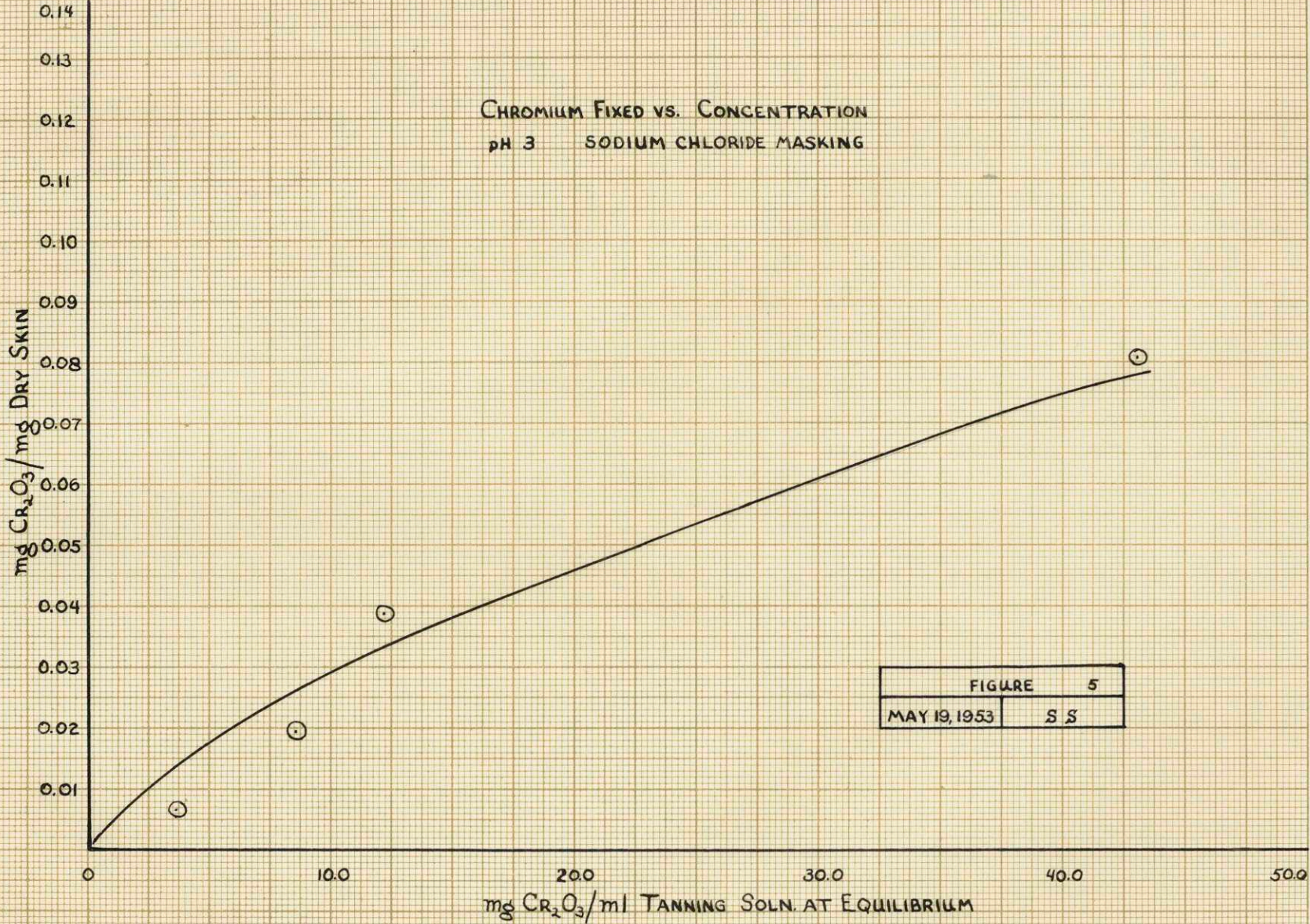
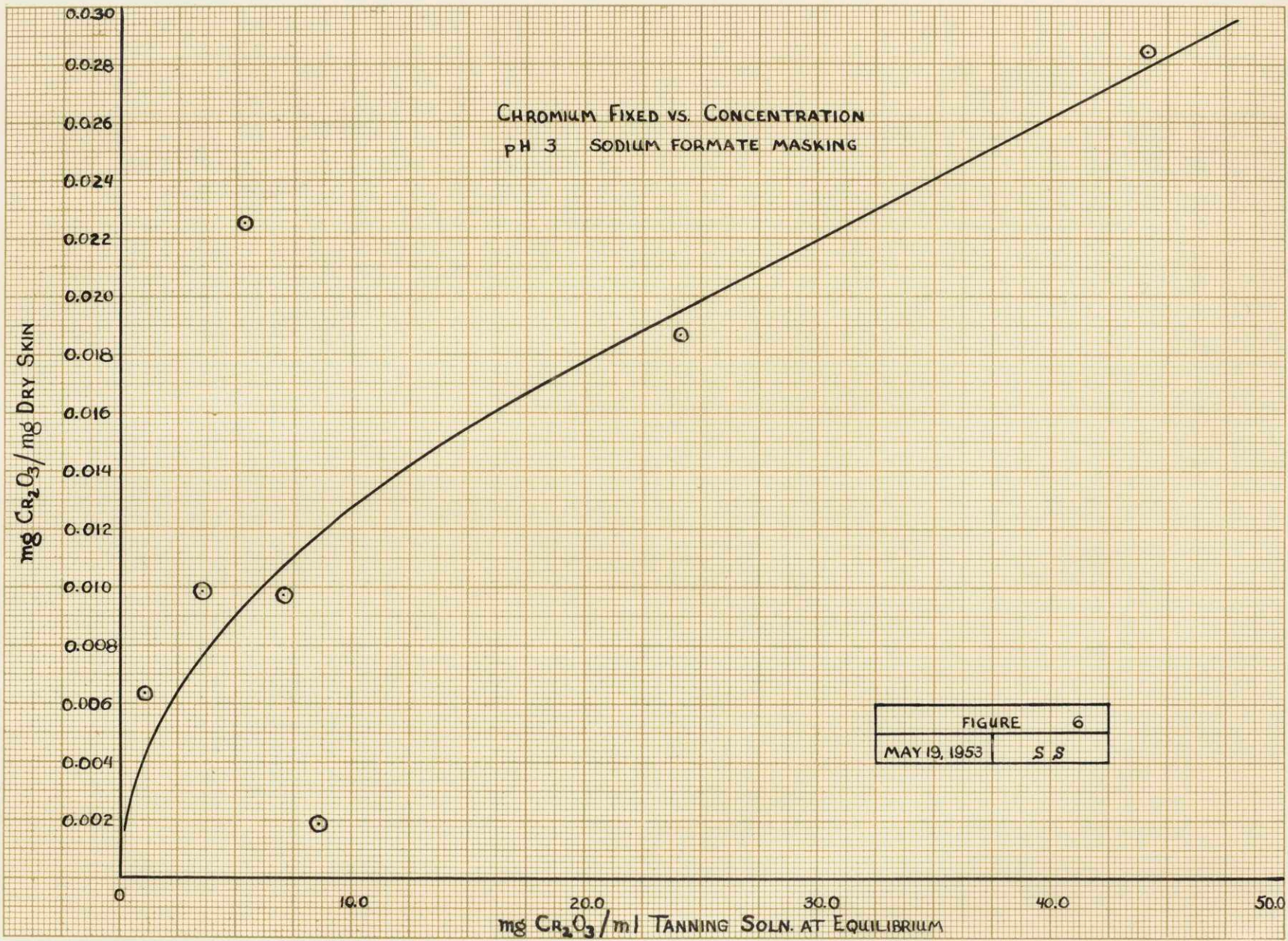


FIGURE 5	
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V. DISCUSSION OF RESULTS

A. TANNING

Distilled Volan--The best tanned leather samples were obtained by the use of distilled Volan with 10% sodium formate (based on weight of 30% Volan) as masking agent. The pH of the liquors was 4.0 ± 0.5 for all twelve runs. Due to the buffering action of sodium formate, the pH did not vary substantially during tannage.

All samples had good "feel" except those tanned in the very low chrome concentration liquors, which were somewhat boardy. The shrinkage temperatures ranged from 84°C to 99°C . The best shrinkage temperature, which was 99°C for three minutes, was obtained for the sample tanned at an equilibrium chrome concentration of $15.2 \text{ mg Cr}_2\text{O}_3/\text{ml}$ liquor.

Leather tanned in very high and very low chrome concentrations did not give as high shrinkage temperatures as those tanned at intermediate concentrations. In the latter case, not enough chromium was fixed on the skin to provide adequate tannage. At the high concentrations, the tanning process was probably too rapid, causing over-tannage at the surface, which prevented good penetration of complex chrome molecules into the center of the sample.

Between chrome concentrations of 30 and $44.5 \text{ mg Cr}_2\text{O}_3/\text{ml}$, the chrome fixation increases more with increasing liquor

concentration than at the lower concentrations. The reason for this is probably due to the method by which the alcohol was distilled from the Volan. In the liquor preparation, all samples were heated until the alcohol was distilled off rather than for a constant period of time. Since the higher chrome concentration liquors had larger amounts of Volan, these were necessarily heated longer to distill all the alcohol. It is known that polymerization of the chrome complex occurs during heating, and that the degree of polymerization increases with the amount of heating. Therefore, the higher chrome concentration liquor was made up of higher molecular weight polymers which gave greater chrome deposition. But because more chromium was deposited on the hide, it does not necessarily follow that the hide was well tanned. Most of the chromium may have been deposited on the hide surface while may have been undertanned.

Volan not distilled--Volan which did not have the alcohol boiled off did not tan leather as well as the distilled Volan. The samples showed shrinkage temperatures between 85 and 92°C and were somewhat more boardy. This is attributed to the fact that the isopropanol, which is a stabilizer as well as a solvent for the chrome complex, prevented hydrolysis and in turn polymerization.

When runs were made at a pH of 3.0 or lower, the chrome fixation was very small. From inspection of the leather samples, it was evident that very little chrome was picked

up by the hide. The leather was very stiff, showed signs of considerable shrinkage upon drying, and was translucent.

This condition was due to the acidity of the liquor and lack of masking agent which caused the skin to undergo a considerable degree of swelling. The swelled skin did not permit enough penetration of chrome complex molecules into the interior. Upon drying, the collagen fibres coalesced, giving a translucent, boardy leather. These samples did have high shrinkage temperatures (90°C) for leather showing little chrome fixation; however, this is attributed to the fact that the leather was initially in a shrunken condition.

Volan with sodium chloride as masking agent--Sodium chloride used as a masking agent, in liquors of pH 3 or lower, showed more chrome fixation than when sodium formate was used at the same pH. Although the chrome fixation closely paralleled that when sodium formate was used at a pH of 4.0 ± 0.5 , the samples masked with sodium chloride were more boardy and did not have a bluish grey color, but appeared brownish.

Three runs were made using Volan without masking agents. The leather tanned in this manner showed little chrome fixation even at high chrome concentrations. Although the leather was not translucent, it was very boardy.

B. Errors in chrome analysis

The probable error in the results of this investigation

is quite high due to the endpoint in titration for iodine with thiosulfate which is the most significant source of error. For the runs which were made in duplicate, it was found that the probable error in chrome fixation ranged from 5 to 20%.

C. Coating

It is evident from weighings that styrene was deposited in the leather. This styrene was probably in the form of polystyrene rather than a copolymer of styrene and methacrylate.

There is evidence, however, of good adhesion of polystyrene to the leather. A sample of this sort was obtained by placing a piece of leather in freshly distilled styrene and allowing it to stand for about 10 hours in an oven at 50°C. This was sufficient time for the styrene to polymerize. Although the coating of polystyrene was about $\frac{1}{4}$ " thick and cracked when the sample was bent, there was no tendency for the polystyrene to become separated from the leather. When a considerable force was applied in attempt to separate the polystyrene from the leather, a thin layer of leather ripped off with the polystyrene. However, upon placing this sample in benzene, all the polystyrene dissolved.

When a solution of polystyrene in benzene was applied to a leather sample and then dried at 50°C, the layer of polystyrene could be easily separated from the leather.

When low molecular weight styrene was used, it was easier

for the styrene molecules to diffuse through the leather fibres. Upon polymerization, these molecules were firmly set among the fibres rather than on the leather surface.

Emulsion polymerization of styrene--The highest styrene content was 21.5%, based on the weight of dry leather. This was obtained by treating the Volan tanned leather in an emulsion with ammonium persulfate catalyst at 50°C for 45 minutes. Upon extraction with benzene, this sample showed a styrene content of 12.4%. Although this sample was placed in hot benzene, it is not believed that the sample was in contact with benzene long enough to extract all of the styrene. When a leather sample was treated with in an emulsion with benzoyl peroxide catalyst, the styrene content was found to be 1.88%. This sample had an identical chrome fixation as that in the sample described above, and was subjected to the same conditions for the same length of time.

Samples treated in an emulsion with a combination catalyst of ammonium persulfate and benzoyl peroxide, showed styrene contents of 6.75 and 4.35%. These samples were subjected to 80°C for 45 minutes.

All samples except the first were soaked in benzene for 6-8 hours and showed no styrene content after extraction.

It is known that styrene from the emulsions penetrated the leather because the leather became translucent during treatment. Evidently the refractive index was such that light could pass through the leather when it was wet with styrene.

After the treated samples were dried, they appeared greenish gray in color and were more boardy than the untreated samples. The grain in the treated samples showed up better than it did in the untreated leather.

Polymerization under pressure and elevated temperature

Samples of leather not treated with styrene, when subjected to 2000-4000psi and 120°C were found to change from a blue grey to a green color. Furthermore, when these samples were bent, the surface was found to crack. These samples paralleled samples treated with styrene in appearance although there was no styrene on the plates when they were subjected to pressure and heat.

Styrene content of leather was found to be 11.7 and 8.68% for samples treated with bulk styrene and then subjected to pressure. The higher styrene content was found in a leather sample with 4.45% Cr₂O₃ fixed. When the samples were placed in benzene, it was found that all the styrene was extracted.

Leather that had styrene deposited from emulsion first and then pressed was found to be more flexible than leather treated with bulk styrene. The color of the leathers after treatment by either method were identical in appearance being dark green in color.

All samples after being treated and subjected to pressure were found to be impermeable to water.

VI. CONCLUSIONS

Good leather, the quality of which depends on the conditions at which tanning is carried out, may be obtained by the use of Volan. The best leather results when the Volan is polymerized, polymerization being accelerated by raising the pH and heating, before tanning is attempted.

Masking agents and pH are important factors for proper tannage by the use of Volan. Sodium formate is a suitable masking agent when used at a pH of about 4. At pH's lower than 4, sodium chloride is a better masking agent.

Styrene does not copolymerize with the methacrylate of the chrome complex probably because oxygen inhibits such a polymerization. However, styrene may be deposited in the leather either by emulsion or by bulk treatment. Styrene deposited in this manner adheres well to Volan tanned leather.

VII. RECOMMENDATIONS

When leather is to be tanned by the use of Volan, it is recommended that 1. isopropanol be distilled off before the liquor is made up; 2. sodium formate be used as a masking agent with about 10% (based on the weight of 30% Volan) being added; 3. the pH of the liquor be kept between 4 and 5; 4. the chrome concentration of the liquor be between 15.0 and 30.0 mg Cr_2O_3 /ml liquor for good tannage.

Further work should be done to determine the effect of the length of time Volan is heated on the chrome fixation in leather.

Since oxygen probably has a tendency to inhibit copolymerization, it is recommended that leather be treated with styrene emulsions immediately after tannage and neutralization to permit only a minimum time of contact with free oxygen. Oxygen should be expelled from the emulsion by bubbling nitrogen through it.

The possibility of using other vinyl or allyl compounds to coat Volan leather should be investigated. Also, chrome complexes with reactive groups other than the methacrylate might be suitable for tanning leather to provide a better bonding with reactive compounds.

APPENDIX

VIII. APPENDIX

A. Details of Procedure for Tanning

The types of liquors used in this investigation to tan leather were:

1. Volan and sodium formate
2. Volan and sodium chloride
3. Volan without masking agents
4. Chromium sulfate and sodium chloride

Solutions were made up in 250 or 100 ml lots. The procedure used in analysis for chromium is as follows:

1. With the use of a pipette, 5 or 10 ml samples were extracted from the liquor.
2. To these solutions, about 4 g of Na_2O_2 was added.
3. The solutions were boiled for 20 minutes and allowed to cool.
4. The solutions were neutralized with concentrated HCl.
5. After the solutions cooled, 20 ml of 10% KI was added.
6. The liberated iodine was titrated with 0.04642 N sodium thiosulfate.

Tanning was carried out at room temperature for 24 hours in 750 ml glass bottles which were placed in a shaker to provide constant agitation.

The pH of solutions was determined with Hydrion Paper which could be read to an accuracy of 0.5 pH units.

After tannage, the leather samples were washed in water to remove residual liquor and then placed in a solution of sodium bicarbonate to neutralize the leather. The leather, after neutralization, was washed again and stretched out by tacking to a board. The stretched sample was then placed in an oven to dry at 50°C . The dry sample was weighed.

A small sample (about $2 \times \frac{1}{2}$ ") was clamped in the upper part of the shrinkage temperature apparatus (fig. 1) and the water was heated until the sample began to shrink. The temperature was increased at a rate of about 4°C per minute.

B. Details of Procedure for Coating

In this investigation, styrene was polymerized on the leather by means of emulsions and by treatment under pressure and temperature. Emulsions were made up as follows:

1. The styrene, which contained an inhibitor, was distilled.

2. The styrene was emulsified in water by means of agitation in a centrifugal pump for about 2 minutes.

Styrene (50 g) was emulsified with 100 g of water, sodium oleate (0.5-1.0 g) being used as a stabilizer. The catalysts (benzoyl peroxide and ammonium persulfate) were added in 0.5 g quantities. Benzoyl peroxide was dissolved in the styrene before emulsification while ammonium persulfate was dissolved in water. Runs were also made using combinations of both catalysts.

As soon as an emulsion was made, a piece of leather (about 1 g) was placed in a beaker of the emulsion. The sample was then allowed to stand in the emulsion at a constant temperature of 50°C for 45 minutes. After this time, it was taken out of emulsion and allowed to dry.

When polymerization was carried out under pressure and elevated temperature, the procedure was as follows:

1. About 0.5 g of benzoyl peroxide was dissolved in 20 ml of freshly distilled styrene.
2. The leather sample was immersed in the styrene.
3. The sample was then placed between 4"x4" steel plates, the edges of which were taped together to prevent evaporation of the styrene at high temperatures.
4. The plates were then placed between the faces of a hydraulic press and the sample was subjected to a pressure of 2000-4000psi and temperature of 120°C for about 20 minutes.
5. The sample was quickly cooled in cold water.

Dry samples which had previously been treated in an emulsion were also subjected to temperature and pressure.

Styrene content was determined by weighing the oven dried leather before and after polymerization. Styrene was extracted from the leather with benzene.

The coated samples were tested for water proofness. This was done by fastening a sample between the disks of the apparatus shown in fig. 2 and filling the column with water. If the samples were not water proof, water would be seen to flow from the bottom.

C. Sample calculations

The following are sample calculations for a run made using distilled Volan.

1 ml 0.04642N $\text{Na}_2\text{S}_2\text{O}_3 \rightleftharpoons 1.1758 \text{ mg Cr}_2\text{O}_3$.

$154.62 \pm 1.33 \text{ ml S}_2\text{O}_3^2-$ needed to titrate 5 ml sample of liquor before tanning.

$137.95 \pm 1.34 \text{ ml S}_2\text{O}_3^2-$ needed to titrate 5 ml sample of liquor after tanning.

90 ml of tanning liquor used.

$$(154.62 \pm 1.33 \text{ ml})(1.1758 \frac{\text{mg}}{\text{ml}}) = 181.6 \pm 1.56 \text{ mg} = 181.6 \pm 0.86\%$$

$$\frac{181.6 \pm 0.86\%}{5 \pm 0.1\%} = 36.3 \pm 0.96\% = 36.3 \pm 0.349 \frac{\text{mg}}{\text{ml}}$$

$$(137.95 \pm 1.34 \text{ ml})(1.1758 \frac{\text{mg}}{\text{ml}}) = 162 \pm 1.58 \text{ mg} = 162 \pm 0.97\%$$

$$\frac{162 \pm 0.97\%}{5 \pm 0.1\%} = 32.4 \pm 1.07\% = 32.4 \pm 0.347 \frac{\text{mg}}{\text{ml}}$$

$$(36.3 \pm 0.349) - (32.4 \pm 0.347) = 3.9 \pm 0.696 \frac{\text{mg}}{\text{ml}}$$

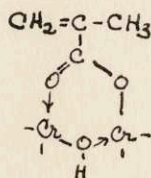
$$(3.9 \pm 0.696 \frac{\text{mg}}{\text{ml}})(90 \text{ ml}) = 351 \pm 62.6 \text{ mg Cr}_2\text{O}_3$$

$$(351 \pm 62.6 \text{ mg Cr}_2\text{O}_3) \left(\frac{206 \text{ gm/gm mol VOLAN FIXED}}{1528 \text{ gm/gm mol Cr}_2\text{O}_3} \right)^* = 476 \pm 85 \text{ mg VOLAN FIXED}$$

$$5915 \text{ mg LEATHER} - 476 \pm 85 \text{ mg VOLAN} = 5439 \pm 85 \text{ mg SKIN} = 5439 \pm 1.5\%$$

$$(351 \pm 18\% \text{ mg Cr}_2\text{O}_3) \div 5439 \pm 1.5\% = 0.0644 \pm 20\% \frac{\text{mg Cr}_2\text{O}_3 \text{ FIXED}}{\text{mg DRY SKIN}}$$

* VOLAN FIXED IS CONSIDERED TO BE



D. Literature Citations

1. McLaughlin, G. D., and Theis, E. R., The Chemistry of Leather Manufacture, 3rd ed, Reinhold Publishing Corporation, page 421, (1945).

2. Wilson, J. A., The Chemistry of Leather Manufacture, vol. II, Chemical Catalog Company, Inc., page 666-669, (1929).

3. "Volan", Product Information Brochure, E. I. DuPont De Nemours & Company, page 5, January 1950.

4. op. cit., Wilson, J. A., page 680.

5. op. cit., "Volan", page 4.