

# A STUDY OF DIFFUSION IN CHROME TANNING

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## ABSTRACT

Mathematical equations were obtained relating free and fixed chrome under equilibrium conditions. Using these empirical equilibrium equations and assuming that tanning involves simultaneous diffusion and reaction, with the reaction being reversible and very rapid as compared to diffusion, the appropriate partial differential equation was integrated by a numerical technique. Computer-derived results are presented for two different ratios of solution volume (in ml.) to pickled hide weight (in g.). Studies of the overall rate of penetration, as well as of the effect of agitation and temperature, indicate that particle diffusion is the rate-determining step. On the other hand, experimentally observed chrome distribution within the hide differs considerably from that predicted by theory. The most probable reason for the discrepancy observed is believed to be the fact that tanning not only follows the laws of kinetics but is also influenced by a combination of other factors which result in pH changes and concomitant changes in composition and basicity of the chromium complexes.

—x—x—

## INTRODUCTION

Studies in ion exchange, dyeing, and other heterogeneous systems have shown that the rate of reaction is controlled by one of the following three mechanisms: (a) diffusion of reactant through the "Nernst film" to the surface of the solid (liquid diffusion), (b) diffusion of the reactant through the solid (particle diffusion), and (c) chemical reaction at fixed sites within the solid.

There have been several attempts in the past to elucidate the mechanism which controls the rate of chrome tanning (1-3). However, in all these attempts the first two mechanisms were completely ignored and chrome tanning was considered to be a chemical phenomenon in which the chemical reaction is the rate-controlling step. These studies failed to describe the process satisfactorily; therefore, the effect of the diffusion mechanisms on tanning rate was investigated and is reported in this paper.

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According to the most recent theories of chrome tanning by Gustavson (4), the principal step involves introduction of carboxyl groups of collagen as ligands into cationic chrome sulfate complexes. Grassman and Stadler (5) showed that chrome tanning, unlike vegetable tanning, is not an instantaneous reaction. These authors reacted procollagen fibrils which had been pretreated with formaldehyde. From their data it is evident, however, that the pretreatment slowed down the reaction rate. Without pretreatment tanning probably proceeds at a much faster rate. Nayudamma and Ramaswamy (6) were able to remove 50 percent of chrome from tanned collagen with ethylenediaminetetracetic acid without affecting its shrinkage temperature. Their results indicate that, in addition to the reaction with carboxyl groups, adsorption and/or some nonspecific deposition of chrome inside the hide takes place which is reversible and probably quite rapid.

Commercially, tanning is carried out by contacting hides with a finite amount of tanning liquor. Thus, diffusion of chrome into the hides proceeds from a variable surface concentration. In this respect tanning is similar to dyeing, which was treated mathematically by Crank (7), who used a numerical method of integrating the appropriate partial differential equation. Crank assumed that dyeing is a reversible process, that particle diffusion is the rate-controlling mechanism, that deposition is rapid compared with diffusion, and that a mathematical relationship between the concentrations of deposited and of free dye can be obtained. In this paper the applicability to chrome tanning of Crank's method of solution is investigated, since chrome tanning is at least partially reversible, and the reaction or deposition of chrome may be rapid as compared to diffusion. Also, McLaughlin *et al.* (8) showed that the relation of fixed and unfixed chrome at equilibrium can be described by an equation resembling the Freundlich adsorption isotherm.

The tanning operation, as carried out in practice, is a dynamic process in which the hide pH and possibly even the basicity of the chrome sulfate undergo continuous changes. In this study these changes were minimized by using a hide pH of about 3.0 to 3.2, which is approximately equal to that of the chrome solution used. To simplify the mathematical treatment, the grain and flesh layers of the hide were removed. The remaining hide corium that was used was fairly uniform in thickness, but it is known to differ in fiber structure over the area of the same hide, as well as from hide to hide. It also undergoes physical and chemical changes during storage. To minimize the effect of the fiber structure variability on the diffusion rate studies, the hide corium was frozen, and small samples from the same areas of the same hide were used in any given series of experiments.

## EXPERIMENTAL

### Preparation of Hides for Tanning

In all experiments the hide samples to be tanned were prepared the same way. Limed flesh splits of cowhide, which were obtained from a local tannery, were

re-split to ensure complete removal of subcutaneous tissue. Samples of this hide corium were frozen with dry ice and stored at about 10°F. They were thawed immediately before use by exposure to ambient temperatures, then washed three times for 20 minutes with fresh distilled water (using eight ml. water per one g. of hide) in a large jar which was shaken by means of a wrist-action shaker (Burrel†). This jar was submerged in a constant temperature bath at 85°F. The shaker speed was about 100 strokes per minute. Bating was carried out by placing 50 g. of washed hide in a one-quart jar containing 228.5 g. distilled water, 2.5 ml. of 3.5 percent HCl solution, 19 ml. of four percent boric acid solution, and 0.075 g. Oropon N (Rohm and Haas). The jar was then shaken for two hours as during washing, using a constant temperature bath of 85°F. and a shaker speed of 100 strokes per minute. Pickling was performed by adding 180 ml. water, 12.5 g. table salt, and 12.5 ml. of 1 M H<sub>2</sub>SO<sub>4</sub> solution to a one-quart jar, mixing the contents, and then placing 50 g. of hide in the solution and pickling it overnight for about 16 hours at 85°F. with shaking. The pickled hide pH was determined by measuring the pH of the equilibrium solution.

### Tanning Studies

In all runs Tanolin R (Diamond Shamrock Chemical Co.†) was used. It has a basicity of 34-37 percent. A stock solution containing approximately eight percent Cr<sub>2</sub>O<sub>3</sub> was prepared from the commercial powder by dissolving it in boiling water with stirring. The stock solution was stored at least one month before use. The conditions of tanning were varied from run to run.

#### *A. Equilibrium Distribution of Chrome at Different Bath Ratios*

To obtain distribution equations relating the amount of reacted and unreacted chrome, three series of experiments were performed using different bath ratios. The bath ratio as used in this work is the ratio of the solution volume (in ml.) to pickled hide weight (in g.). In the first series the bath ratio was 13.3:1. Solutions with varying amounts of Tanolin R were first prepared. Then 7.5 g. of pickled hide corium, which had a pH of 3 and was cut into 1/8 in. squares, was added to glass jars containing 100 ml. of these solutions. Reaction was carried out for one month at 95°F. The jars were shaken by hand once every day. After tanning, the solutions were separated by pouring the contents of each jar into a funnel containing coarse filter paper. Chrome and protein analyses were performed on the hide samples after they had been dried and comminuted. The equilibrium solutions were analyzed for chrome.

The second series was conducted at a bath ratio of 8:1. 6.25 g. of 1/8 in. hide squares at pH 3.09 were added to 50 ml. solutions containing varying amounts of Tanolin R. All the other operating conditions were the same as in the first series.

†Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

In the third series of experiments the bath ratio was 1:1. The pH of the hide was 3.14. Twenty-g. samples of hide corium were reacted with 20 cc. Tanolin R solutions varying in chromic oxide concentration up to eight percent. The reactions were carried out for one month in glass jars which were immersed in a constant temperature bath at 95°F. and were shaken by means of a wrist-action shaker (Burrel) at 50 strokes per minute. Each of the reacted hide samples was then divided into two portions. One portion was pressed for one minute in a hydraulic press using 20,000 p.s.i.g. pressure. The unpressed hide was analyzed for chrome, as were the reaction solution, the pressed hide, and the solution that was pressed out.

### *B. Kinetics of Tanning*

1. *"Interruption test."* Three hide corium slabs were reacted for two, six, and 24 hours without interruption. Another three slabs were reacted for two hours, taken out of the solution and equilibrated in closed jars for two days, then returned to the same solutions and reacted for an additional four, eight, and 22 hours, respectively. All slabs were 0.150 in. thick. The bath ratio in all runs was 1:1, the starting chromic oxide concentration was two percent, the Burrel shaker speed was 112 strokes per minute, the reaction temperature was 95°F., and the pH of the pickled hide was 3.02.

2. *Effect of agitation.* Two methods of agitation were studied. The first method involved the use of the Burrel wrist-action shaker to shake the jar containing the hide and the tanning solution horizontally and in the direction of the cylindrical axis of the jar. This was the method used in practically all the experiments reported in this paper. A set of experiments using this method of agitation was carried out by tanning 0.145 in. thick corium slabs for two hours at shaker speeds ranging from 0 to 150 strokes per minute, a bath ratio of 8:1, and a hide pH of 3.2.

The other method of agitation was used to simulate more closely the tumbling which occurs inside drums during commercial tanning. It involved rotating the jar containing the hide slab and the tanning solution in such a way that the slab tumbled along its cylindrical axis. A small stainless steel weight was attached to the hide to prevent it from adhering to the jar wall. An experiment was conducted using this agitation method at a bath ratio of 1:1. The slab thickness was 0.105 in., the hide pH was 3.14, the tumbling speed ranged from 0 to 50 revolutions per minute, and the reaction time was four hours.

In all agitation experiments, the starting chromic oxide concentration was two percent and the temperature was 95°F.

3. *Effect of time on tanning rate.* One series of experiments was carried out to study the variation in tanning rate with time. In these experiments the reaction temperature was 95°F., the Burrel wrist-action shaker speed was 110 strokes per minute, and the starting chromic oxide concentration in the solution was

two percent. The bath ratio was 8:1, and the hide slabs were 0.196 in. thick and had a pH of 3.3. The reaction times ranged from two hours to one month. The hide slabs were lifted from the solutions, blotted, and then analyzed.

4. *Stratigraphic distribution of chrome.* Three 0.19 in. thick hide slabs at pH 3.5 were reacted with two percent chrome solutions in separate glass jars, using a bath ratio of 1:1. The reaction temperature was 95°F., and the Burrel shaker speed was 112 strokes per minute. Reaction was terminated after four, 18, and 168 hours. The samples were quickly blotted and cut into five thin slices with a 30 in. Randall band knife splitter. Each of the slices was then analyzed for chrome.

5. *Effect of temperature.* Hide slabs of various thicknesses were reacted for two and 720 hours at temperatures ranging from 75 to 125°F. The hides and the solutions were preheated to the desired temperature before reaction was started. The pH of the pickled hide was about 3.1, the bath ratio was 8:1, the starting chromic oxide content of the solution was two percent, and the shaker speed was 116 strokes per minute.

### Chemical Analyses

At the end of each of the experiments described above, the wet hide slabs were cut into small squares, dried in a gravity-convection oven for one day at 80°C., weighed, ground in a Wiley Mill by being passed twice through a #20 screen, then re-dried in a vacuum oven overnight at 70°C., and finally analyzed for chrome and protein. The protein analyses were performed by the Kjeldahl method. Chrome analyses on the tanned hide corium and the chrome solutions were made by the atomic absorption method described by DellaMonica *et al.* (9).

## RESULTS AND DISCUSSION

### A. Equilibrium Distribution of Chrome

Tanning involves simultaneous diffusion and reaction of chrome complexes within the hide. The study of the kinetics of tanning is difficult, primarily because there is no direct method of measuring the extent of the reaction. By chemical analysis it is impossible to distinguish between the free chrome in the interstices of the hide and that which has reacted with, *e.g.*, the carboxyl groups of the hide. Shrink temperature measurements are used by tanners as a measure of the extent of the reaction. But this test is not accurate enough for use in kinetic studies. It involves heating a piece of hide and determining the temperature at which it contracts. It is quite possible that, in a freshly tanned hide, some or most of the reaction might occur during this heating, and an experimental sample at pH of 3.0 will always show a high shrink temperature as long as the chrome is well distributed throughout the hide piece. Chrome complexes used in tanning precipitate at a pH above 4. Washing a tanned hide piece with tap water is, there-

fore, not going to remove all the unreacted chrome; some of it may precipitate inside the hide. On the other hand, washing the hide with acid water may remove some of the fixed chrome because the reaction may be reversible.

Table I gives the results obtained in the third series of tanning equilibrium experiments, which were carried out at a bath ratio of 1:1 and involved pressing of hides after tanning. This table shows that the chrome concentration of the external solution is approximately the same as in the solution pressed out of the hide when hide is reacted with chrome for a period of time long enough to

TABLE I  
CHROME CONTENT OF INTERNAL AND  
EXTERNAL SOLUTIONS AT EQUILIBRIUM\*

Run No.	Final pH of Tanning Solution	% Cr <sub>2</sub> O <sub>3</sub> in Hide (Collagen Basis)	% Cr <sub>2</sub> O <sub>3</sub> in Tanning Liquor	% Cr <sub>2</sub> O <sub>3</sub> in Internal Solution†
128-5	3.16	1.49	.0114	.0017
-6	3.10	2.02	.0152	.0170
-7	3.06	2.53	.0192	.0195
-8	2.96	3.70	.0359	.0383
-9	2.90	4.34	.0593	.0594
-10	2.85	6.87	.171	.1746
-11	2.95	9.46	.471	.502
-12	2.98	12.17	1.18	1.21
-13	2.99	16.56	3.40	3.45

\*Conditions of reaction: 95°F. and a bath ratio (ratio of solution volume, in ml., to pickled hide weight, in g.) of 1:1.

†Internal solution is the solution pressed out of the hide with a hydraulic press.

establish equilibrium. Consequently, if the concentration of chrome in the external solution is known, the amount of free chrome associated with the water inside the hide can be calculated. By subtracting this amount of chrome from the total chrome present in the hide, the amount fixed can be obtained. This type of calculation is shown in Table II for the first series of experiments, in which the bath ratio was 13.3:1. Columns 1 to 4 of this table give experimental results which were used to calculate the other two columns. Columns 5 and 6 give the free and reacted chrome, respectively, per g. of collagen. From these last two columns it can be readily seen that very little free chrome is present in the hide when the chrome concentration in the external solution is low. As the chrome concentration is increased, the amount of free chrome inside the hide increases continuously, while the amount of reacted chrome reaches a maximum value and then drops rapidly with increase in chrome concentration of the chrome liquor. This phenomenon has been observed previously. Gustavson (10) states that this

TABLE II  
FREE VS. REACTED CHROME AT EQUILIBRIUM\*

Column 1	2	3	4	5†	6‡
g. Cr <sub>2</sub> O <sub>3</sub> per ml. Tanning Solution, Z <sup>∞</sup>	Total g. Cr <sub>2</sub> O <sub>3</sub> per g. Collagen, y	g. Water per g. Dry Hide	g. Collagen per g. Dry Hide	g. Free Cr <sub>2</sub> O <sub>3</sub> per g. Collagen, C <sup>∞</sup>	g. Reacted Cr <sub>2</sub> O <sub>3</sub> per g. Collagen, S <sup>∞</sup>
.0000061	.0167	2.172	.9575	.000014	.0167
.0000302	.0304	2.000	.9258	.000065	.0305
.0000733	.0420	1.900	.9014	.000155	.0418
.00081	.0916	1.586	.8076	.001590	.0916
.00186	.1117	1.514	.7797	.003610	.1081
.00304	.1265	1.430	.7761	.005600	.1209
.00462	.1422	1.368	.7305	.008650	.1336
.00778	.1548	1.419	.7391	.014936	.1398
.01104	.1628	1.346	.7074	.021000	.1418
.01953	.1607	1.346	.7135	.036850	.1238
.03129	.17525	1.250	.6729	.058125	.1171
.04484	.1838	1.209	.6668	.081320	.1025
.07338	.2105	1.111	.6086	.133970	.0765

\*Bath ratio 13.3:1.

†Column 5 = Column 1 × Column 3/Column 4.

‡Column 6 = Column 2 - Column 5.

maximum zone is a function of the concentrations of chromium and neutral sulfate. This author also points out that the solution inside the hide consists of: (a) bound water held by the protein, which amounts to about 20 percent of the weight of collagen, and (b) free water. Free chrome, according to Gustavson, is present only in the free water. The relative amounts of reacted and unreacted chrome were, therefore, recalculated by considering the presence of bound water. They were very similar to those given in Table II.

A plot of the logarithm of the total chromic oxide present inside the hide vs. the logarithm of the chromic oxide concentration of the equilibrium liquor can be mathematically fitted by two empirical equations of the following form:

$$y = R_1 Z^{\infty n_1} \quad (1a)$$

and

$$y = R_2 Z^{\infty n_2} \quad (1b)$$

where y = g. Cr<sub>2</sub>O<sub>3</sub> per g. of collagen, at equilibrium,  
Z<sup>∞</sup> = g. Cr<sub>2</sub>O<sub>3</sub> per cc. outer solution, at equilibrium,  
and R<sub>1</sub>, R<sub>2</sub>, n<sub>1</sub>, n<sub>2</sub> are constants.

Equation (1a) is valid in the lower concentration range and Equation (1b) in the higher. This is shown in Figure 1 for the data of the second and third series of experiments, which were carried out at bath ratios of 8:1 and 1:1,

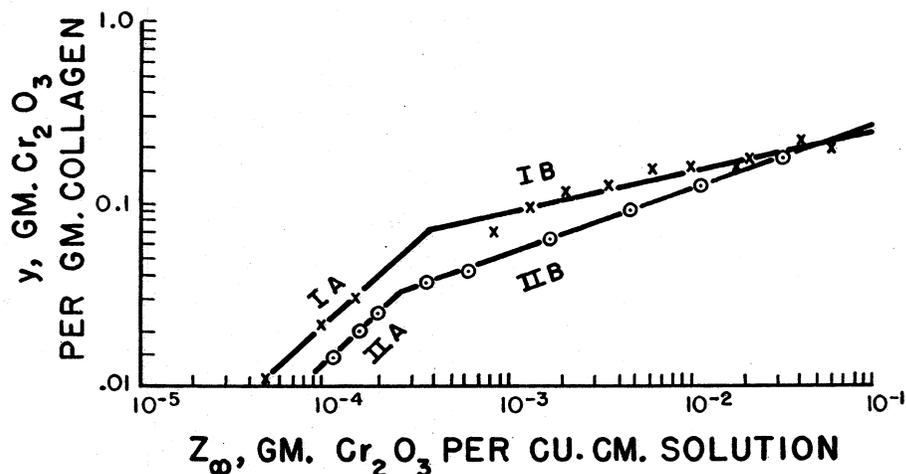


FIGURE 1.—Logarithmic plots of equilibrium chrome content in hide and solution.

IA and IB. Bath ratio 8:1. Equations of curves

$$\text{IA: } y = 108.65 Z^{\infty 0.92628}$$

$$\text{IB: } y = 0.40121 Z^{\infty 0.21636}$$

IIA and IIB. Bath ratio 1:1. Equations of curves

$$\text{IIA: } y = 194.23 Z^{\infty 1.0443}$$

$$\text{IIB: } y = 0.54387 Z^{\infty 0.33426}$$

respectively. Using the method of least squares, the following equations were found to fit the data of the second series of experiments (8:1 bath ratio):

$$y = 108.65 Z^{\infty 0.92628} \text{ for } Z^{\infty} < 0.00038 \quad (2)$$

and

$$y = 0.40121 Z^{\infty 0.21636} \text{ for } Z^{\infty} > 0.00038$$

In the third series of experiments (1:1 bath ratio) the equations were

$$y = 194.2 Z^{\infty 1.0443} \text{ for } Z^{\infty} < 0.00026$$

$$\text{and } y = 0.54387 Z^{\infty 0.33426} \text{ for } Z^{\infty} > 0.00026 \quad (3)$$

This type of plot was first prepared by McLaughlin *et al.* (8), who concluded that tanning follows the Freundlich adsorption law. However, these authors obtained only one line instead of two because they limited their experiments to relatively high chrome concentrations.

Rewriting Equation (1a) using different terminology one obtains

$$y = R_1 \left( \frac{C^\infty}{Q} \right)^{n_1} \quad (4)$$

where  $\frac{C^\infty}{Q} = \text{g. Cr}_2\text{O}_3 \text{ per cu. cm. outer solution,}$

$C^\infty = \text{g. unreacted Cr}_2\text{O}_3 \text{ per cu. cm. hide,}$

$Q = \text{cu. cm. solution per cu. cm. hide.}$

$Q$  is a partition factor showing that the mass concentration of chrome within the hide is  $Q$  times that in solution.

Multiplying both sides of equation (4) by  $A = \text{g. collagen per cu. cm. of hide,}$  one obtains

$$yA = R_1 A \left( \frac{C^\infty}{Q} \right)^{n_1} \quad (5)$$

where  $yA = \text{g. Cr}_2\text{O}_3 \text{ per cu. cm. hide, at equilibrium.}$

As mentioned previously, the solution pressed out of the hide has the same chrome content as the exterior solution when equilibrium has been established. Consequently, Equation (1a) becomes finally

$$C^\infty + S^\infty = yA = R_1 A \left( \frac{C^\infty}{Q} \right)^{n_1} \quad (6a)$$

or

$$S^\infty = R_3 C^\infty^{n_1} - C^\infty$$

where  $C^\infty = \text{g. unreacted Cr}_2\text{O}_3 \text{ per cu. cm. hide,}$

and  $S^\infty = \text{g. reacted Cr}_2\text{O}_3 \text{ per cu. cm. hide.}$

Equation (1b) similarly yields

$$S^\infty = R_4 C^\infty^{n_2} - C^\infty \quad (6b)$$

It is interesting to point out that Equation (6b) predicts the maximum value or zone of reaction of chrome observed and calculated in Table I.

## B. Kinetics of Tanning

Cursory observation of tanning indicates that it involves simultaneous diffusion and reaction of chrome complexes. For diffusion accompanied by reaction, a general equation of the following type applies:

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta X^2} - k[C]^\alpha [\text{collagen}]^\beta \quad (7)$$

where [collagen] = the number of unreacted groups in collagen

C = the chrome concentration in collagen

$\alpha$  &  $\beta$  = constants.

Equation (7) is nonlinear and not amenable to formal solution. Lack of information about  $\alpha$  and  $\beta$  makes this equation nonsolvable by any technique. Only an approximate solution has been obtained for a bimolecular reaction where both  $\alpha$  and  $\beta$  are equal to 1 (12). If it is assumed that tanning is reversible and much faster than diffusion, the following equation should apply:

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta X^2} - \frac{\delta t}{\delta S} \quad (8)$$

where C = concentration of chrome inside the hide which is free to diffuse,

S = reacted chrome,

both C and S being expressed as amount per unit volume of hide.

To solve Equation (8) a relationship between S and C must be known. If the reaction of chrome complexes with collagen is very rapid compared to the diffusion process, local equilibrium can be assumed to exist between S and C, and Equations (6a) and (6b) are applicable. Under these local equilibrium conditions the subscripts in these equations may be dropped. Equation (6a), for example, may then be rewritten as follows:

$$C + S = R_1 A \left( \frac{C}{Q} \right)^{n_1}$$

But these equations are nonlinear; hence, it is not possible to get an exact solution of the differential equation (8). A numerical method which involves changing the differentials to finite differences has been described by Crank (7). By following Crank's procedure, Equation (8) was solved for the complicated case of reaction equilibria described by two nonlinear equations. The diffusion coefficient D was assumed to be constant. A slab of hide was assumed to occupy the space  $-L \leq X \leq +L$ , while the chrome solution, which was of limited extent, was assumed to occupy the spaces  $-L-a \leq X \leq -L$ ,  $L \leq X \leq L+a$ . The concentration of chrome in the solution was initially  $Z_0$ , while initially the slab was free from chrome. The boundary condition at  $X = \pm L$  and any given time was thus

$$\frac{aC}{Q} + \int_0^L (C + S) dX = \frac{aC_0}{Q} \quad (9)$$

where  $C_0 = Z_0 Q$  and  $C = ZQ$ .

The initial condition was

$$C = 0 \text{ at } t = 0 \text{ } (-L < X < +L). \quad (10)$$

To solve Equation (8) with the boundary condition (9) and the initial condition (10), reduced variables  $c = C/C_0$  and  $s = S/C_0$  were introduced,  $t$  was changed to  $\tau = Dt/L^2$ ,  $X$  was changed to  $x = X/L$ , the hide thickness  $L$  was divided into thin slices of thickness  $dx$ , and the time was divided into intervals  $d\tau$ .

The other details of the numerical solution are given by Crank (7). Solution of the finite difference equations was accomplished by the Gauss-Seidel iterative method. This method is applicable to the solution of simultaneous linear equations, whereas the finite difference equations to be solved are nonlinear, since the relationship between  $S$  and  $C$  is nonlinear. The usual Gauss-Seidel method was, therefore, modified by utilizing the interval halving method to calculate the roots of each of the finite difference equations. The computer program which was written to simplify the rather tedious calculations may be obtained from the authors. It was written in Fortran IV for an IBM 1130 digital computer.

Figure 2 gives calculated values of  $M_t/M^\infty$  vs.  $\tau = Dt/L^2$  for reactions carried out at bath ratios 8:1 (Curve I) and 1:1 (Curve II), when the total exhaustion of chrome from the tanning solution was 30 percent and 90 percent, respectively. In this figure  $M_t$  = total amount of chrome in hide at time  $t$ , and  $M^\infty$  = total amount of chrome in hide after an infinite reaction time. Figure 3 gives the calculated overall concentration,  $(C + S)/C_0$ , as a function of time and position for a bath ratio of 1:1 and 90 percent exhaustion of the tan liquor.

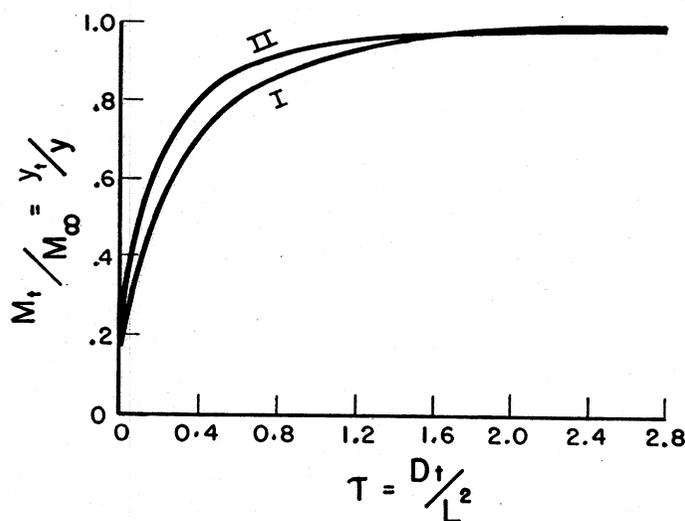


FIGURE 2.—Computer calculations of diffusion of chrome into a slab of thickness  $2L$ .

- I. 30 percent exhaustion of chrome from solution using bath ratio 8:1.
- II. 90 percent exhaustion of chrome using bath ratio 1:1.

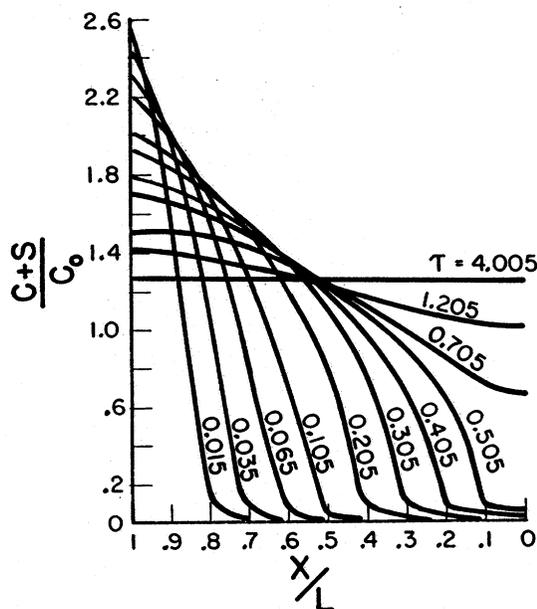


FIGURE 3.—Computer calculations of the overall concentration distribution of reacted and unreacted chrome for different  $Dt/L^2$  values, a bath ratio of 1:1, and 90 percent exhaustion of chrome at equilibrium. Numbers on curves are values of  $Dt/L^2$ .

It should be pointed out that Equations (6a) and (6b) are valid for equilibrium conditions, and in the integration procedure it was assumed that there is an immediate equilibrium established between S and C at all points within the hide. Consequently, the experimental data will be in agreement with the calculated results only if tanning is reversible and much faster than diffusion, although it does not necessarily have to be instantaneous.

The curves in Figure 2 can be used to determine the diffusion coefficient from experimental data. A hide piece is tanned for a prolonged time to obtain the value  $M^\infty$ . Another tanning is then carried out for a shorter time, yielding  $M_t$ . The ratio  $M_t/M^\infty$  is then calculated and the corresponding value of  $Dt/L^2$  is read from the appropriate graph in Figure 2. Since  $t$  and  $L$  are known,  $D$  can be immediately calculated.

In practice, of course,  $M_t$  and  $M^\infty$  values are not determined, since only a small sample of the hide is analyzed. If the chrome analyses are on collagen basis, however, then

$$\frac{M_t}{M^\infty} = \frac{y_t}{y} \quad (11)$$

where  $y_t$  = g.  $\text{Cr}_2\text{O}_3$  per g. of collagen after reaction time,  $t$ ,

and  $y$  = g.  $\text{Cr}_2\text{O}_3$  per g. of collagen after an infinitely long reaction time.

1. "Interruption test." The best technique for distinguishing between particle diffusion and film diffusion control is the so-called "interruption test" (13). In this test hide slabs were removed and allowed to remain out of contact with the solution for two days to allow the concentration gradient within the hide to level out. As can be seen from Figure 4, the rate of diffusion was found to be

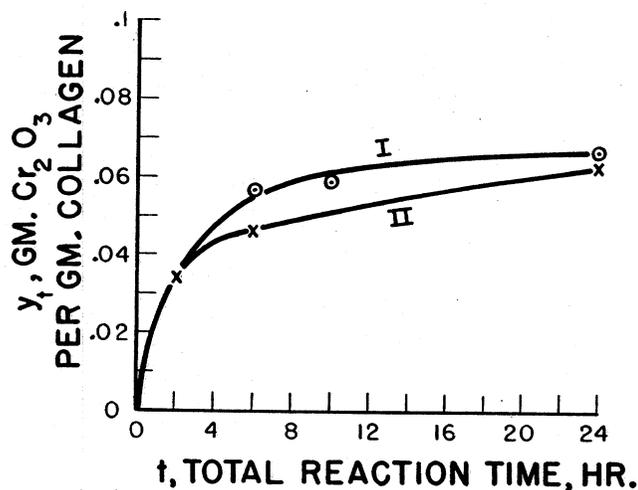


FIGURE 4.—"Interruption Test" to determine particle diffusion control.  
 I. After two hours, reaction was interrupted for two days.  
 II. Reaction without interruption.

considerably greater on reimmersion (Curve I) than in an identical experiment without interruption (Curve II). The result supports the conclusion that, in tanning, particle diffusion is the controlling mechanism. With film diffusion control no concentration gradient would exist and no effect on tanning rate would have been observed on reimmersion.

2. *Effect of agitation.* The reaction rate is sensitive to agitation if the process is influenced by liquid or film diffusion. From Tables III and IV, which give the experimental data and the calculated  $D$  values, it can be readily seen that in both methods of agitation the diffusivity increases with increase in the rate of agitation until a maximum value is reached. When using the wrist-action shaker and a bath ratio of 8:1, the maximum diffusivity was reached at about 100 strokes per minute. When tumbling a hide piece in a flask at a 1:1 bath ratio, the maximum diffusivity was reached at about 30 revolutions per minute. The difference in the maximum  $D$  values obtained by the two different methods of agitation is most probably due to the variability of the fiber structure of the different hide pieces which were used. Film diffusion may be considered to be negligible when the maximum diffusivity is reached. Particle diffusion is then the rate-controlling mechanism.

TABLE III  
EFFECT OF SHAKING ON TANNING RATE\*

Run No.	Reaction Time t (hr.)	Slab Thickness, 2L (in.)	Shaker Speed s.p.m.†	% Cr <sub>2</sub> O <sub>3</sub> (Collagen Basis) 100y <sub>t</sub> ‡	Diffusion Constant D·10 <sup>7</sup> (cm. <sup>2</sup> per sec.)
43-2	2	0.143	0	2.56	.8
44-15	2	0.146	30	3.09	1.7
46-1	2	0.140	70	2.91	1.4
48-1	2	0.149	70	2.87	1.5
49-1	2	0.149	90	3.56	2.1
47-1	2	0.141	100	4.10	2.6
47-2	2	0.140	100	4.52	3.5
45-1	2	0.149	150	3.94	2.4
45-2	2	0.151	150	3.67	2.2

\*Tanning rate represented by diffusion coefficient, D. Tanning conditions: 95°F., bath ratio 8:1, 30 percent exhaustion of chrome after one month, initial Cr<sub>2</sub>O<sub>3</sub> conc. in solution two percent.

†Strokes per minute using wrist-arm shaker.

‡100y = 14.125 percent (collagen basis) attained after one month of tanning.

TABLE IV  
EFFECT OF TUMBLING ON TANNING RATE\*

Run No.	Reaction Time t (hr.)	Slab Thickness, 2L (in.)	Tumbler Speed r.p.m.	% Cr <sub>2</sub> O <sub>3</sub> (Collagen Basis) 100y <sub>t</sub> ‡	Diffusion Constant D·10 <sup>7</sup> (cm. <sup>2</sup> per sec.)
133-2,0	4	.1053	0	4.46	1.6
-2,10	4	.1053	10	5.72	3.6
-2,30	4	.1053	30	5.74	3.7
-2,31	4	.1053	30	6.09	4.4
-2,50	4	.1053	50	6.01	4.2

\*Tanning rate represented by diffusion coefficient, D. Tanning conditions: 95°F., bath ratio 1:1, 90 percent exhaustion of chrome after one month, initial Cr<sub>2</sub>O<sub>3</sub> conc. in solution two percent.

‡100y = 7.96 percent Cr<sub>2</sub>O<sub>3</sub> (collagen basis) obtained after one month of tanning.

3. *Effect of time on tanning rate.* Table V gives a summary of experiments performed in which hide corium slabs were tanned for different lengths of time and the change in chrome content of the hide phase was determined. A bath ratio of 8:1 was used. The chrome content after one month of reaction was considered to be equal to  $y$ , the maximum concentration attainable. After this tanning time the exhaustion of the tanning liquor was 30 percent.

TABLE V  
EFFECT OF TIME ON TANNING RATE\*

Run No.	Reaction Time, t (hr.)	Slab Thickness 2L (in.)	% Cr <sub>2</sub> O <sub>3</sub> (Collagen Basis) 100y <sub>t</sub>	Diffusion Constant D · 10 <sup>7</sup> (cm. <sup>2</sup> per sec.)
21-2	2	.205	5.51	11.8
23-2	6	.197	5.72	3.9
24-3	17	.193	7.63	2.3
19-3	24	.218	7.98	2.3
22-2	26	.194	10.60	3.1
24-2	26	.190	10.90	3.1
24-1	48	.187	13.56	5.2
25-1	72	.189	11.90	1.7
23-1	97	.194	12.61	1.7
22-1	168	.190	13.70	1.6
58-3	720	.197	14.12†	

\*Tanning rate represented by diffusion coefficient, D. Tanning conditions: 95°F., bath ratio 8:1, 30 percent exhaustion of chrome after one month, initial Cr<sub>2</sub>O<sub>3</sub> conc. in solution two percent.

†Assumed to be equal to 100y, the equilibrium concentration.

Using Curve 1 of Figure 2,  $\tau = Dt/L^2$  values were obtained for each experimental  $M_t/M^\infty$  value. Note that  $y_t/y = M_t/M^\infty$  from Equation (11). Diffusion constants, D, were then calculated from the  $\tau$  values, using experimental t and L values. The diffusion constants thus obtained are summarized in the last column of Table V. The arithmetic average of the D values, equal to  $3.7 \times 10^{-7}$  sq. cm. per sec., was then used to make a plot of  $M_t/M^\infty$  vs. t with the help of Figure 2. This "theoretical" curve of  $M_t/M^\infty$  vs. t is shown in Figure 5 to pass through the experimental points. This fact again indicates that particle diffusion is the controlling mechanism during tanning. It is apparent, however, from Table V that diffusion of chrome complexes through hide is somewhat concentration-dependent, as the D values decrease with increase in time and in concentration within the hide.

4. *Stratigraphic study of chrome distribution.* Having calculated the diffusion coefficient, D, with the help of Figure 2, it is possible to obtain the chrome dis-

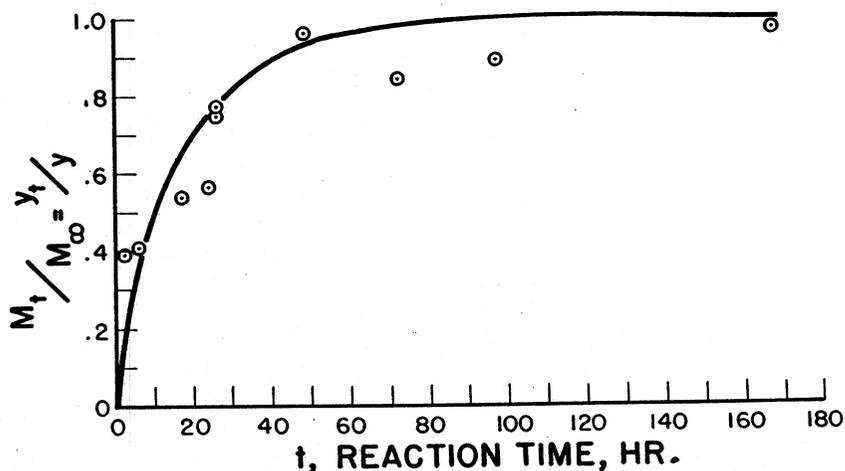


FIGURE 5.—Fractional attainment of equilibrium,  $M_t/M_\infty$ , as a function of time  $t$ . Theoretical line passed through experimental points. Operating conditions: Initial  $\text{Cr}_2\text{O}_3$  concentration in solution two percent, bath ratio 8:1, reaction temperature 95°F., 30 percent exhaustion of chrome from solution at equilibrium.

tribution at different times and positions within the hide by using Figure 3. To calculate  $y_t$  from  $(C + S)/C_0$  values the latter have to be multiplied by  $C_0 = Z_0Q$ , and divided by  $A$ , where  $Z_0$  is the initial chrome concentration in the solution,  $Q$  is a partition factor defined by Equation (4), and  $A$  gives the g. of collagen per g. of hide.

Figure 6 shows stratigraphic determinations of chrome penetration as plots of chrome content *vs.* distance from the surface for four, 18, and 168 hours of reaction. In this figure the crosses, circles, and triangles are experimental points for four, 18, and 168 hours of reaction, respectively. The three lines shown give the theoretical chrome distribution for these reaction times. To obtain the theoretical chrome distribution curves, an average diffusivity,  $D$ , of  $3.7 \times 10^{-7}$  sq. cm. per sec. was used. This  $D$  value is approximately equal to the values obtained in other experiments reported in this paper. Using this  $D$  value, the appropriate  $\tau$  values were calculated;  $(C + S)/C_0$  values were then read off from Figure 3, from which  $y_t$  values were finally calculated by multiplying by the factor  $Z_0Q/A$ . In this experiment  $Z_0$  was equal to 0.02 g.  $\text{Cr}_2\text{O}_3$  per g. of solution,  $Q$  was determined experimentally to be equal to 0.7125 cu. cm. solution per cu. cm. of hide, and  $A$  was determined to be approximately 0.324 g. collagen per cu. cm. of hide. Actually, the authors used in their calculations the more detailed computer data. However, Figure 3 contains sufficient information to illustrate the calculation procedures. As can be seen from Figure 6, the experimental points do not fall exactly on the theoretical lines. For the two lower reaction times the center of the slab has a higher chrome content than predicted

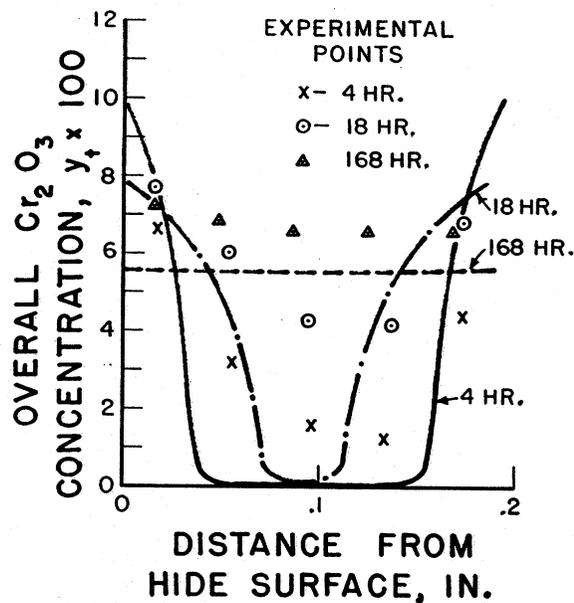


FIGURE 6.—Concentration distribution of chrome in hide after four, 18, and 168 hours of reaction. Lines indicate theoretically predicted concentration distributions through experimental points. Operating conditions: Initial  $\text{Cr}_2\text{O}_3$  concentration in solution two percent, bath ratio 1:1, reaction temperature  $95^\circ\text{F}$ ., 90 percent exhaustion of chrome from solution at equilibrium.

by theory. This may be due to the fact that reaction of chrome complexes with carboxyl groups causes a drop in pH inside the hide (14). This drop in pH results in lowered fixation in the reacted regions, but faster movement of chrome complexes through the hide. In other words, the use of Figure 1, which was obtained for pH equal to approximately 3.0 to 3.2, is probably not strictly valid, since the pH inside the hide may be much lower during reaction.

5. *Effect of temperature.* Table VI lists the experimental data and the diffusion coefficients obtained at different reaction temperatures. It is readily seen that the diffusion constant increases with increase in temperature up to  $115^\circ\text{F}$ . At  $125^\circ\text{F}$ ., a slight decrease in the diffusion constant was observed. This effect is probably due to an interplay of many antagonistic factors (15), such as incipient shrinkage of collagen, formation of non-ionic complexes, etc. This result could be of practical importance, since it gives the maximum temperature which should be used during tanning.

A plot of the logarithm of the diffusion coefficients *vs.* the reciprocal of the absolute temperature yields a fairly straight line if the value obtained for  $125^\circ\text{F}$ . is excluded. From the slope of this line the activation energy of diffusion was found to be equal to 18 kcal./mole. This value for the activation energy again supports the particle diffusion mechanism.

TABLE VI  
DIFFUSION COEFFICIENTS AT DIFFERENT TEMPERATURES\*

Run No.	Reaction Time t (hr.)	Slab Thickness, 2L (in.)	% Cr <sub>2</sub> O <sub>3</sub> Fixed Collagen Basis) 100y <sub>t</sub>	Reaction Temp. (°F.)	Diffusion Constant D·10 <sup>7</sup> (cm. <sup>2</sup> per sec.)
51-2	2	.142	1.72	75	0.27
58-1	720		13.55†	75	
50-2	2	.142	2.33	85	.55
58-2	720		14.34†	85	
34-2	2	.141	3.08	95	1.76
58-3	720		14.11†	95	
57-2	2	.147	2.98	105	1.59
61-4	720		14.43†	105	
64-1	2	.153	3.1	115	1.99
61-5	720		13.52†	115	
64-2	2	.147	2.84	125	.92
96-1	720		15.35†	125	

\*Tanning conditions: Bath ratio 8:1. Wrist-action shaker speed approx. 110 strokes per minute, initial Cr<sub>2</sub>O<sub>3</sub> conc. in solution two percent.

†Values considered maximum which can react after infinite length of time.

#### CONCLUSION

The results of this study are in agreement with many processing facts which are more or less known in the tanning industry. For example, this study brings out the importance of such variables as agitation, temperature, and hide thickness. Diffusion of chrome increases with increase in agitation until film diffusion becomes negligible and particle diffusion becomes the controlling mechanism. Further increase in agitation will not result in a significant increase in diffusion rate.

The results of this paper also indicate that increased chrome penetration is accomplished during the initial tanning stages with increase in temperature up to 105-115°F. A decrease in chrome penetration rate was observed at 125°F., which is indicative of some denaturation of untanned hide at this temperature. However, the total amount of chrome which reacts with collagen after a long period of time increases with increase in temperature over the whole temperature range studied. Thus, it is advantageous to increase the temperature at the end of the tanning operation to remove the maximum amount of chrome from the chrome liquor.

The tanning experiments reported here were conducted under idealized conditions: the grain and the flesh layers were removed and the remaining hide corium slabs, which were tanned, had a uniform thickness and a relatively uni-

form fiber structure. Also, the pH of these hide corium slabs was equal to that of the tanning solution. Despite these facts, a discrepancy between the theoretical and the experimental chrome distributions was observed. It is possible, of course, that faulty assumptions were made in the derivation and integration of the diffusion equation. According to De Wijs (16), the changes in the properties of the chrome liquors and in the pH level which occur during tanning have great influence on the speed of reaction and the total amount of chrome fixed. It is thus quite probable that the discrepancy observed is due to, *e.g.*, the lowering of the hide pH during tanning.

Tanning reactions are very complex, involving many chemical and physical factors. For a thorough understanding of the tanning mechanism all these factors have to be considered. Unfortunately, the complex nature of these factors makes mathematical treatment of the kinetics of tanning rather difficult. Nevertheless, the application of the principles of kinetics to tanning must not be neglected. As evidenced by this work, tanning rate studies are useful as a general guide even in cases where perfect agreement with theory is not achieved.

In dyeing, which involves simultaneous diffusion and adsorption, many experiments (17) have shown that the diffusion coefficient varies with dye concentration and neutral salt content. It is not surprising, therefore, that perfect quantitative agreement between theory and experiment was not obtained in this work on the kinetics of tanning, which is much more complex than dyeing.

#### ACKNOWLEDGMENT

The authors wish to thank Pauline McDowell for carrying out the analytical work, and George F. Thompson, Jr. and Helen Lew for conducting many of the tanning experiments.

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#### NOMENCLATURE

A	= weight of collagen per unit volume of hide.
a	= $\frac{1}{2}$ cross section of space occupied by chrome solution.
C	= weight of unreacted $\text{Cr}_2\text{O}_3$ per unit volume of hide at time t.
$C_0$	= $Z_0Q$ .
$C^\infty$	= $Z^\infty Q$ = weight of unreacted $\text{Cr}_2\text{O}_3$ per unit volume of hide at equilibrium.
D	= diffusion constant.
L	= $\frac{1}{2}$ thickness of hide slab.
$M_t$	= total amount of chrome in hide at time t.
$M^\infty$	= total amount of chrome in hide at equilibrium.
$n_1, n_2$	= constants.
Q	= partition factor giving volume of solution per unit volume of hide.
$R_1, R_2$	= constants.
$R_3, R_4$	= constants.
S	= weight of reacted $\text{Cr}_2\text{O}_3$ per unit volume of hide at time t.
$S^\infty$	= weight of reacted $\text{Cr}_2\text{O}_3$ per unit volume of hide at equilibrium.
t	= reaction time.
X	= distance from center of hide slab.
y	= weight of $\text{Cr}_2\text{O}_3$ per unit weight of collagen at equilibrium.
$y_t$	= weight of $\text{Cr}_2\text{O}_3$ per unit weight of collagen at time t.
Z	= $\text{Cr}_2\text{O}_3$ concentration in solution at time t.
$Z_0$	= initial $\text{Cr}_2\text{O}_3$ concentration in solution.
$Z^\infty$	= $\text{Cr}_2\text{O}_3$ concentration in solution at equilibrium.
$\tau$	= $Dt/L^2$ .