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I hereby recommend that the thesis prepared under my supervision by Robert W. Fleming *entitled* "Some Studies on Iron and Combination Iron Furnaces" -

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SOME STUDIES ON IRON AND COMBINATION IRON-CHROME TANNAGES

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by

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INTRODUCTION

Late in 1941, shortly after the country's entry into war, the leather industry was confronted with a most serious problem: a shortage of chromium. This situation resulted from the curtailment of chrome imports. While the problem is no longer acute due to the development of domestic ores for chemical chrome uses, it then received the attention of a number of interested firms and individuals, including this laboratory. This study is a report of the work begun under those emergency conditions and work more recently undertaken designed to further elucidate the nature of iron tanning.

PART I

A STUDY OF THE FERROUS SULFATE - SODIUM DICHROMATE REACTION AS APPLIED TO COMBINATION IRON-CHROME TANNAGE

As means of coping with the emergency, the following were considered:

(1) Conservation of chromium by greater efficiency in existing processes and by recovery from waste liquors;

(2) The development of substitutes capable of replacing chromium in tanning; and

(3) The reduction of chromium consumption by partial replacement with other materials.

Consideration of these alternatives indicated that in combating an immediate emergency, where the chromium supply was not completely shut off, the first and third were the most important. Since the first alternative depends largely upon circumstances in the individual plant, and can be realized by methods already more or less familiar to the industry, it was felt that results of immediate value would be most likely obtained by concentrating on the partial replacement of chromium by other materials.

It was obvious, of course, that the material chosen to replace chromium had to be readily available in a condition convenient and practical to use, not prohibitively expensive, and that, in addition to possessing the necessary tanning qualities, its use could not involve radical changes in existing processes. Moreover, since it had been indicated by Government authorities that about 50% of the existing level of chromium consumption would probably be maintained available, the replacement material would have to supplant approximately half the normal chromium content of the leather and still yield a product of satisfactory quality.

Among the most widely discussed methods of realizing these possibilities was the use of a combination iron-chrome tannage. The use of iron salts as tanning agents had been the subject of investigation by many workers for years, but it is well known that no particular success had ever attended these efforts. (Part II will attempt to examine the causes of these failures in the light of present-day knowledge, and to offer some suggestions for future improvements.) Even with the apparent shortcomings of iron tanning, the opinion was expressed by a number of persons of wide practical experience in the leather industry that a combination iron-chrome tannage might well prove to be a successful solution of the problem of emergency reduction in chromium consumption by the industry. For these reasons, and because iron salts met so admirably the other requirements mentioned above, such as availability, cheapness, etc., it was decided to undertake to gather some useful data on this type of tannage.

There were a number of ways in which a combination iron-chrome tannage might conceivably be carried out. One of the most promising methods appeared to be by utilization of the well-known reaction between ferrous salts and sodium dichromate. Previous work on iron tannage had established that whatever tanning properties iron salts may have, are possessed exclusively by the ferric, or oxidized, salts. The ferrous salts apparently have no tendency at all to combine with hide substance. The advantage of the reaction just mentioned lies in the fact that by the interaction of the iron salts with the dichromate, both are brought into the necessary condition for tanning, the iron being oxidized to the ferric state, while the dichromate is reduced just as in the preparation of an ordinary one-bath chrome liquor.

This reaction has already been discussed to some extent in the literature of iron tanning. It is mentioned in the patent of Frey (3), assigned to the Government and people of the United States; Jackson and Hou (5) investigated its possibilities in their study of iron tannage; it has been the subject of a French patent issued to Gottschalk (4); and very recently Ruppenthal and Malik (22) used this method, and others, in conjunction with sodium phosphate and sodium gluconate to produce a leather, samples of which have been examined by this laboratory and found to be very satisfactory. No systematic study seems to have been made, however, of the effects of various factors on the fixation of iron and of chrome by hide substance in the utilization of this reaction, and it is to this end that the present work was directed. It must be pointed out that this work is not meant in any way as an advocacy of this type of tannage, the merits of which must await further examination. The data presented are intended only to be of use to those who wish to experiment further and on a larger scale.

EXPERIMENTAL METHODS

In all of this work the 1/2 inch, bated, calf-skin squares described by McLaughlin (16) were used. Samples containing 10.00 grams of hide substance, as calculated from Kjeldahl nitrogen determinations on representative samples from the batch, were soaked 24 hours in 100 ml. portions of distilled water. After soaking, the samples were drained for 5 minutes on funnels before being placed into the subsequent solutions.

With the exception of the soaking, all of the treatments were carried out in closed glass jars, with continuous mechanical agitation. Pickles and the first baths of the two-bath processes were used in 100 ml. portions to the above skin samples. For the second baths, and the single bath liquors, 50 ml. portions were used. Further experimental details are given under the descriptions of the individual experiments.

Analytical Methods

After the desired time periods of tannage, the samples were removed to funnels, and squeezed free from as much of the liquor as possible by hand. They were then transferred to clean jars containing 100 ml. portions of distilled water, in which they were shaken for 30 minutes. The whole squeezing and washing process was then repeated, after which the samples were pressed twice in a hydraulic press, at a pressure of 5,000 lbs. The samples were wrapped in filter cloth before pressing, and the pressure was maintained for 1 minute. This procedure is based on that used by McLaughlin (17) in his studies of chrome tanning, and is designed to remove as much as possible of the uncombined material. In the present work it has been assumed that iron and chromium remaining in the skin samples after this treatment are combined with the hide substance.

Determination of Iron and Chromium

After pressing, the samples were dried in the air at room temperature, shredded in the large Wiley mill, and reground in the medium Wiley mill to 20 mesh. Samples of the ground material were then weighed out for the determination of nitrogen and of iron and chromium. All samples were weighed at the same time to eliminate error caused by loss of moisture. Nitrogen determinations were run in duplicate, using the ordinary boric acid modification of the Kjeldahl method. Percentages of nitrogen were converted to the hide substance basis by multiplying by the factor 5.62.

For the determination of iron and chromium, approximately 2 gram samples of the air dry material were used. These were heated, in 250 ml. Erlenmeyer flasks, with 25 ml. of 70 per cent perchloric acid until oxidation was complete, as indicated by the color change from green to red. After a further 10 to 15 minute heating at just below the boiling temperature, the solutions were immediately diluted with distilled water, and washed into 400 ml. beakers. The diluted solutions were boiled for several minutes, cooled, and treated with ammonium hydroxide until they were alkaline to litmus paper. The precipitated ferric hydroxide was then filtered off, and the beaker and precipitate washed with several portions of hot distilled water, the filtrate and washings being received in a clean 400 ml. beaker. The precipitate was dissolved on the filter with hot 1 to 1 hydrochloric acid, and washed into the original beaker. After dilution to a suitable volume, the precipitation and washing of the ferric hydroxide was repeated. This double precipitation of the iron was found to be necessary in order to effect a complete separation from the chromium.

Chromium was determined in the combined filtrates and washings, after acidification and cooling, by the usual iodometric procedure, using potassium iodide and 0.05N sodium thiosulfate solution. For the determination of iron, the final ferric hydroxide precipitate was dissolved in the minimum amount of hot hydrochloric acid, washed into the original beaker, and concentrated to 15-20 ml. on the water bath. The iron was then determined by a modification of the Zimmermann-Reinhardt procedure (10) using .05N $KMnO_4$.

RESULTS AND DISCUSSION

The Ferrous Salt - Sodium Dichromate Reaction

The reaction between ferrous sulfate and sodium dichromate is represented by the equation:

$$6FeSO_4 + Na_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

One part by weight of $Na_2Cr_2O_7 \cdot 2H_2O$ therefore requires, for complete reaction, 3.06 parts of $FeSO_4$ (or 5.60 of $FeSO_4 \cdot 7H_2O$), and 2.30 parts of H_2SO_4, and will yield 1.61 parts of Fe_2O_3 and 0.51 parts of Cr_2O_3.

Since the above reaction proceeds readily at room temperature, and without the development of heat, it is evident that it may be used in a two-bath procedure for tanning. It is obvious that there are three general methods of procedure: a single bath method in which the reaction is allowed to take place before the introduction of the skins, and two two-bath methods, differing from each other only in that the order of the baths is reversed. It has been the object of the present work to collect comparative data on all three of these methods.

The Absorption of Ferrous Sulfate by Calf-Skin

For the proper regulation of conditions in the two-bath procedure where the ferrous sulfate is used in the first bath, it is obviously necessary to know the influence of concentration and of time on the absorption of this iron salt by the skin. Soaked calf-skin squares, containing 10.00 grams of hide substance per sample, were agitated with 100 ml. portions of solutions containing, in addition to ferrous sulfate, 5.00 grams H_2SO_4, and 150 grams NaCl per liter. Ferrous sulfate concentrations ranged from 25 to 150 grams per liter. At the end of the desired time intervals the samples were removed, drained for 5 minutes on funnels, blotted lightly between towels, air dried, ground, and analyzed for hide substance and iron as described above. (In this case a single iron precipitation was used.) The results are given in Table I.

It will be noted that the solutions used in these experiments correspond approximately to an ordinary pickle liquor to which ferrous sulfate is added. This was based on the idea that such a two-bath process could be conveniently carried out by merely adding the iron salt to the usual pickle liquor, thus not increasing the number of processes required.

In Figure I, the absorption of ferrous sulfate by calf-skin under these conditions is plotted as a function of time. In the

TABLE I

ABSORPTION OF FERROUS SULFATE BY CALF-SKIN FROM SOLUTIONS CONTAINING 5.00 GRAMS H_2SO_4 AND 150 GRAMS NaCl PER LITER

Grams $FeSO_4$ Per Liter	Grams $FeSO_4$ per 100 Grams Hide Substance at			
	1 Hour	3 Hours	5 Hours	24 Hours
25	4.00	4.11	4.12	4.50
50	7.28	8.10	7.37	9.29
100	13.14	15.65	15.56	16.56
150	22.32	23.17	20.08	26.17

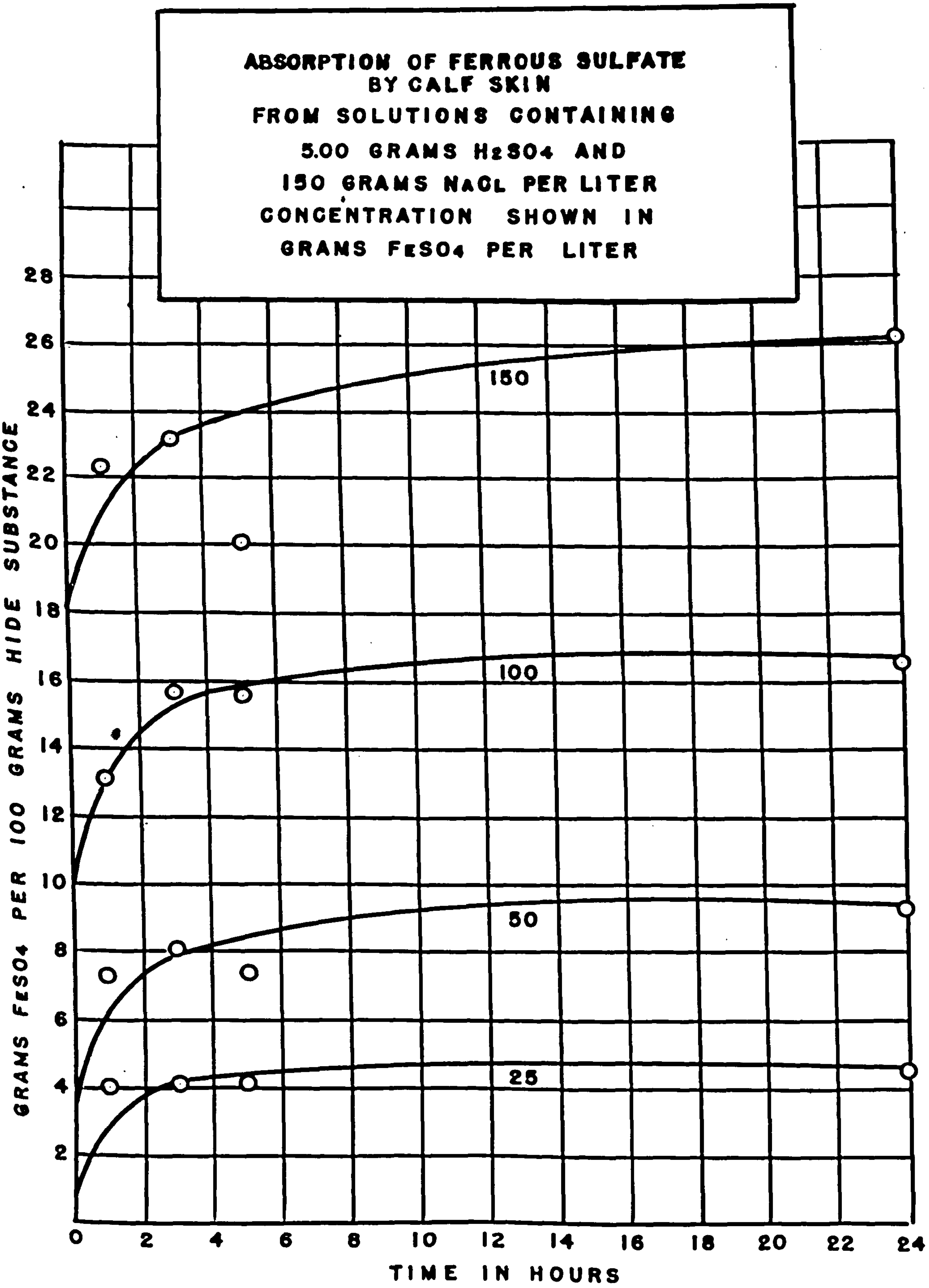
ABSORPTION OF FERROUS SULFATE
BY CALF SKIN
FROM SOLUTIONS CONTAINING
5.00 GRAMS H_2SO_4 AND
150 GRAMS NACL PER LITER
CONCENTRATION SHOWN IN
GRAMS $FeSO_4$ PER LITER
150
100
50
25
GRAMS $FeSO_4$ PER 100 GRAMS HIDE SUBSTANCE
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME IN HOURS

FIGURE I

lowest concentration, equilibrium is practically established at the end of 4 to 6 hours. In the higher concentrations, however, absorption of ferrous sulfate continues over the whole 24 hours period, although the increase is much slower after the first few hours. Other experiments have shown that in the higher concentrations this slow absorption continues practically indefinitely, and have indicated that this apparent lack of an equilibrium is due to the continuous air oxidation of the ferrous sulfate, with fixation by the calf-skin of the ferric salt.

In Figure II, the absorptions at 24 hours are plotted against the initial concentrations of ferrous sulfate. The slope of the resulting straight line is, of course, greater than it would be in the absence of the air oxidation effect noted above. There appears to be no convenient method available for distinguishing between the ferrous and the ferric iron present in the skin under these conditions.

The Fixation of Iron and Chrome in the Two-Bath Method Using Ferrous Sulfate First

Figure II provides the necessary data for controlling the conditions in the two-bath procedure where the ferrous sulfate is used in the first bath, so that the resulting amounts of ferric and chromic salts available for tanning will be in the desired range. On the basis of the considerations given previously, a fixation of around 2 to 3 grams of Cr_2O_3 per 100 grams of hide substance would appear to be the desired range in this type of tannage. For the purposes of the present work, the lower figure has been arbitrarily assumed. From the

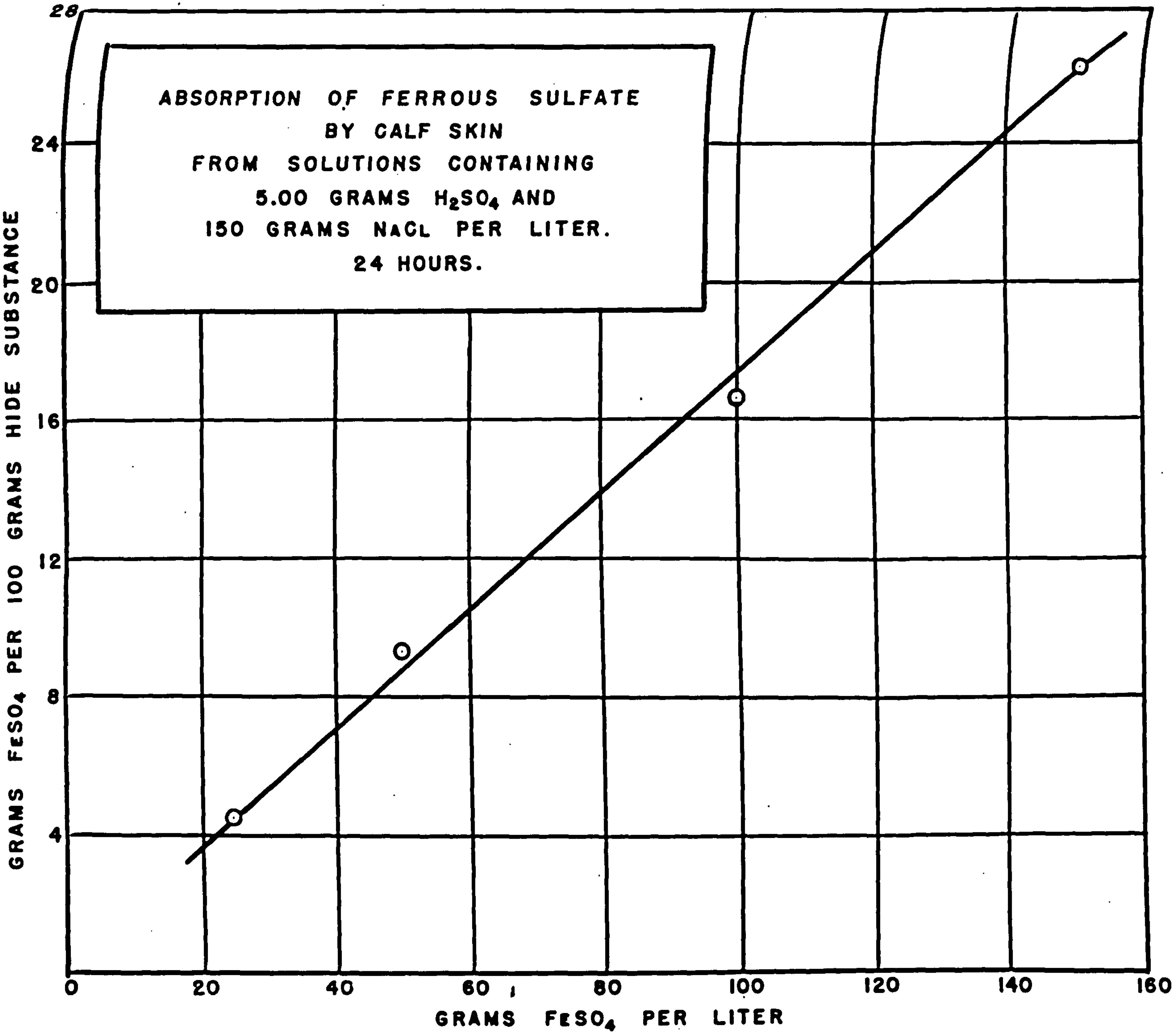
ABSORPTION OF FERROUS SULFATE
BY CALF SKIN
FROM SOLUTIONS CONTAINING
5.00 GRAMS H_2SO_4 AND
150 GRAMS NACL PER LITER.
24 HOURS.
GRAMS $FeSO_4$ PER 100 GRAMS HIDE SUBSTANCE
4
8
12
16
20
24
28
0
20
40
60
80
100
120
140
160
GRAMS $FeSO_4$ PER LITER

FIGURE II

stoichiometric relations discussed in a previous section, 2.00 grams of Cr_2O_3 are produced from 3.92 grams of $Na_2Cr_2O_7$-$2H_2O$, and this amount of dichromate requires 12.00 grams of $FeSO_4$ to reduce it.

In order to have the desired amount of chromic salt available for tanning, therefore, 12 grams of $FeSO_4$ per 100 grams of hide substance must be absorbed in the first bath. Reference to Figure II shows that this condition is reached in 24 hours at a concentration of 75 grams of $FeSO_4$ per liter, under the given conditions. In studying the fixations of iron and chrome in this two-bath process, calf-skin samples containing 10.00 grams of hide substance were accordingly agitated for 24 hours in 100 ml. portions of a pickle liquor of the previously given composition, containing this concentration of ferrous sulfate. At the end of this period the samples were removed, given the usual drainage, and transferred to 50 ml. portions of a second liquor containing 7.84 grams $Na_2Cr_2O_7$-$2H_2O$, 50 grams NaCl, and 15 grams H_2SO_4 per liter. This solution contains the theoretical amount of dichromate to react with the ferrous sulfate present, while the acid is calculated to be slightly in excess of the theoretical amount required, when that which is carried over from the pickle liquor is included.

At the end of 3 hours of continuous agitation in the second bath, adjustment of the basicity was started with the gradual addition of a solution containing 100 grams of Na_2CO_3 per liter. This was added in portions of 2 ml. at a time, at hourly intervals over a period of 6 hours, so that a total of 12 ml. was added to the most basic liquor. The experiment was so arranged that samples of all six degrees of basicity were available, as well as controls to which no sodium carbonate was added. The pH values of the liquors were taken with the glass electrode 30 minutes after the last addition of sodium carbonate in each case. Tannage was allowed to continue for a total of 24 hours in all cases, after which the samples were removed and analyzed as previously described. The pH values of the exhaust liquors were also determined.

The results thus obtained are given in Table II, and shown graphically in Figure III. In common with ordinary chrome tannage, very little tanning power, as judged by combination with the hide substance, is shown until the basicity is increased. In the present experiments the over-all basicities ranged from about 12 to about 72 per cent.

The Absorption of Sodium Dichromate by Calf-Skin

For the two-bath process in which the solutions are used in the reverse order, it was necessary to determine the absorption of sodium dichromate by calf-skin. This was carried out in the same manner as already described, except that in this case no salt was added to the solutions. Some swelling was noted in the lower concentrations of sodium dichromate for this reason, but for the comparative purposes of the present work this was ignored. Other experiments have indicated that in the presence of added salt the absorption of the dichromate is markedly reduced.

The results of these experiments are given in Table III, and shown graphically in Figures IV and V.

TABLE II

TWO-BATH METHOD USING FERROUS SULFATE FIRST

CONTROL SERIES, 0 PER CENT BASICITY

(Averages of two determinations)

Time in Hours	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
1	1.71	0.187	9.15
3	2.02	0.209	9.67
5	2.07	0.204	10.15
8	2.09	0.223	9.38
24	1.96	0.258	7.60

BASICITY ADJUSTED WITH SOLUTION CONTAINING 100 GRAMS Na_2CO_3 PER LITER

Fixations at 24 Hours

ml. Na_2CO_3 Solution Added	pH 30 Minutes After Na_2CO_3 Addition	Final pH	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
2	2.00	-	2.86	0.347	8.24
4	2.31	1.90	3.86	0.458	8.43
6	2.62	1.96	5.00	0.522	9.58
8	3.21	2.05	5.92	0.943	6.28
10	3.70	2.30	6.24	1.08	5.78
12	4.51	2.96	6.47	1.40	4.62

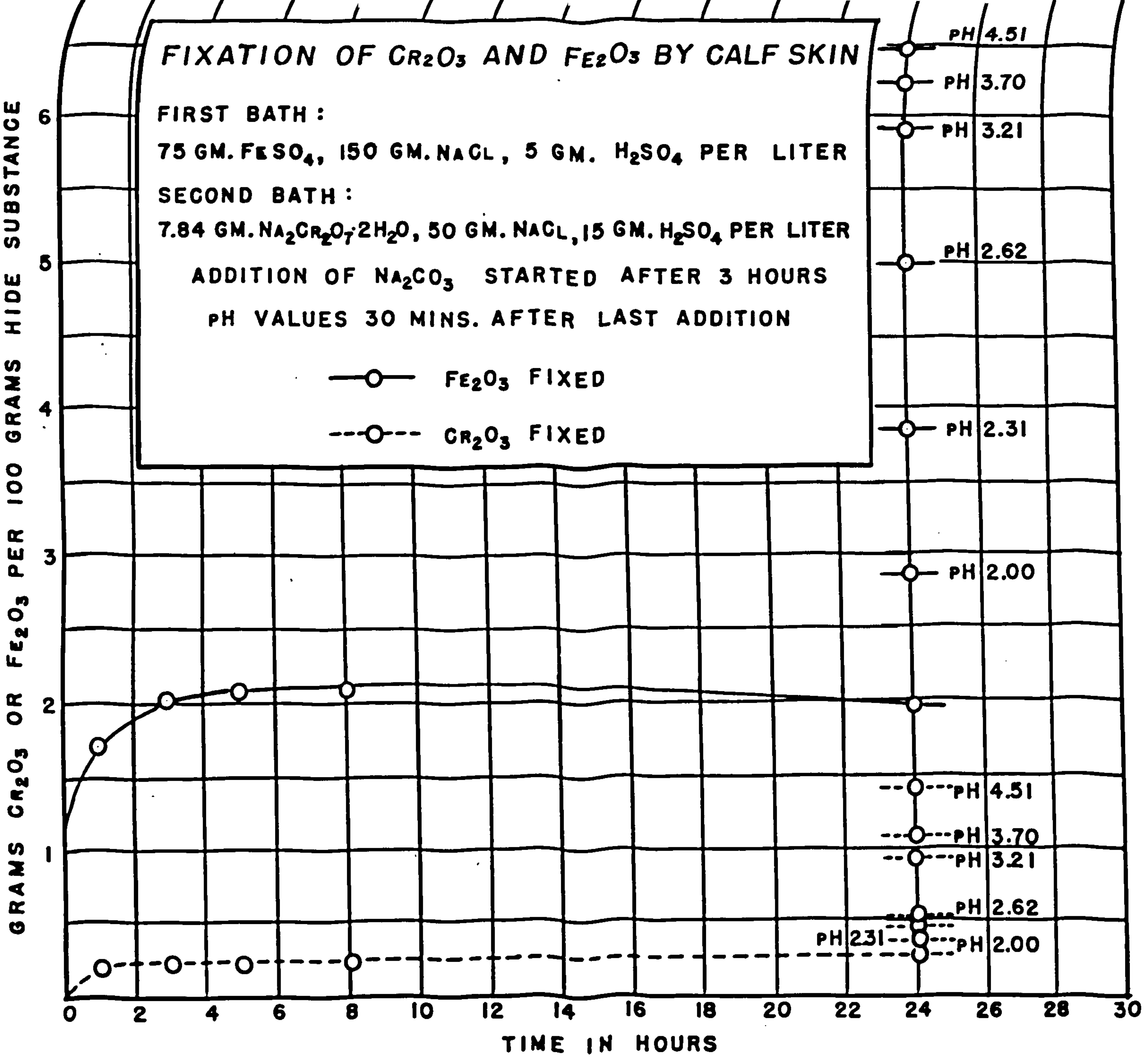
FIXATION OF Cr_2O_3 AND Fe_2O_3 BY CALF SKIN
FIRST BATH:
75 GM. $FeSO_4$, 150 GM. NaCl, 5 GM. H_2SO_4 PER LITER
SECOND BATH:
7.84 GM. $Na_2Cr_2O_7 \cdot 2H_2O$, 50 GM. NaCl, 15 GM. H_2SO_4 PER LITER
ADDITION OF Na_2CO_3 STARTED AFTER 3 HOURS
pH VALUES 30 MINS. AFTER LAST ADDITION
Fe_2O_3 FIXED
Cr_2O_3 FIXED
pH 4.51
pH 3.70
pH 3.21
pH 2.62
pH 2.31
pH 2.00
pH 4.51
pH 3.70
pH 3.21
pH 2.62
pH 2.31
pH 2.00
GRAMS Cr_2O_3 OR Fe_2O_3 PER 100 GRAMS HIDE SUBSTANCE
1
2
3
4
5
6
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
TIME IN HOURS

FIGURE III

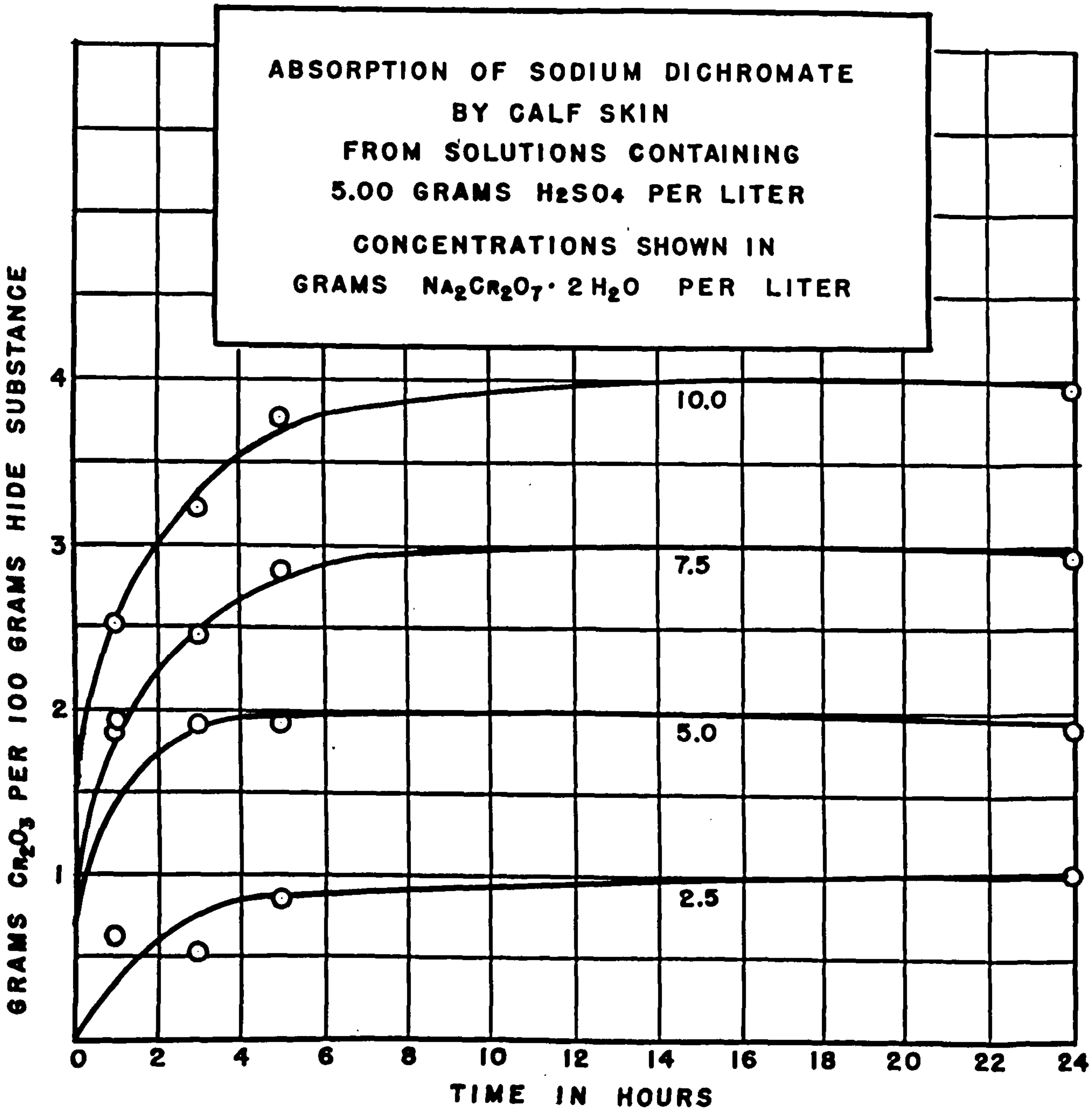
ABSORPTION OF SODIUM DICHROMATE
BY CALF SKIN
FROM SOLUTIONS CONTAINING
5.00 GRAMS H_2SO_4 PER LITER
CONCENTRATIONS SHOWN IN
GRAMS $Na_2Cr_2O_7 \cdot 2H_2O$ PER LITER
GRAMS Cr_2O_3 PER 100 GRAMS HIDE SUBSTANCE
TIME IN HOURS
10.0
7.5
5.0
2.5
0
1
2
3
4
0
2
4
6
8
10
12
14
16
18
20
22
24

FIGURE IV

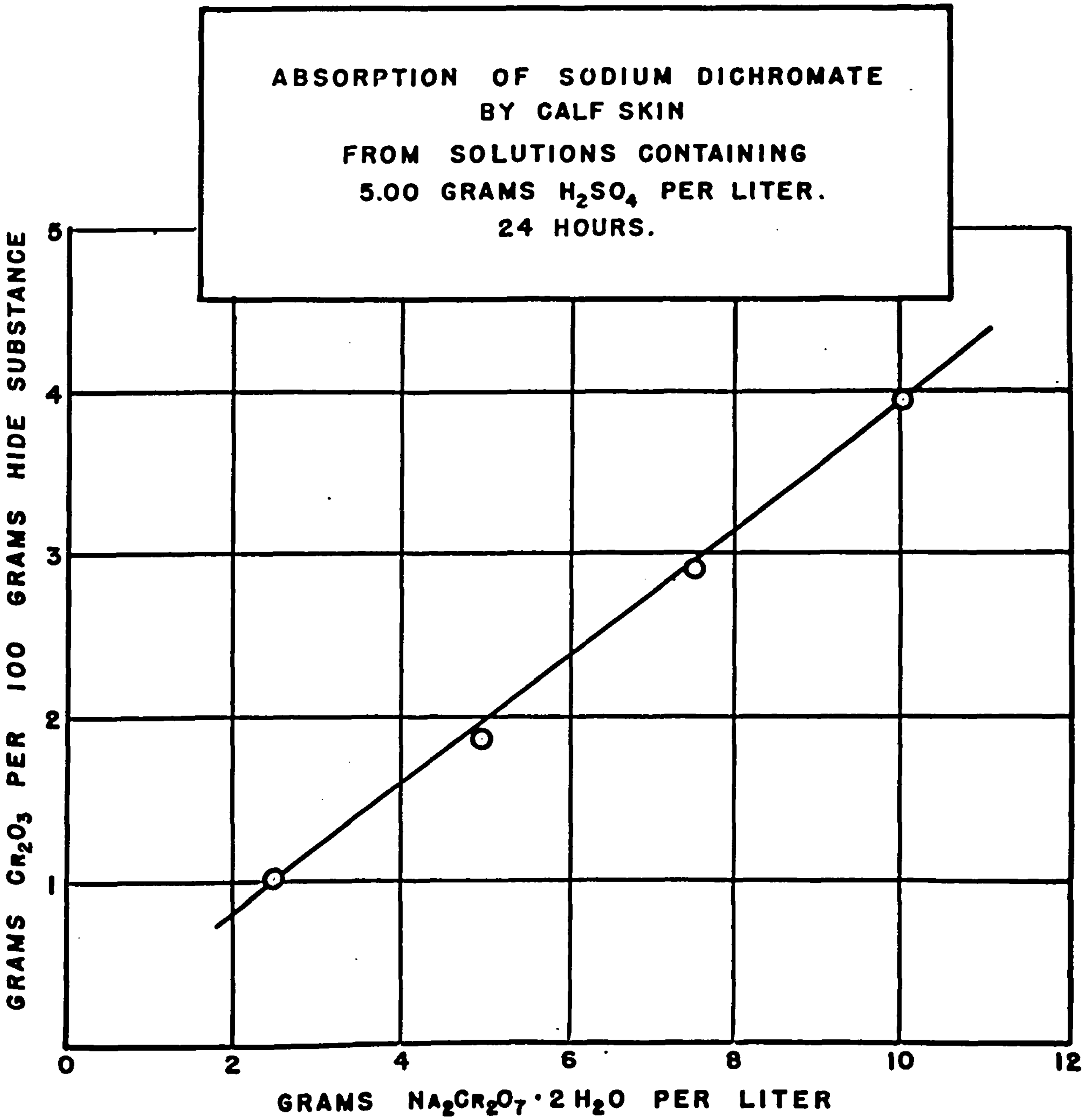
ABSORPTION OF SODIUM DICHROMATE BY CALF SKIN
FROM SOLUTIONS CONTAINING
5.00 GRAMS H_2SO_4 PER LITER.
24 HOURS.
GRAMS Cr_2O_3 PER 100 GRAMS HIDE SUBSTANCE
5
4
3
2
1
0
2
4
6
8
10
12
GRAMS $Na_2Cr_2O_7 \cdot 2H_2O$ PER LITER

FIGURE V

The Fixation of Iron and Chrome in the Two-Bath Method Using Sodium Dichromate First

Figure V contains the necessary data for setting up the alternative two-bath method. From the graph it can be seen that in order for 100 grams of hide substance to absorb the required 2 grams of Cr_2O_3 under the given conditions in 24 hours, an initial concentration of 5.30 grams per liter of $Na_2Cr_3O_7$ $2H_2O$ is necessary.

The experiment was carried out exactly as before, except for the obvious necessary changes. The second baths consisted of 50 ml. portions of a solution containing 24.00 grams $FeSO_4$, 50 grams NaCl, and 15 grams H_2SO_4 per liter. The results are given in Table IV and Figure VI. As might be expected, the fixation of iron in this case is somewhat lower, and that of chrome somewhat higher, than in the previous method.

The Fixation of Iron and Chrome in the One-Bath Method

The third possibility to be investigated was the one-bath tannage in which the ferrous sulfate and sodium dichromate are allowed to react before the skin is placed in the liquor. In investigating this method, under conditions such that the results could be compared with those previously obtained, the skin samples were first pickled for 24 hours in a pickle liquor containing 5.00 grams H_2SO_4 and 150 grams NaCl per liter. After drainage, the samples, equivalent to 10.00 grams of hide substance, were agitated in 50 ml. portions of the one-bath tan liquor. This was prepared by allowing 24.0 grams $FeSO_4$, 7.84 grams $Na_2Cr_2O_7$ $2H_2O$, and 18.04 grams H_2SO_4 to react, and adjusting the final volume to 1 liter. The amounts of iron and chrome available for tannage were thus exactly the same as in the previous

TABLE IV

TWO-BATH METHOD USING SODIUM DICHROMATE FIRST

CONTROL SERIES, 0 PER CENT BASICITY

(Averages of two determinations)

Time in Hours	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
1	1.80	0.564	3.19
3	1.95	0.454	4.30
5	2.15	0.550	3.91
8	2.28	0.605	3.77
24	2.14	0.598	3.58

BASICITY ADJUSTED WITH SOLUTION CONTAINING

100 GRAMS Na_2CO_3 PER LITER

Fixations at 24 Hours

ml. Na_2CO_3 Solution Added	pH 30 Minutes After Na_2CO_3 Addition	Final pH	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
2	1.91	2.02	2.94	0.654	4.50
4	2.13	2.18	3.69	0.806	4.58
8	2.98	2.44	5.00	1.30	3.84
10	3.30	2.71	5.33	1.59	3.35
12	5.62	3.28	5.68	1.74	3.26

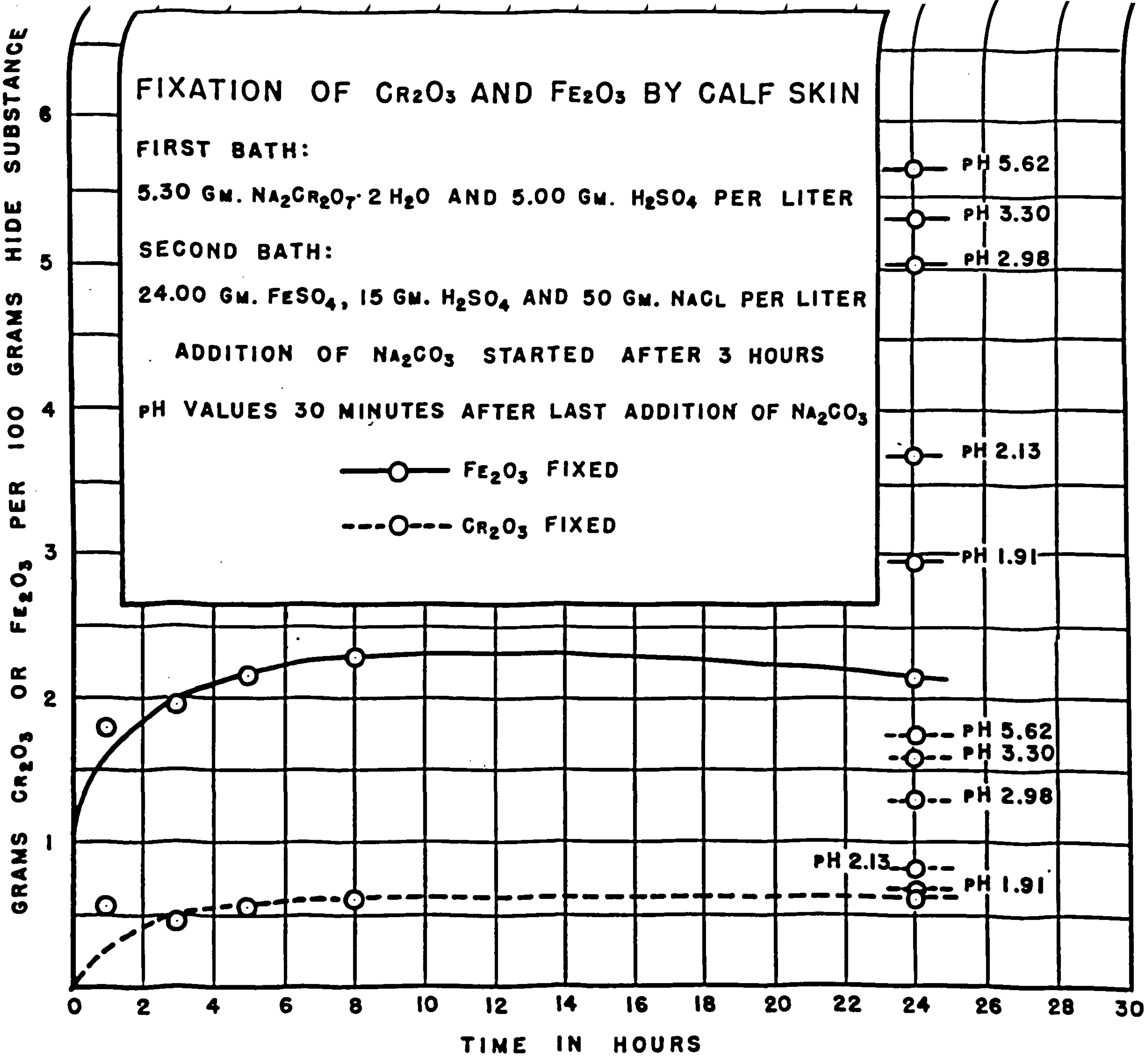
FIXATION OF Cr_2O_3 AND Fe_2O_3 BY CALF SKIN
FIRST BATH:
5.30 GM. $Na_2Cr_2O_7 \cdot 2H_2O$ AND 5.00 GM. H_2SO_4 PER LITER
SECOND BATH:
24.00 GM. $FeSO_4$, 15 GM. H_2SO_4 AND 50 GM. NaCl PER LITER
ADDITION OF Na_2CO_3 STARTED AFTER 3 HOURS
pH VALUES 30 MINUTES AFTER LAST ADDITION OF Na_2CO_3
Fe_2O_3 FIXED
Cr_2O_3 FIXED
pH 5.62
pH 3.30
pH 2.98
pH 2.13
pH 1.91
pH 5.62
pH 3.30
pH 2.98
pH 2.13
pH 1.91
GRAMS Cr_2O_3 OR Fe_2O_3 PER 100 GRAMS HIDE SUBSTANCE
1
2
3
4
5
6
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
TIME IN HOURS

FIGURE VI

cases. Adjustment of basicity was carried out as before.

The results obtained in this experiment are given in Table V and Figure VII.

Comparison of the Three Methods

In order to compare the results obtained by the various methods, the fixations of iron and chrome found in all three experiments are plotted, in Figure VIII, against the pH values of the 24 hours exhaust liquors. From this graph the much greater fixation of iron when the ferrous sulfate is used in the first bath will be noted. It will also be seen that at the higher basicities the one-bath method and the ferrous sulfate first two-bath method yield approximately equal fixations of both iron and chrome, while the dichromate first two-bath method gives lower iron and higher chrome fixations. It is also evident that increasing basicity increases the fixation of iron in all cases at a faster rate than that of chrome.

If the ferric and chrome salts were fixed by the hide substance in exact proportion to their production in the reaction between the ferrous sulfate and sodium dichromate, the ratio of Fe_2O_3 to Cr_2O_3 in the leather would be 3.16. In all cases in the present work the actual ratio found is higher than this, due to at least two factors. The first of these is the fact, already noted by other workers, that iron salts are fixed more rapidly than chrome. This is shown, for example, by the data in Table V for the one-bath control samples of 0 per cent basicity. Here the ratio in the early stages of tanning reaches values of the order of ten times the theoretical, showing the much more rapid fixation of iron. The other factor involved is the

TABLE V

ONE-BATH METHOD

CONTROL SERIES, 0 PER CENT BASICITY

(Averages of two determinations)

Time in Hours	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
1	1.43	0.045	31.8
3	1.50	0.098	15.3
5	1.54	0.123	12.5
8	1.60	0.128	12.5
24	1.49	0.167	8.92

BASICITY ADJUSTED WITH SOLUTION CONTAINING

100 GRAMS Na_2CO_3 PER LITER

Fixation at 24 Hours

ml. Na_2CO_3 Solution Added	pH 30 Minutes After Na_2CO_3 Addition	Final pH	Grams Fe_2O_3 per 100 Grams Hide Substance	Grams Cr_2O_3 per 100 Grams Hide Substance	Ratio $\frac{Fe_2O_3}{Cr_2O_3}$
2	1.80	1.87	2.16	0.282	7.66
4	2.18	2.12	3.03	0.355	8.54
6	2.30	2.22	3.97	0.478	8.31
8	2.52	2.37	4.73	0.788	6.00
10	2.74	2.51	5.47	1.06	5.16
12	3.61	2.82	6.23	1.34	4.65

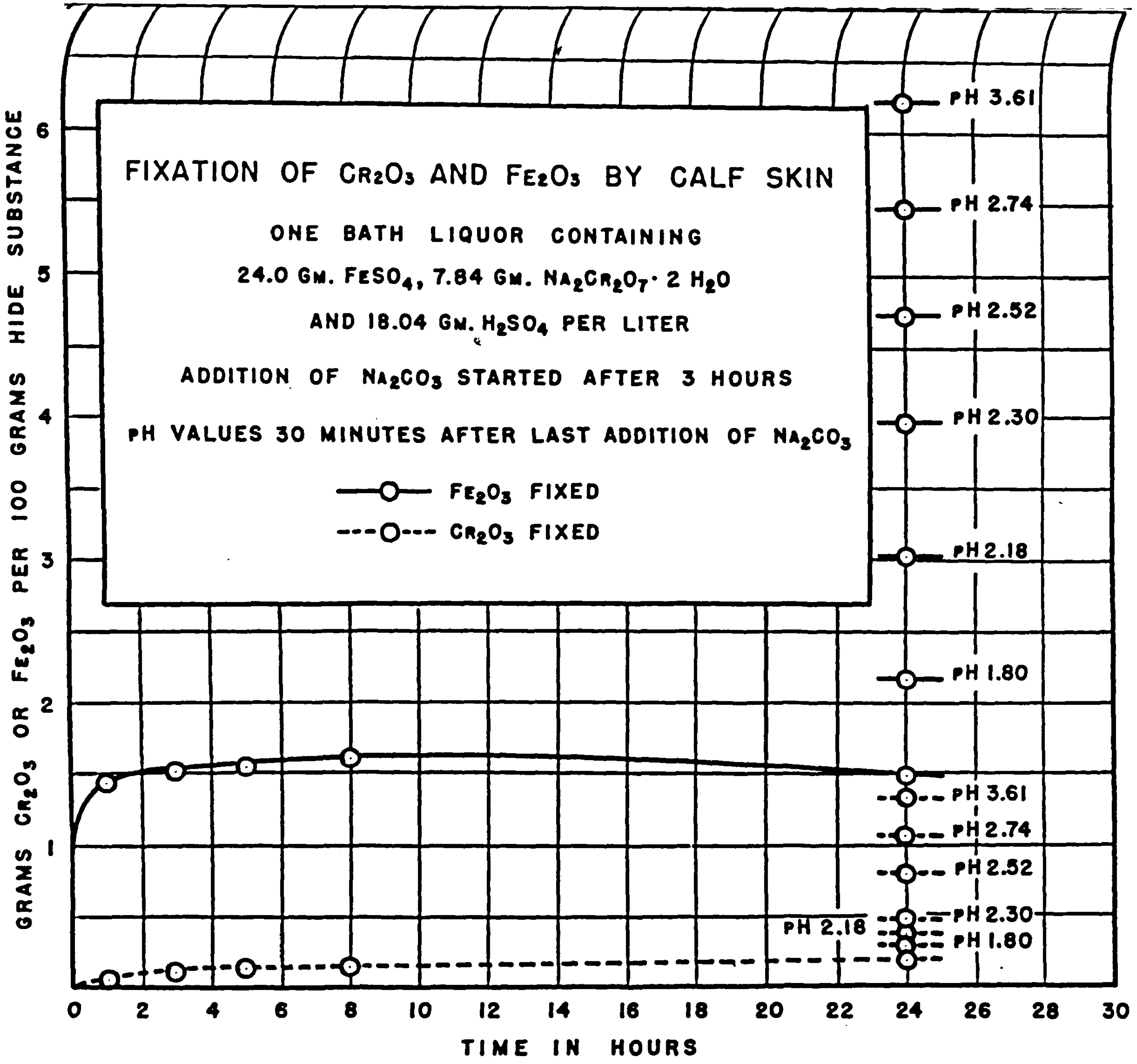
FIXATION OF Cr₂O₃ AND Fe₂O₃ BY CALF SKIN
ONE BATH LIQUOR CONTAINING
24.0 GM. FeSO₄, 7.84 GM. Na₂Cr₂O₇ · 2 H₂O
AND 18.04 GM. H₂SO₄ PER LITER
ADDITION OF Na₂CO₃ STARTED AFTER 3 HOURS
pH VALUES 30 MINUTES AFTER LAST ADDITION OF Na₂CO₃
Fe₂O₃ FIXED
Cr₂O₃ FIXED
pH 3.61
pH 2.74
pH 2.52
pH 2.30
pH 2.18
pH 1.80
pH 3.61
pH 2.74
pH 2.52
pH 2.30
pH 2.18
pH 1.80
GRAMS Cr₂O₃ OR Fe₂O₃ PER 100 GRAMS HIDE SUBSTANCE
1
2
3
4
5
6
TIME IN HOURS
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

FIGURE VII

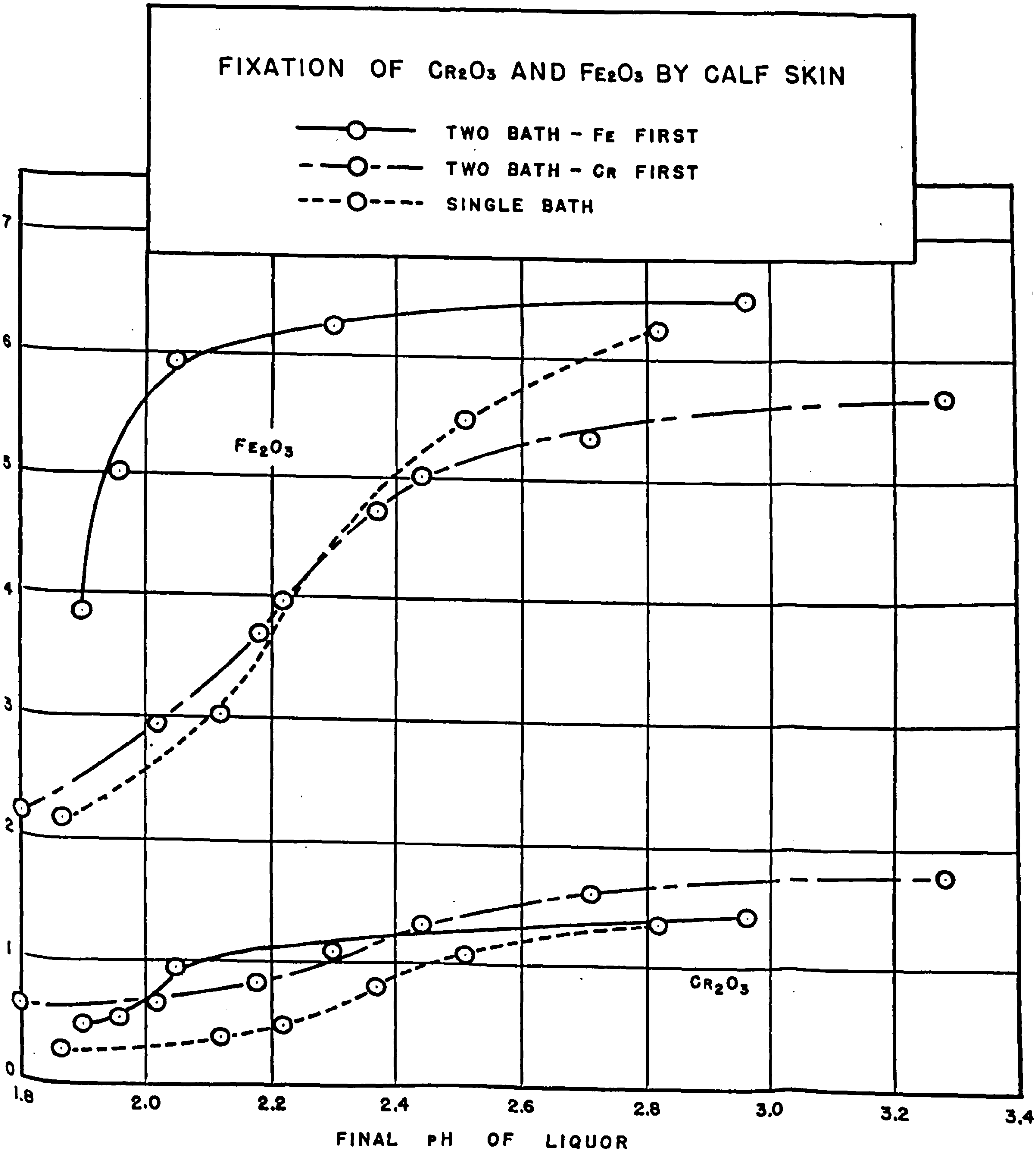
FIXATION OF Cr_2O_3 AND Fe_2O_3 BY CALF SKIN
TWO BATH - Fe FIRST
TWO BATH - Cr FIRST
SINGLE BATH
Fe_2O_3
Cr_2O_3
0
1
2
3
4
5
6
7
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
FINAL pH OF LIQUOR

FIGURE VIII

previously mentioned air oxidation of the ferrous sulfate in the cases of the two-bath methods. Since in the present study theoretical proportions of ferrous sulfate and sodium dichromate were used, air oxidation of the former tends to increase the fixation of iron, and decrease that of chrome, as insufficient ferrous salt will remain to reduce the dichromate completely.

It will be noted from Table IV that, in the case of the two-bath method using the dichromate first, the fixation ratio approaches the theoretical fairly closely, especially in the most basic liquors. This is evidently due to a fortuitous combination of circumstances peculiar to this method. Here the chrome fixations are higher, and the iron fixations lower, than in the other methods, as might be expected from the order of procedures used.

On the basis of the general experience gained thus far, it would appear that the one-bath method and the two-bath method using ferrous sulfate first show the best practical possibilities. A further point, indicated by limited small scale experiments, is that leathers made by these methods need especial attention to the fat-liquoring. Larger amounts of fat-liquor appear to be necessary than are used with ordinary chrome leathers. These and other aspects of the problem, such as the use of organic hydroxy acids, are considered in the previously referred to paper of Ruppenthal and Malik.

PART II

THE FIXATION OF IRON FROM FERRIC SULFATE SOLUTIONS BY HIDE SUBSTANCE AS APPLIED TO IRON TANNAGE

As was mentioned in Part I, the use of iron salts as tanning agents has long been a subject for experimentation. The cheapness and universal availability of iron, as well as the advantages of a mineral tanning process, have repeatedly enticed both practical tanner and chemist to endeavor to succeed where his predecessors had failed. The pressure of war-time economies has also contributed in several periods to the efforts expended in this direction. Robert Lindet reported to the National Congress of France on September 20, 1794, that the urgent need for leather by the army during the great French Revolution had been met by a rapid iron tanning process (7). It is well known that during World War I Germany was faced with an acute shortage of tanning materials, and there have been various reports as to the use of iron-tanned leather by the country at that time. More recently this situation has again arisen in Germany, and, indeed, the present work, as well as that of several other investigators in this country, was prompted by the prospect of a shortage of chromium. However, although the literature on iron tannage has thus assumed rather large proportions, there is no conclusive evidence at the time of writing that the method is in practical use.

It would serve no good purpose to review completely this literature here, as such reviews not only are to be found complete to 1920 (8), (6), but also contain much data of no theoretical or practical interest today. While there have been numerous patents issued on iron tanning since 1920, especially in the field covering the use of iron-organic complexes, only three studies of a systematic nature, made under controlled laboratory conditions acceptable to the present-day standards, have been published in the available literature. (There are abstracts indicating that considerable work in this field has been undertaken in Russia, but it is difficult to determine just to what extent these experiments have been made systematic. The work of Casaburi also comes under this category, although the patriotic motif, "A Contribution to Italian Self-Sufficiency," seems to cloud much of his effort.) Due to their importance, it might be well to survey briefly the content of each of the three papers mentioned above.

The first paper in which systematic study is shown is that of Jackson & Hou (5). These chemists made an extended investigation of the various factors involved in the iron tanning of sheep skins, including the best method of oxidizing ferrous sulfate to ferric sulfate, the hydrolysis and decomposition of ferric and chromic salts compared, the relation of basicity to stability in iron liquor, the behavior of the pelt toward iron tan liquor, experiments in tanning with ferric hydroxide hydrosol, general experimental work on iron tanning, chrome-iron joint tannage, pure iron tannage, and iron phosphate tannage. From their work they drew the following conclusions:

(1) Iron must be completely oxidized to its ferric state and maintained there by using an excess of proper oxidizing agent, and by means of an after-oxidation.

(2) Adjustment of proper basicity by the addition of a proper amount of alkali is essential, a basicity between 16-2/3% and 25% (Schorlemmer) being the proper range for tanning.

(3) Gradual neutralization should be effected so that the iron may be uniformly fixed in the pelt throughout its thickness.

(4) After tanning, the leather must be dried before subsequent treatment to minimize the reactions between the iron and the substances employed later that would react with the iron to give an undesirable color.

It should be mentioned that their work on tanning with ferric hydroxide hydrosol showed this material to have absolutely no tanning properties. Wintgen and Meyer (26) also made a study of this nature and concluded that such colloidal dispersions were unable to penetrate hide and could therefore not be expected to tan.

The second paper, that of Thomas and Kelly (23), approaches the problem from a somewhat different viewpoint. Using hide powder and a modified Wilson-Kern technique, they determined the irreversible fixation of iron by hide substance from solutions of ferric sulfate. The experimental variables investigated were changes of basicity and concentration of ferric sulfate, time of tannage, and effect of added sodium chloride and sodium sulfate. Due to the experimental technique employed, they had to limit the ranges of concentration and basicity to those which would yield only clear solutions. This somewhat detracts from the value of their researches, since the basicities involved are generally more acid than would ordinarily be used in tanning practice, the highest basicity being 16%. The method also involves the disadvantage in that it measures the so-called "irreversible" fixation, i.e., the fixed iron which is not removable by washing with large quantities of water. This is not only contrary to actual tanning practice, but does not give a true picture of the iron take-up by hide substance. The prolonged washing would cause extensive hydrolysis of the iron salt, remove the large part of the acid, and leave as "irreversibly fixed" only precipitated iron oxide which could not escape the filtering apparatus. Thus it is not at all surprising to find that by this technique the authors found greater fixation of iron from the more dilute tan liquors, as it is well known that ferric sulfate is very susceptible to hydrolysis, and this salt in the more dilute solutions would be practically 100% hydrolyzed under these conditions, while the more concentrated solutions would tend to wash out before hydrolysis could take place to the extent where precipitation occurs. The data showing increased fixation with increasing basicity and the attainment of equilibrium at a fixed basicity and concentration in about 6-8 hours, are entirely in accord with those of the present work. It was found that sodium chloride diminished the amount of iron fixed while sodium sulfate showed less inhibitory effect; in fact, in solutions of the normal ferric salt it actually favored the degree of fixation of iron when small amounts of the sodium salt were used.

Ruppenthal and Malik (22) have attacked the problem from yet another viewpoint: that of the practical tanner. That their interest lay solely in the practical aspects, is evidenced by their introductory remarks: "... to develop an iron tannage that will stand upon its own merits, or else, can be combined with chrome, decreasing the amount of chrome necessary, without unduly impairing the quality of chrome leather." The paper is divided into two parts: iron tanning, and combination iron-chrome tanning. These investigators first established a tannage using ferric sulfate and conditions so adjusted as to give a fair picture of the potentialities of this material when used alone as a tanning agent. They then proceeded, by a long series of tests, to modify the ferric sulfate tan liquor by the addition of various sodium salts of organic acids and various sodium phosphates, keeping the conditions the same as far as possible. The use of various neutralizing agents was also studied. As a criterion of tanning, the shrink temperature test was employed throughout. It was found that the substitution of phosphate from various phosphate compounds showed that all but metaphosphate gave approximately the same results. Metaphosphate formed a precipitate that would not dissolve. The iron phosphate tanned skins had a shrink temperature approximately 20 F.° higher than when iron alone was used. The leather also dried out softer and with a stronger grain. The modifications with sodium salts of organic acids indicated rather conclusively that the use of such a salt was very beneficial provided the acid contained a hydroxy group in the molecule. It was possible to raise the shrink temperature as much as 55 F.° by this type of addition. As a result of this, the authors recommend the use of sodium gluconate, which contains five hydroxy groups, along with disodium phosphate. According to their procedure, it is possible to obtain an iron tanned leather with a shrink temperature of approximately 205° F. In their work on combination iron-chrome tannage, these investigators employed tan liquors prepared both from ferric sulfate and chromic sulfate and by the ferrous sulfate - sodium dichromate reaction, using all three methods as outlined in Part I of this paper. Experiments were run with and without the incorporation of the improvements found for iron tannage. They concluded:

(1) The use of phosphate and gluconate was very beneficial and should be included in an iron-chrome tannage.

(2) Very little choice existed between the oxidation-reduction method and the ferric sulfate - chromic sulfate method.

(3) Leather first tanned with iron and then retanned with chrome gave the highest shrinkage temperature in all cases.

There is then supplemented practical procedures for preparation of both straight iron and iron-chrome leather. As was mentioned in Part I, this laboratory has examined samples of this leather and has found it to be very satisfactory. Accelerated aging tests have shown this material to stand up fully as well as a straight chrome leather prepared under similar conditions of a small-batch process.

It is evident from the above, which has attempted to give a fair picture of the status of systematic study of iron tanning at the present time, that knowledge of the effects of various factors on the fixation of iron by hide substance is very imperfect. It is the purpose of this Part to gather such data, under controlled laboratory conditions, which will contribute materially to this knowledge.

EXPERIMENTAL METHODS

The methods employed throughout this Part are in general very similar to those of Part I. However, due to the desire to have as far as possible only one variable in each test, certain modifications and refinements were incorporated.

As standard technique it was decided to use exactly 10.00 grams of hide substance in the form of the calf-skin squares described before. These were soaked back in 100 ml. portions of distilled water for 24 hours, then drained for five minutes on funnels before being placed into the pickle.

Pickling was carried out by a standardized method described in a following section. The pickled calf-skin squares were then drained on funnels, blotted in a clean towel, and put into the tan liquor.

All treatments except soaking were conducted in the Launderometer, standard laboratory testing instrument of the American Association of Textile Chemists and Colorists. With this apparatus it is possible to obtain constant agitation and temperature. The temperature was arbitrarily set at 30° C. (86° F.) which was always slightly above room temperature, a necessary criterion if constant temperature is to be attained with this apparatus since it has no cooling facilities. The operations were carried out in closed pint jars which were completely immersed in the Launderometer water bath.

Concentrations in all cases were calculated on an over-all basis; i.e., the quantities of Na_2SO_4, H_2SO_4 and water carried over into the tan liquor by the pickle as well as the Na_2SO_4 formed by neutralization were taken into account. This was made possible by the standardized pickling procedure in which the quantity of pickle used was so large as to overcome slight variables in water content or alkaline residue of the soaked stock.

On this basis the hide substance-water ratio was arbitrarily set at 9.7-1; i.e., 97 grams of water to 10 grams of hide substance. Since the pickled stock contained by analysis 22 grams of water, the volume of tan liquor used was 75 ml.

The tan liquors were made up by taking a measured quantity of a concentrated stock solution of analytical grade ferric sulfate, previously analyzed for iron and H_2SO_4 content. To this was added the requisite quantity of Na_2SO_4 in the form of a concentrated solution and then the calculated quantity of Na_2CO_3 solution to produce the desired basicity. After diluting to volume and thoroughly mixing, they were ready for use. These liquors were always prepared just prior to addition to the pickled stock, as ferric sulfate solutions of the degrees of basicity involved are somewhat unstable and would precipitate on standing. At no time was a precipitated liquor employed in these investigations, all solutions being examined for clarity before using. Due to the H_2SO_4 and Na_2SO_4 carried over from the pickle, it is, of course, necessary to prepare a liquor of greater basicity and lesser Na_2SO_4 content than that desired in the equilibrium system. As a consequence of this, liquors in which a low concentration of iron is used will be of higher basicity at the beginning of the tanning period than those in which a high concentration of iron is used. However, the important consideration is that once equilibrium has been established, all the systems have the same known basicity and Na_2SO_4 content.

Analytical Methods

Here, as above, the methods were very similar to those employed in Part I; however, again certain modifications were incorporated. The squeezing and washing techniques were eliminated and blotting in a clean towel substituted. The pressure at which the samples were pressed to remove uncombined liquor was increased to 22,000-23,000 pounds, the manipulation being otherwise the same. After drying and grinding, the Kjeldahl nitrogen and iron were determined as previously, but one precipitation of ferric hydroxide was considered sufficient in the absence of chromium. The perchloric acid digestion was found to be complete after 2-2½ hours at boiling temperature.

Any variance from the above experimental methods is noted in the experiment involved.

Standardization of Pickling Procedure

Since the neutralization of ferric sulfate by sodium carbonate during the preparation of the tan liquors produces sodium sulfate, it was decided to use a pickle containing sodium sulfate instead of the somewhat more customary sodium chloride. With this modification it is thereby possible to eliminate the chloride ion and any possible effects of it from the tanning procedure.

Wilson (25) has stated in his Chemistry of Leather Manufacture that a satisfactory pickle liquor is obtained by using a molar solution of sodium chloride to which sulfuric acid is added in the desired amounts. Reasoning along the same lines, a molar (142 grams per liter) solution of sodium sulfate was chosen, using enough sulfuric acid to bring the pH value to 2.0 (4.00 grams H_2SO_4 per liter).

Now, since it was desired to obtain from the pickling operation a stock containing known quantities of hide substance, water, Na_2SO_4, and H_2SO_4, and of known pH value, the following procedure was set up and standardized. The standardization was accomplished by putting three samples through the operations involved, weighing them after each step, and finally analyzing them as well as the spent pickle liquor to determine the quantities of the three variables present, it being assumed that there was negligible loss of hide substance in the process. Especial note was made of the deviations in weights and analyses in order to determine to what extent the process was reproducible.

Three samples of exactly 10.00 grams of hide substance were weighed out, soaked back in 100 ml. of distilled water for 24 hours, drained on funnels for five minutes, and weighed. They were then pickled at 30° C. in the Launderometer for 24 hours, using 300 ml. of the sulfate pickle solution. This volume was taken as it represents about 1 to 8 by weight on the soaked skin and should be large enough to take care of slight differences in the water content of the soaked stock. After pickling the samples were drained for 5 minutes, weighed, blotted without squeezing in a clean towel and reweighed. The observed weights at the end of each operation were:

Sample No.	1	2	3
Soaked samples, drained	37 grams	37 grams	37 grams
Pickled samples, drained	39 "	39 "	38 "
Pickled samples, blotted	34.5 "	34.5 "	34.5 "

Since there is no convenient and accurate method for determining the quantity of acid in a sample of pickled stock in the presence of a large amount of the salt of that acid, it was decided that the best determination of this quantity could be made by measuring the loss of acid from the pickle liquor. This method is, of course, not a good determination of the bound acid, as it does not distinguish between the bound and mechanically entrained acid contents; however, in this work all that was required was a method for determining the total acid carried over into the tan liquors. Each pickle bath originally contained 300/1000 x 4.00 grams, or 1.20 grams, H_2SO_4. The water carried over into the pickle bath by the soaked stock was 37 grams minus 10 grams, or 27 grams, assuming that all water is available for dilution. The original concentration, therefore, was equal to 1.20/327 or 0.00367 grams H_2SO_4 per ml. The final concentration after pickling was determined by titrating 50 ml. samples of the spent liquor with 0.1 N NaOH to a phenolphthalein endpoint. This concentration was determined as 0.00235 plus or minus .00001 gram H_2SO_4 per ml. for the three samples. The difference in concentration is accordingly 0.00132 grams per ml. and the total acid taken up by the hide substance is 0.432 grams per sample.

The sodium sulfate content was determined by ashing and igniting the blotted pickled stock at a dull-red heat. The normal ash of the sample was subtracted from the percentage obtained to give the desired result. This method is subject to several errors: the original ash may have dissolved in the soak water or pickle liquor, or it may have been appreciably altered in composition by the sulfuric acid. In either case, the error involved would not be large, and a difference of several hundredths of a per cent of sodium sulfate would have negligible effect on the fixation of iron by hide substance. The quantity of sodium sulfate thus determined was 2.18 plus or minus 0.2 grams per sample.

The pH values of the three spent liquors, and therefore of the samples, were 2.20, 2.19, and 2.20.

To summarize: It is possible to prepare by the above standardized procedure a pickled stock of pH 2.20 and of the following composition:

10.00	grams hide substance
2.18	grams sodium sulfate
0.432	grams sulfuric acid
22.0	grams water (by difference)

The Pressing Method

The technique of the pressing method has already been described and references given in Part I. It was the purpose of this investigation to assure that a pressure of that used throughout the work was sufficient to remove for practical purposes all occluded and mechanically entrained tan liquor from the sample. The procedure used was that of obtaining data over a wide range of pressures, and demonstrating that material increases of pressure caused only slight changes in the fixed iron content of the samples. Pressures chosen were 2,500, 5,000, 10,000, 15,000, 20,000, and 22,500 pounds gauge. The surface over which pressure was applied was not determined but was the same as that used throughout the investigation and amounted to approximately 9 square inches.

Six 10.00-gram samples of hide substance were weighed out, soaked, pickled, and tanned in a 1/6 basic $Fe_2(SO_4)_3$ system containing 10% Fe_2O_3 on the weight of the hide substance and 5% Na_2SO_4 on the volume of the tan liquor, observing all standardized techniques. An example of the data necessary to prepare a tan liquor such as this is here included. This information will not be given for each experiment; however, all calculations were made by this method.

Grams Fe_2O_3 Required	Ml #2 Stock Solution	Grams H_2SO_4 Total	Grams H_2SO_4 1/6 Basic	Grams H_2SO_4 to be Neutralized	Grams Na_2CO_3 Required	Grams Na_2SO_4 Formed
1.000	10.04	1.769	1.535	0.234	0.253	0.339

Each sample of pickled stock contained 0.432 grams H_2SO_4 and 2.18 grams Na_2SO_4. This requires 0.466 grams Na_2CO_3 to neutralize it, which yields 0.626 grams Na_2SO_4, making a total of 2.81 grams Na_2SO_4 from this source. So for 75 ml. the materials required are:

10.04 ml. #2 stock solution of ferric sulfate
7.19 ml. 10% sodium carbonate
6.00 ml. 10% sodium sulfate
Water to volume

After tanning for twenty-four hours, these samples were drained, blotted of the excess tan liquor, and pressed at the above pressures, one sample per pressure. After air drying and grinding to 20 mesh, they were analyzed for Fe_2O_3 and hide substance. It can be easily seen from Table VI that the method gives results which can be interpreted to indicate that practically complete removal of the uncombined

TABLE VI

THE PRESSING METHOD

Sample Number	Pressure in Pounds Gauge	Grams Fe_2O_3 Fixed Per 100 Grams Hide Substance
1	2,500	6.37
2	5,000	6.42
3	10,000	6.29
4	15,000	6.26
5	20,000	6.18
6	22,500	6.13

Fe_2O_3 is obtained at even moderate pressures, an increase of 20,000 pounds causing removal of only 0.24% more Fe_2O_3. Since the overall experimental error has been estimated from experiments involving reproducibility of results at approximately 10%, it can be seen that this technique is acceptable to the present work.

RESULTS

The Effect of Time and Concentration on Iron Fixation

Due to the experimental technique employed by which a tan liquor of high basicity and a pickled stock of high acidity are allowed to neutralize each other and produce a system of desired overall basicity, it was necessary at the outset of this investigation to determine the time period required for an equilibrium to be established. This period would also involve, of course, the time necessary for the complete diffusion of the tan liquor through the stock, and the time required for the iron to precipitate and become fixed there.

The experiment was carried out by tanning the pickled calf-skin squares in tan liquors containing various concentrations of iron over varying time periods, the overall basicity being maintained at 16-2/3%. All the previously outlined techniques were employed and the Na_2SO_4 concentration was maintained at 5% of the tan liquor volume (3.75 grams Na_2SO_4 per tan bath). The results obtained are tabulated in Table VII and plotted in Figure IX.

It can be seen from these data that equilibrium has been essentially established after six hours, any fixation occurring after this time being small. It has been concluded, therefore, that a tanning period

TABLE VII

EFFECT OF TIME AND CONCENTRATION ON IRON FIXATION FROM 1/6 BASIC FERRIC SULFATE SOLUTIONS

% Fe_2O_3 on Hide Substance	Grams Fe_2O_3 Fixed per 100 Grams Hide Substance at 1 Hour	3 Hours	6 Hours	24 Hours
5	2.36	3.47	4.32	4.50
10	3.02	4.70	5.61	6.13
15	4.32	-	6.65	7.31
20	5.38	7.04	7.46	7.95
25	5.69	7.55	8.05	8.11

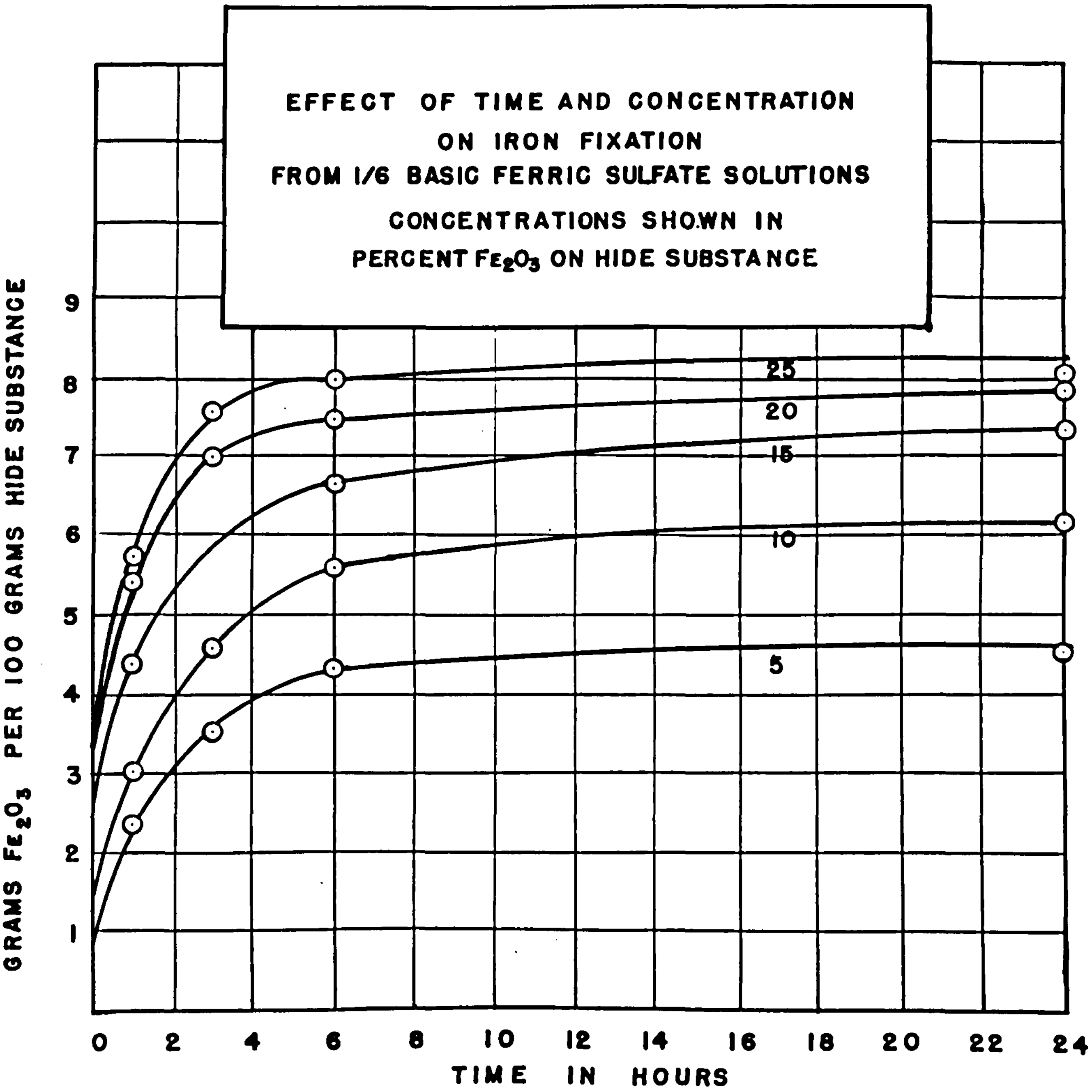
EFFECT OF TIME AND CONCENTRATION ON IRON FIXATION FROM 1/6 BASIC FERRIC SULFATE SOLUTIONS
CONCENTRATIONS SHOWN IN PERCENT Fe_2O_3 ON HIDE SUBSTANCE
GRAMS Fe_2O_3 PER 100 GRAMS HIDE SUBSTANCE
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME IN HOURS
25
20
15
10
5

FIGURE IX

of twenty-four hours is ample for the establishment of an equilibrium system under the present conditions, and this time interval has been used in succeeding experiments.

On further examination of Table VII and Figure IX it can be seen that at a definite basicity the fixation of iron is proportional to the concentration of iron in the tan liquor. It is also evident that this proportionality is not direct, but the iron is fixed to a much greater degree from the more dilute solutions. Thus from the 5% concentration 90% of the Fe_2O_3 is fixed in twenty-four hours; from the 10%, 61.3%; 15%, 48.7%; 20%, 39.8%; and from the 25%, only 32.4%.

The Effect of Sodium Sulfate on Iron Fixation

In the foregoing section the concentration of Na_2SO_4 was arbitrarily set at 5% of the tan liquor volume (3.75 grams per tan bath), or, if the water carried over into the system by the pickled stock is considered, 3.87% on the total water basis. However, other work has shown that while Na_2SO_4 seems to have only a slight effect on the basicity at which precipitation of $Fe_2(SO_4)_3$ solutions occurs, it does have the effect of raising the pH of such solutions and at the same time causes them to be slower in precipitating. In view of these noticeable effects, and since it is known that Na_2SO_4 causes decreased Cr_2O_3 fixation in chrome tanning, it was deemed advisable to determine the effect of Na_2SO_4 on the fixation of iron by hide substance.

The procedure was exactly like that previously employed for the twenty-four hour samples except that the Na_2SO_4 concentration was varied instead of maintained constant, the concentrations chosen being 4, 6, 8, and 10% Na_2SO_4 on the total water (97 ml.) basis. This effect could not be studied at much less than the 4% concentration because of the salt carried over from the pickle and formed by neutralization in the basicity adjustment.

There are several points to be noted upon examining Table VIII and Figure X:

First, the effect of Na_2SO_4 on iron fixation over the range of concentration studied is generally not very great; in fact, with the experiments being reproducible only to within approximately 10% of the given fixation value, the curves of Figure X would not be possible except that the whole of the study was made at one time and the experimental error under these conditions is much less.

Second, with increasing iron concentration the effect of Na_2SO_4 becomes more pronounced, causing a considerable decrease in fixation at the 25% concentration but only slight decrease at 5%.

Third, on going from 20% to 25% Fe_2O_3 the effect of increasing concentration of Na_2SO_4 is such that less and less iron is fixed until finally at the 10% concentration there is a maximum in the curve, showing less Fe_2O_3 fixed from the 25% concentration than from the 20%.

The Effect of Basicity on Iron Fixation

Since it was shown that the fixation of iron is indirectly proportional to its concentration at a given basicity, it was decided to extend this study to other basicities. In addition, since iron tanning could be expected to be somewhat similar to chrome tanning in its

TABLE VIII

EFFECT OF SODIUM SULFATE ON IRON FIXATION FROM 1/6 BASIC FERRIC SULFATE SOLUTIONS

% Fe_2O_3 on Hide Substance	Grams Fe_2O_3 Fixed per 100 Grams Hide Substance at Na_2SO_4 Concentration of			
	4%	6%*	8%	10%
5	4.37	4.40	4.33	4.31
10	6.33	6.07	5.96	5.88
15	7.17	7.16	6.68	6.58
20	8.06	7.89	7.67	7.48
25	8.59	8.25	7.67	7.28

*Average of two determinations

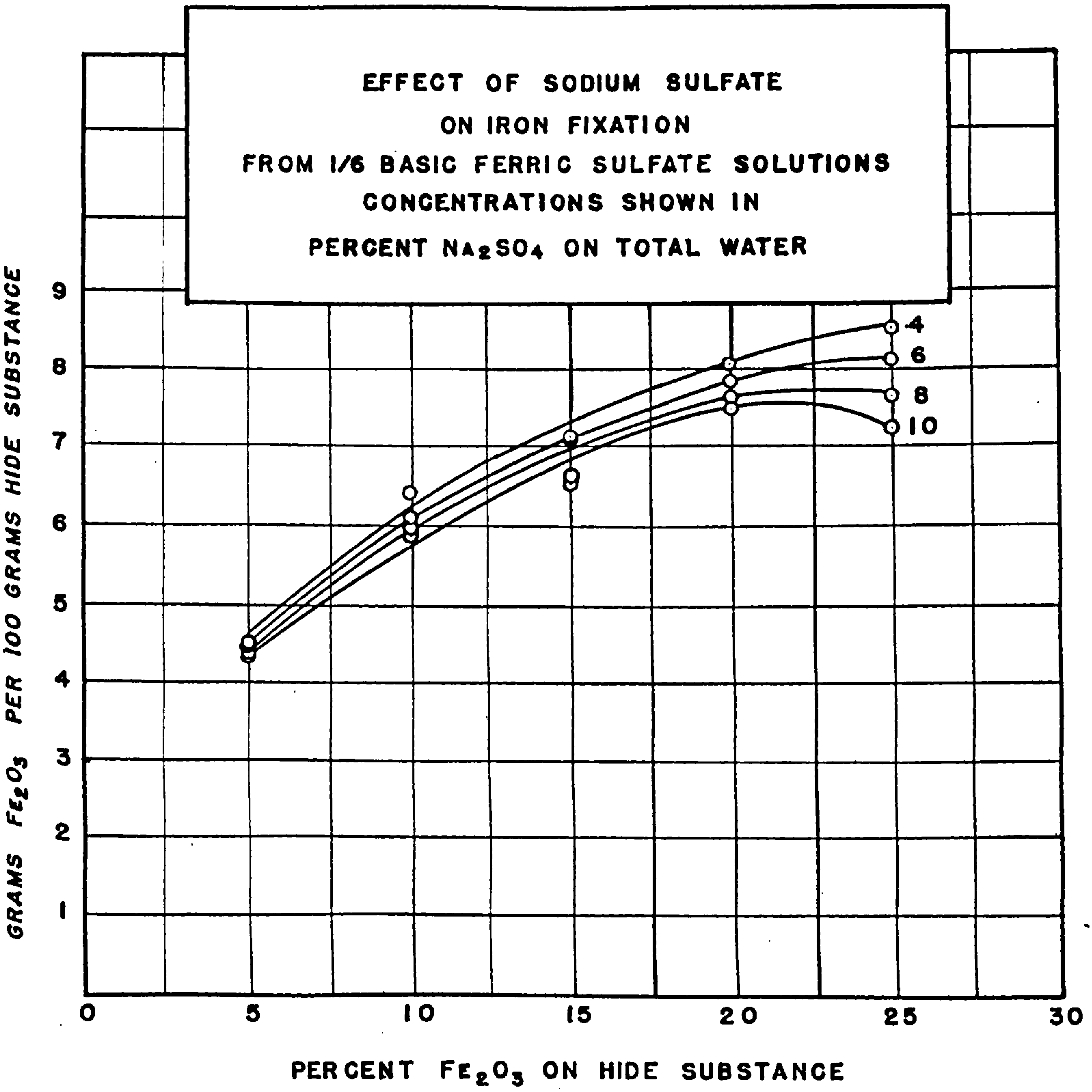
EFFECT OF SODIUM SULFATE
ON IRON FIXATION
FROM 1/6 BASIC FERRIC SULFATE SOLUTIONS
CONCENTRATIONS SHOWN IN
PERCENT NA_2SO_4 ON TOTAL WATER
GRAMS FE_2O_3 PER 100 GRAMS HIDE SUBSTANCE
1
2
3
4
5
6
7
8
9
0
5
10
15
20
25
30
PERCENT FE_2O_3 ON HIDE SUBSTANCE
4
6
8
10

FIGURE X

mechanism, it was desired to show that the fixation of iron is an adsorption process following the requirements as set forth by Langmuir (15) and Freundlich (2). Also it was hoped to obtain data on the shrinkage temperatures of the samples, and, if shrinkage temperatures can be used as a criterion of good tannage, to find the best concentration and basicity for iron tanning from solution of basic ferric sulfate.

The procedure used was the same as that outlined previously except for certain modification made desirable by the higher basicities employed, the basicities chosen for study being 8-1/3%, 16-2/3%, 25%, and 33-1/3%. The use of basicities over 33-1/3% is inadvisable in iron tanning due to the pronounced hydrolysis of ferric sulfate solutions which causes precipitation to occur very rapidly at a basicity much over this value in dilute solutions. Even at this value, difficulty was expected in the low iron concentration sets, since the procedure employed throughout requires a much more basic initial tan liquor than the stated overall basicity of the system. To combat this, the tan liquors were made up containing the requisite amounts of Na_2SO_4 and $Fe_2(SO_4)_3$ and diluted to 50 ml. These solutions were then added to the pickled stock in the tanning jars and allowed to stand. Then the required quantities of Na_2CO_3 were added in 25 ml. of solution and the whole quickly mixed. Tanning was carried out as usual for twenty-four hours after the addition of the alkali. It can be seen that this method offsets the difficulties involved in neutralizing the H_2SO_4 of the pickled stock without having a precipitated tan liquor.

In order to keep results comparable, the Na_2SO_4 concentration was maintained at 6% on the total water basis. This is the lowest possible concentration that will correspond to previously determined data, since in the 33-1/3% basic, 25% Fe_2O_3 experiment, the total sulfate formed and carried over from the pickle amounts to 4.92 grams.

At the end of the tanning period, the samples were drained as usual but the equilibrium liquor was collected in clean flasks which were stoppered immediately and saved for analysis. The condition of the liquors was noted and the pH was determined on the glass electrode within an hour. Aliquot samples were taken after thorough mixing and were analyzed for total Fe_2O_3 by digesting in perchloric acid, precipitating with NH_4OH, redissolving, and running the iron as usual by the Zimmermann-Reinhardt procedure, using 0.05 N $KMnO_4$.

The shrinkage temperatures were determined on air-dried, unpressed samples selected as representative of each tanning experiment. The instrument employed was the Theis Shrinkage Meter, and the heat transfer medium was water. These measurements generally showed considerable variation within each set. For example, the 25% Fe_2O_3 concentration at 25% basic gave values of 71.0 C, 66.5 C, and 67.0 C, which, on averaging, gives 68.2 C. The results reported are averages of three determinations.

Table IX contains the data determined in this section. Figure XI shows the effect of basicity on iron fixation, while Figure XII shows these data plotted according to the requirements of Freundlich and Langmuir.

TABLE IX

THE EFFECT OF BASICITY ON IRON FIXATION

(a) Original concentration, % Fe_2O_3 on hide substance
(b) Grams Fe_2O_3 fixed per 100 grams hide substance = x/m
(c) Grams Fe_2O_3 unfixed per ml. of equilibrium liquor = C
(d) C/x/m
(e) pH of equilibrium liquor
(f) Condition of equilibrium liquor
(g) Average shrinkage temperature of three air-dried unpressed samples, °C

8-1/3% Basic

a	b	c	d	e	f	g
5	3.96	0.00126	0.000318	2.60	clear	62.3
10	5.29	0.00567	0.001071	2.37	"	65.5
15	5.72	0.01080	0.001890	2.27	"	69.0
20	5.85	0.01662	0.00284	2.11	"	71.5
25	5.88	0.0219	0.00372	2.00	"	70.0

16-2/3% Basic

a	b	c	d	e	f	g
5	4.40*	0.00114	0.000240	2.62	"	60.2
10	6.07*	0.00471	0.000752	2.39	"	65.7
15	7.16*	0.00924	0.001293	2.30	"	67.5
20	7.89*	0.01448	0.001831	2.23	"	66.7
25	8.25*	0.01978	0.00238	2.19	"	67.5

*Average of two determinations

25% Basic

a	b	c	d	e	f	g
5	4.38	0.00077	0.000175	2.70	"	62.0
10	7.07	0.00381	0.000539	2.43	"	65.0
15	8.26	0.00781	0.000946	2.33	sl. ppt.	66.3
20	9.64	0.01231	0.001278	2.27	ppt.	69.5
25	10.13	0.01800	0.001774	2.22	"	68.2

33-1/3% Basic

a	b	c	d	e	f	g
5	4.73	0.00063	0.000133	2.79	clear	60.3
10	7.19	0.00404	0.000562	2.50	ppt.	64.3
15	9.03	0.00755	0.000835	2.39	"	65.8
20	10.38	0.01200	0.001157	2.31	"	68.3
25	10.57	0.01750	0.001654	2.27	"	67.3

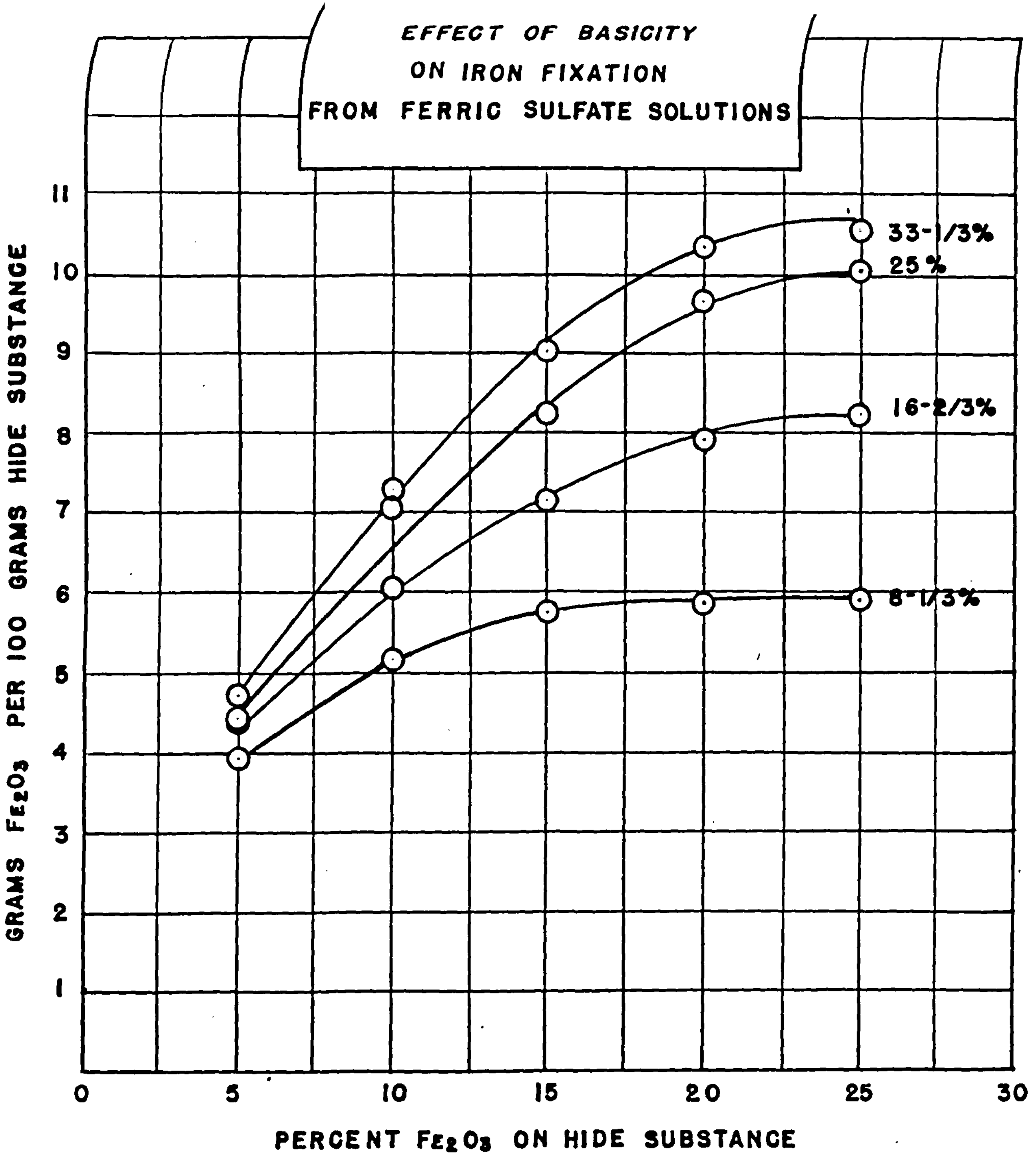
EFFECT OF BASICITY
ON IRON FIXATION
FROM FERRIC SULFATE SOLUTIONS
GRAMS Fe₂O₃ PER 100 GRAMS HIDE SUBSTANCE
PERCENT Fe₂O₃ ON HIDE SUBSTANCE
0
5
10
15
20
25
30
1
2
3
4
5
6
7
8
9
10
11
33-1/3%
25%
16-2/3%
8-1/3%

FIGURE XI

EFFECT OF BASICITY ON IRON FIXATION

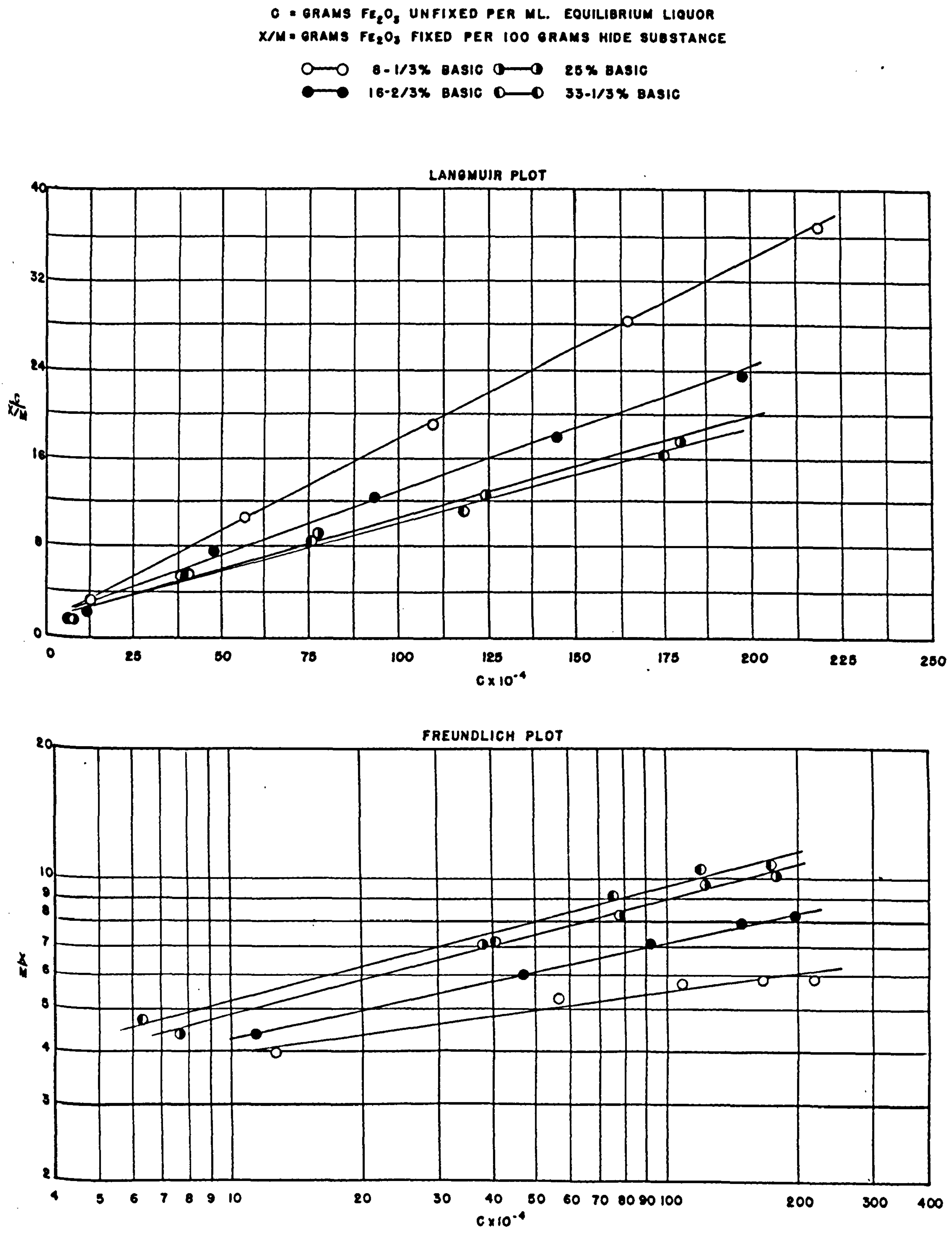

FIGURE XII

DISCUSSION

These data clearly indicate that the fixation of iron by hide substance is an adsorption process dependent upon the basicity of the iron liquors and (from the preceding section) the sodium sulfate concentration. Since it is difficult to conceive of any process of adsorption dependent upon these variables other than that demonstrated by McLaughlin (16) for chrome tanning in which he has shown that the deposition of chrome is dependent on the adsorption of acid by the hide substance, it is logical to assume that the mechanism of iron tanning is similar to that found for chrome tanning.

Several factors which have been considered in making this assumption should be mentioned:

1. Iron salts are similar to chrome salts in that they are readily hydrolyzable to free acid and a more basic insoluble compound. This mechanism is thereby possible.

2. It is known that ferric hydroxide hydrosol is incapable of tanning and cannot penetrate skin. Other experiments have also shown that any insoluble product formed by precipitation of ferric solutions is incapable of penetration. Since it is known that iron tanning involves complete penetration, it cannot be assumed that precipitated iron salts are responsible for the adsorption-type phenomenon which has been observed. It is necessary to eliminate this as a possibility because it is known that precipitation of ferric sulfate solutions is dependent upon basicity and sodium sulfate concentration, the variables upon which the adsorption is dependent.

3. Ferric sulfate, ferric ion, or any other soluble factor, the concentration of which is not dependent upon basicity and sodium sulfate concentration, cannot be the adsorbed material. It is possible, however, that the hide substance may have a specific adsorption capacity for a certain type of soluble basic ferric sulfate, as there is evidence in the literature that thie type of compound does exist in solution, and it is known that adsorption phenomena are very specific in nature. The present data are not extensive enough to further examine this possibility, and it must await future work. However, it is felt that at this time it is better to accept the mechanism so well worked out by McLaughlin rather than postulate a new one with insufficient data.

Upon accepting the assumption that the fixation of iron is dependent upon the adsorption of acid by hide substance, the question of the nature of the iron compound which is fixed should be discussed. In order to shed more light on this problem, it is perhaps well to summarize briefly the known facts concerning the nature of ferric sulfate solutions and basic ferric sulfate compounds.

The literature of these subjects is a maze of conflicting claims and counterclaims. Investigators have repeatedly denied the existence of basic compounds found by their predecessors and have postulated new compounds of their own. Other workers have denied the existence of any basic salts and have regarded them all as mixtures or solid solutions whose composition depends upon arbitrary conditions of temperature and concentration at formation. Mellor (19) in his Comprehensive Treatise has come to the conclusion that for straight hydrolysis of ferric sulfate solutions "so far as chemical analysis can tell, there might be an indefinitely large number of products where there is no break in the continuity of the process of transformation, by hydrolysis, from pure ferric sulfate to pure ferric hydroxide." In this regard, Wieser (24) has recently shown that ferric hydroxide as such does not exist, but the compounds previously known as this are various forms of ferric oxide with varying amounts of entrained water. He has also indicated that the insoluble compounds formed by hydrolysis of ferric sulfate solutions are either $\alpha Fe_2O_3.H_2O$ (yellow) or αFe_2O_3 (red-brown) depending upon the age of the solution and the rate of precipitation, the hydrate being formed by slow precipitation from old solutions and the non-hydrated oxide by rapid precipitation from freshly-prepared solutions.

The factor which has caused so much confusion in the literature with regard to the postulation of so many basic ferric sulfate salts is that these ferric oxides are now known to adsorb considerable quantities of sulfate, the actual quantity of which being dependent on concentration, and rate and other conditions of precipitation. Kolthoff and Sandell (11) have explained this phenomenon: "It should be realized that from solutions having an acid reaction there will be primarily an anion adsorption. The surface of the hydrous oxide attracts the protons (H^+) and consequently an equivalent amount of anion is adsorbed. The adsorbability of the anions increases with increasing valence. Thus, for example, it is found that sulfate, chromate, and oxalate are much more strongly adsorbed than chloride, nitrate, etc. In addition, the adsorption increases with increasing hydrogen ion concentration. Therefore, a coprecipitation of anions can be expected if the precipitate is formed in acid medium."

Further evidence to support this proposition can be found in the paper of Kraus (12) who has shown that the precipitates formed by adding various quantities of alkalies (KOH, NaOH, NH_4OH, Na_2CO_3, K_2CO_3, $NaHCO_3$ or $C_6H_5NH_2$) to ferric sulfate solutions containing 1.16% Fe_2O_3 are of variable Fe_2O_3/SO_3 ratio depending upon the hydroxyl ion concentration, and that a pH of 7.7 must be attained before these precipitates are SO_3 free.

It should not be inferred from the above discussion that basic ferric sulfate compounds do not exist, as there is good evidence in the literature that such compounds do exist in solution and may be formed as stable solid products under certain conditions of Fe_2O_3 and SO_3 concentration. With regard to this some experiments conducted by the writer have shown that there is a definite maximum at approximately 30% basicity in the curve relating pH and basicity of ferric sulfate solutions, the Fe_2O_3 and Na_2SO_4 concentration being kept constant. This maximum could be interpreted to indicate that a basic compound is formed in solution.

However, examination of the conditions at which such basic ferric sulfates are formed as the stable solid phase (or precipitate) rather clearly indicates that they are not the conditions to be found in iron tanning, but are conditions of much greater Fe_2O_3 and SO_3 concentration. In this respect the work of Posnjak and Merwin (20) on the system $Fe_2O_3 \cdot SO_3 \cdot H_2O$ seems to be the most reliable study on the subject. These investigators have made a careful examination of this system at equilibrium over the temperature range of 50° C. to 300° C. They have drawn isotherms for each of the temperatures studied showing the solid phases in equilibrium with the saturated solutions over the entire possible range of concentration, and have constructed a solid model for the system over the whole range of temperature. It is recognized, of course, that it is somewhat dangerous to try to extrapolate these data from their temperatures to 30° C., the temperature of tanning used throughout this study. However, the data presented are such that it appears extremely unlikely that the rather dilute basic solutions used in tanning would have other than $\alpha Fe_2O_3 \cdot H_2O$ as the stable solid phase. This is especially true when it is considered that the hide substance adsorbs more acid from the system causing even higher basicities.

In the above discussion it has been pointed out that the solid phase to be expected from solutions of ferric sulfate of concentration and basicity such as are used in tanning is probably $\alpha Fe_2O_3 \cdot H_2O$ or αFe_2O_3 with entrained water and adsorbed sulfate. It would seem very probable, therefore, that this is the type of compound which is fixed by the skin in iron tanning with solutions of basic ferric sulfate, unless, of course, the hide substance has a specific adsorption capacity for a certain type of soluble basic compound as was mentioned before as a possibility which could not be examined further with present data. From this it is possible to propose that the iron tanning mechanism takes the course of adsorption of acid from the tan liquor by the hide substance causing deposition of the iron compound which is probably ferric oxide with varying amounts of occluded sulfate. This proposition does not necessarily hold, of course, if material other than pure ferric sulfate, such as organic acids, phosphate, etc.

are employed.

Assuming that this proposition is correct, there are several anomalies in the present work which must be explained. In the section on the effect of sodium sulfate on iron fixation, it was noted that this salt had only a slight effect on iron fixation at the 5% Fe_2O_3 concentration level, while the effect was rather pronounced at the 25% level. It was also noted that on going from 20% to 25% Fe_2O_3 the effect of increasing quantities of Na_2SO_4 is such that less and less iron is fixed until finally at the 10% Na_2SO_4 concentration there was a maximum in the curve showing less Fe_2O_3 fixed from the 25% concentration than from the 20%. McLaughlin (18) has shown that Na_2SO_4 causes decreased H_2SO_4 fixation, which thereby explains the decreased chrome (or, in this case, iron) fixation, and it seems to be entirely possible, within the limits of experimental error, that this fully explains the first effect noted above. However, the second effect resulting in a maximum in the 10% Na_2SO_4 concentration curve cannot be explained on this basis, and is probably due to the fact that insufficient time was allowed for an equilibrium to be established under these high concentration conditions, since McLaughlin has stated that a longer time (48 hours) and higher temperature (120° F.) were necessary for equilibrium when high concentrations of Na_2SO_4 were employed. These points, then, do not indicate the maximum of Fe_2O_3 that can be fixed under these conditions of concentration and basicity, but merely show the amount fixed in 24 hours' tanning time.

From Figure XI it can be seen that an increase of basicity from 8-1/3% to 16-2/3% causes a certain increase in iron fixation, from

16-2/3% to 25% a slightly less increase in fixation, and from 25% to 33-1/3% only a small increase even though the tan liquors were far from being exhausted. At first this may appear to be a somewhat anomalous condition. However, if Table IX, Column f, is examined, it can be seen that the final equilibrium liquors of the 25% and 33-1/3% sets were not always clear, but in some cases contained precipitated iron oxide. Since it is known that these precipitates cannot penetrate skin, the full amount of iron employed in these cases was not available for tanning, resulting in the somewhat irregular appearance of these data.

SUPPLEMENT

THE INSTABILITY OF IRON-TANNED LEATHER

In view of the large volume of literature on iron tannage, it is perhaps somewhat surprising that up to the present time a satisfactory leather has not been produced, the principal defects of an iron-tanned skin having been variously described by the terms thin, brittle, hard, and unstable to storage or water. The ascribed causes for these defects which have been proposed are just as varied as the defects themselves.

Procter (21) suggested that "iron salts often act as carriers of oxygen, and oxidizers of organic matter, absorbing oxygen from the air, and giving it up again under the influence of light or heat." Acting along these lines Johnson (9) patented the use of antioxidants such as are used in the rubber industry. These materials were to be incorporated in an iron-tanned leather and thus give it the stability to storage which so often had been reported as lacking.

Jackson and Hou (5) also had an oxidation-reduction mechanism in mind when they recommended the incorporation of a slight excess of oxidizing agent in the tanned stock. However, they believe that the tannage failure was due to the reduction of the ferric salt to the ferrous state, the latter compounds being known to have no tanning properties. It can be seen that with regard to oxidation these workers had exactly the opposite idea to that of Procter as to the cause of failure. Since they report that their leathers were completely stable to storage, it does not seem probable that the instability can be ascribed to oxidation of the hide fibers.

In several cases poor stability has been attributed to the fats and greases used in finishing. Casaburi (1) believed that uncombined ferric salts oxidized these fats, resulting in a general degradation of the stock over long periods of time. Kubelka and Nemec (13), working with a combination iron-chrome tanned leather, reported that highly unsaturated greases or those containing much free fatty acid caused appreciable loss in tensile strength in an hydrothermal aging test of this type of stock, while unstuffed leather or leather stuffed with completely saturated and acid free materials were practically unaffected. They believed that perhaps the fats converted the iron salts into insoluble soaps, whereby the acid in the original complexes was liberated and attacked the hide substance. They also discussed the possible effect of atmospheric oxidation but came to no conclusion. Ruppenthal and Malik (22) have noted that the fat liquoring of iron and combination iron-chrome tanned leathers requires special attention. They have employed a light syntan after-treatment of these leathers in order to retard the rate of exhaustion of the fat liquor. It was noted that if the fat liquor went on the leather too rapidly, it was fixed on the surface and resulted in a smeary grain and flesh. The leather dried out hard and dark and in many cases had a tender grain and flesh. In this connection it should be mentioned that at the Columbus meeting of the American Leather Chemists Association a number of persons of recognized experience expressed the opinion that while the fat liquoring of iron-tanned leather required special attention, it does not matter what fats are used provided the leather itself is of good tannage. It would thus appear that any instability found in iron-tanned leather is not due to the fat or grease content but is due to the tannage itself. It may be that a poor tannage may have iron in a form that makes possible the degradation of unsaturated fats or free fatty acids, but at the same time it appears that a good tannage may be fat liquored with any type of fat.

The question is, then, what constitutes a "good" or a "poor" iron tannage, and what is the factor in a poor tannage which causes the instability? Küntzel (14) has briefly mentioned the subject, at the same time pointing out that, in general, scientific iron tannage has been only very slightly worked out. He stated that it was still undecided whether the instability of iron leather depends on an oxidated disintegration of the protein fibers, catalytically influenced by the iron salts, or a hydrolytic destruction through free mineral acid in the hard-to-neutralize leather. However, he goes further in saying, "... it is very probable that the structure instability depends on hydrolytic acid destruction." In view of the previously mentioned adsorption of sulfate by the precipitated iron oxide, it would seem very likely that Küntzel's viewpoint is close to the truth. It will be recalled that the mechanism of the sulfate adsorption involves first the adsorption of hydrogen ion with consequent take-up of the sulfate ion. The iron oxide tanning agent contains, then, an appreciable quantity of free sulfuric acid which could be slowly given off, causing hydrolytic decomposition on aging. It would thus seem that the difference between a "good" and a "poor" tannage lies, at least in part, in the quantity of free sulfuric acid occluded by the precipitated iron tanning agent. Any mechanism whereby this quantity of free acid can be reduced should result in a better tannage, other factors being the same. It has been shown that the pH of the precipitation predetermines to a degree how much SO_3 will be occluded in the precipitate; the higher the pH, the less SO_3. The writer has also found that the rate of precipitation influences this factor, a precipitate formed rapidly occluding more SO_3 than one formed more slowly at the same pH value. The concentration of the ferric sulfate and sodium sulfate could also be expected to have some effect. Ruppenthal and Malik as well as others have succeeded in producing a very satisfactory leather by employing organic hydroxy acids. It would seem probable that these materials may act in one of two ways, or both. They may form complexes with the iron, causing it to be fixed as a compound other than ferric oxide, or they may act by forming unstable complexes from which the iron oxide may be precipitated more slowly and at a higher pH.

SUMMARY

In Part I a study has been made of the fixations of iron and of chrome by calf-skin in combination tannage based on the reaction between ferrous sulfate and sodium dichromate. Data are given for three alternative methods: (1) the two-bath method using ferrous sulfate first; (2) the two-bath method using sodium dichromate first; and (3) the one-bath method.

Part II undertook the study of iron tannage from a more theoretical viewpoint. The variables of time of tannage, basicity of tanning liquor, and sodium sulfate concentration were investigated, and data were presented showing the fixation of Fe_2O_3 by hide substance from basic ferric sulfate solutions in experiments involving each of these three variables. It was proposed that iron tanning from basic ferric sulfate solution takes place by a mechanism similar to that demonstrated by McLaughlin for chrome tanning, sulfuric acid being adsorbed by the hide substance with consequent deposition of the iron as either $\alpha Fe_2O_3 . H_2O$ or αFe_2O_3.

A supplement has been appended which presents a critical discussion of the various postulations as to the cause of the apparent instability of iron-tanned leather.

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