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Current Efficiency of Electrolytic

Chromium Processes

A Thesis Submitted to the Faculty of the Michigan State College

By

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Candidate for the Degree of

M.S.

June, 1927.

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In Appreciation

I wish to express my sincere appreciation to Dr. Dwight Tarbell Ewing, Professor of Chemistry, for the kind assistance, supervision, and ready suggestions which have made possible the successful completion of this investigation.

T.H.K.

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Geuther (Leibig's Ann. <u>99</u>, 314, (1856)) electrolysed solutions of chromic acid and noted that the formation of electrolytic chromium is accompanied by the evolution of hydrogen at the cathode and of oxygen at the anode. Geuther stated that, "the amount of metal deposited stands in direct relation to the hydrogen deficiency". Buff (Leib. Ann. <u>1</u>, 101, (1857)) repeated Geuther's work and reports that the results of Geuther are unreliable.

The electrolysis of chromic acid solutions containing various addition agents offers several problems for further investigation. There is produced during electrolysis of such solutions various substances and changes. For example, there is formed chromium, hydrogen, and trivalent chromium (probably some di-valent chromium) at the cathode. Oxygen is evolved and chromium in the lower states of valence is oxidized at the anode. Heat effects are also produced upon the passage of the current.

It is the object of this work to study quantitatively some of these effects. An attempt has been made to account for the total reduction taking place at the cathode and to determine with the aid of Faraday's laws of electrolysis if all such changes are accounted for. Three changes are assumed to take place, namely, the electrolytic deposition of metallic chromium, the evolution of hydrogen, and the reduction of chromium in the chromate-ion to trivalent chromium. The work of the Bureau of Standards indicates that the current efficiency of the bath employed for the formation of electrolytic chromium is about twelve per cent. Obviously this is very low for practical purposes. Other solutions do not offer much greater yields of chromium. Two lines of approach are offered for improving this

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efficiency. One is to alter the composition of the bath; for example, by changing the concentration of the solution or by the addition of various other substances which would effect the decomposition potential of chromic acid, or the over-voltage of chromium and hydrogen. The second line of approach is the study of such physical factors as changes in current density, temperature, etc. This investigation was undertaken from the second viewpoint.

The main points of investigation are as follows:

1. The percentage of the current used for the reduction of six valent chromium to the lower valent chromium, if any reduction takes place.

2. The percentage of the current used in depositing chromium on the cathode.

3. The percentage of the current used for liberating the hydrogen gas at the cathode.

4. The effect of the temperature changes upon the current efficiency of the chromium deposit, and the color of deposit.

5. The effect of current density upon the nature of the deposit of chromium.

In general the chromic acid solution contained about 250 grams of chromic acid per liter of solution. Various addition agents were added, but in general the same type of bath was used throughout the investigation. The record of the composition of the bath was carefully made and referred to as used. A steel anode was used. The vessel containing the electrolyte had a capacity of about one liter. A small porous cup was used for the anolyte. The hydrogen was collected under an inverted short stem funnel and led into a 500 cc. flask as described later.

-2-

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The Analytical Method

The analytical work involved the determination of three valent chromium in the presence of six valent chromium. Several methods were tried. The most successful one was the iodine titration method which is described here. The three valent chromium is oxidized to six valent chromium by sodium peroxide, and then reduced by potassium iodide, whereupon the free iodine is titrated with a standard solution of sodium thiosulphate.

<u>Procedure</u>: Transfer with a 5 cc. pipett a sample of chromic acid into a 500 cc. graduated flask and dilute it up to the 500 cc. mark. Draw out three portions of 25 cc. each. This contains one-fourth of a cc. of original solution. Acidify each with five cc. concentrated hydrochloric acid and dilute it up to about 100 cc. Add 10 cc. of 20% potassium iodide. Shake and titrate with 0.1N sodium thiosulphate until the color changes from yellow to sea green. Add 5 cc. of 10% fresh starch solution and cautiously titrate again with sodium thiosulphate until the sharp light green end point appears.

Formulas:

 $2 H_2 Cr O_4 + 6 KI + 12 H_2 O \longrightarrow 6KC1 + 2CrCl_3 + 8H_2 O + 3I_2$ $Na_2 S_2 O_3 + I_2 \longrightarrow Na_2 S_4 O_6 + 2NaI$ Calculations:

Since 1 cc. 0.1N sodium thiosulphate is equivalent to 0.001733 grams of chromium, then 0.001733 x cc. of sodium thiosulphate used .x 4 equals to grams of chromium per cc. of original solution. Divide the number of grams of chromic acid by 52% to get the metallic chromium in terms of chromic acid in grams per cc.

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Analysis of Trivalent Chromium.

Dilute 5 cc. original solution to 500 cc. Analyze for six valence chromium by previous method. Pipett out three portions of the diluted solution previously analyzed for six valent chromium into an erlenmeyer flask. To these three portions of diluted sample add two grams of sodium peroxide and gently heat for a few minutes until the excess sodium peroxide is decomposed. The trivalence chromium present in the solution is oxidized into the six valence state. Acidify the solution with concentrated hydrochloric acid and add 5 cc. in excess. Analyze again for the total chromium present in the six valence state by the method of the preceding paragrap.

Treat the result as in the preceding paragraph.

Total chromium minus the six valent chromium equals the three valent chromium present in the solution.

There were quite a number of trivalence chromium salts analyzed. The only one which contained a definite amount of water of hydration was chromium sulphate.

Analysis of chromium sulphate:

$Cr_2 (SO_4)_3 \cdot 5H_2O$	Weight taken	Weight found
1	0 .1195 g.	0.1042 g.
2	0.1018 "	0.1012 "

The determination of trivalence chromium in the presence of six valent chromium.

Sample 1.	Weight taken	Weight found
K ₂ Cr0 ₄	0 .2125 g.	0.2121 g.
Cr ₂ (SO ₄)3.5 H ₂ O	0.1025 "	0.1024 *

-4-

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Sample 2.	Weight taken	Weight found
K ₂ Cr0 ₄	0.1615 g.	0.1612 g.
Cr ₂ (SO ₄) ₃ 5H ₂ O	0.1692 *	0 .1609 "



The Electrolysis of the Solutions.

A steel anode was used. A porous cup separated the anolyte from the catholyte.

The cathode was made of a sheet copper held by a copper wire sealed into a glass tube as shown in Fig. I. It was bent in such a shape as to readily go under the funnel. When the current is passing, the chromium is deposited on the copper electrode and the hydrogen gas liberated is lead by the funnel into the flask, as shown in Fig. I.

Procedure

Before each run the cathode electrode is cleaned, dried, and weighed after it is cooled to room temperature. It is then inserted under the short funnel. Fill the flask A with the chromium solution, close the stop cock B, and use the finger to stop the outlet C. Quickly invert the flask over the tip of the inverted funnel in the vessel D. Fill up the vessel D with chromic acid solution until the funnel is immersed in the solution.

Examine the circuit before closing the switch. Be sure to close the stop cock B and let it remain closed until the current is on. Close the circuit and let the current flow a minute or so until the gas liberated forces the level of the solution down to 20-30 cm. Then gently open the stop cock B and adjust to an appropriate point so that the solution can not flow back into the flask A from the gas delivery tube. Open the circuit when the solution in the flask A is displaced by hydrogen gas to the calberated points X and Y on the tube. Note the time required for liberation of the hydrogen gas. Find the amount of the hydrogen gas liberated and the weight of chromium deposited on the

-6-

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copper electrode. Calculated by Faraday's Law, the amount of the current used. The temperature of the vessel D can be controlled by surrounding it with a large vessel filled with water and ice. For higher temperatures a micro-burner was used.

The study of the change taking place in the solution when current passed.

Data f	or bath No. 03:	All results are i	n grams per liter.
Data	Cr. as CrO3	^{Cr} 2 ⁰ 3	Cr ₂ O ₃ in terms of metallic C.
Aug. 6, 1926	243.23 g.	5.439 g.	2.828 g.
Aug. 17, 1926	236 .34 g.	13.467 g.	7.003 g.
Aug. 18, 1926	256 .27 g.	9 .799 g.	5.091 g.
Sept. 6, 1926	288.87 g.	14.69 g.	7.6395 g.
Oct. 9, 1926	254.6 g.	42.6 g.	22 .18 g.
Oct. 18, 1926	26 5.28 g.	15 .33 7 g.	7 .9 94 g.
Nov. ?, 1926	277.06 g.	38.2 g.	19.8 g.

The analysis of trivalent chromium of same solution when the current is passed at an average of 110 ampere minutes on each run.

20 L. Tank	Cr as CrOg	^{Cr} 2 ⁰ 3	Change Cr ₂ 0 ₃ to Cr.
1	221.4 g.	4.252 g.	2.211 g.
2	•	5.115 g.	2.659 g.
3	•	•	•
4	•	6.82 g.	3.546 g.
5	n	5.115 g.	2.659 g.
6	n	6 .82 g.	3.546 g.
7	n	6.82 g.	3.546 g.

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17 L. Tank (Solution prepared by Professor D. T. Ewing, Dec. 20, 1926.)

In this table below are recorded the results of ten consecutive runs without changing the solution 500 cc. of solution from 17 L. tank was taken.

No. of Run	Date	Cr03	Cr203	Cr203 in terms of Cr.
1	12/22, 1926	226.75 g.	5.115 g.	2.659 g.
2.	•		N	•
3	-	248.489 g.	•	· 19
4	12/2 3, 19 26	245.29 g.	Nê.	19
б		247.22 g.	1ê	••
6	12/27 ,19 26	278.2 g.	n	*
7		319.942 g.	6 .82 g.	3.456 g.
8	•	317.935 g.	M	N
9	12/30 ,1926	3 41.87 g.	M	
10	*	319.942 g.	H	n

The following data shows the effect of changing various factors on current efficiency, etc.

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C. D.	Amp.	Time Min.	Ampere Min't.	Volt	Grams Depst.	ocH. Gas	I% on Cr.	I % on H.Gas	Temp. C°.
16.66	2.5	51.5	128 .75	5	.205	553	29.56	58.47	20-21
۳		51.0	127.5	5.5	.1971		28.71	59.3	•
•	*	51.5	128.75	5.3	.1993	Ħ	28.73	58.47	Ħ
20.00	3.0	40.0	120.0	5.7	.1868	Ħ	28.91	62 .75	21.
•		39.7	119.0		.1878	*	29.6	63.5	
		39.4	118.0	W	.1810	•	29.07	63.8	21-22
26.33	3.5	33.5	117.0	6.5	.1805		28.66	64.2	20-21
	M	33 .5	116.5	H	.1814	•	28.8 9	64.5	•
•		33.0	115.5	7.0	.1763		28.35	65.1	
33.33	4.0	28.0	112.0	7.7	.1783	10	29.56	67.24	20.
		28.5	114.0	7.0	.1821		29.66	66.06	Ħ
		28.0	112.0	7.5	.1775	*	29.43	67 .24	
16.66	2.5	39.17	97.85	5.0	.0879	553	16 .67	76.92	29.
		39.0	97.5	5.2	.0873	N	16.17	77.04	•
20.0	3.0	31.3	93.9	6.5	.0891	18	17.41	80.1	29-30
•		•	•	6 .0	.0834	Ħ	16.93	82.7	
26.33	3.5	26 .5	92.75	6 .8	•0854		17.09	81.2	29
	**	26.0	92.0	6 .6	•0836	Ħ	16 .9	82.75	30
33.33	4.0	21.00	84.0	7.5	.0548	W	12.19	88.86	31-32
•	•	21.17	84.68	7.2	•0557		12 .21	89.01	M
		See gi	raphs on	next	page.				

Data of 20 liter tank: (Solution prepared by Dr. D. T. Ewing)

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CYLON uo porn C N D 2 gas Liberated percentage 8 on H usedon 50 100 percentage 5 225 Current 6 Red line = % of Chromium Violetline = 0% of H. gas 5 5 8 ty lood

C. D.	Amp.	Ampere ∐in's	Volt	Grams Depst	CC H Gas	I% on Cr.	I % on H. Gas	Temp. C	Time Min.
13.33	2.0	118.0	5.0	.1624	533	26.1	63.82	20.21	59.0
	181		Ħ	.1668	Ħ	26 .27	63.82	20-22	
20.00	3.00	123.0	7.0	.1850	11	27.95	62.24		41.0
•		123.75	6 .5	.1809	R	27.99	62.31	20-21	41.2
23 .33	3.5	122.5	7.7	.1953		29.61	61.49	20-225	35.0
×	Ħ	126.0	7.6	.2017	Ħ	29.45	59.76	20-21	36.0
26.66	4.0	136.0	7.5	.2309	19	31.53	55.38	N	34.0
W r		126.0	7.3	.2110	19	31.23	59 . 77	20-22	31.5
33.33	5.0	132.5	9.0	.2345	×	32.53	56.83	20-21	26.5
	19	127.5	9.2	•2228	Ħ	32.45	59.04	20.21,	5 25.5
13.33	2.5	114.34	4.7	.1282	553	20.8	65.83	27-29	57.17
×		115.0	10	.1279	Ħ	20.62	65 .48	*	57.5
20.00	3.0	105.0	5.3	.1216		21.7	71.72	28	35.0
Ħ	*	104.0	5.2	.1204	n	21.5	72.42	30.0	34.66
23.33	3.5	113.75	6.5	.1304		21.2	66.24	n	32.5
	11	112.0	Ħ	.1261	Ħ	20.97	67.24	N.	32.0
26.66	4.0	112.0	7.5	.1261	N	20.92	67.24	30- 32	28.0
	Ħ	108.0	7.2	.1257	10	21.07	69 ,73	10	27.0
33.33	5.0	100.85	8.2	.1233	14	22.70	74.7	30.	20.17
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Data of 17 liter steel tank. (Both of Jan. 20, 1927.)

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Conclusions

1. Whether or not the reduction of six valent chromium to trivalent chromium takes place in the chromium bath is entirely dependent upon the content of the bath.

2. The best current density of the bath is 20-30 amperes per square decimeter.

3. The current efficiency of chromium deposit is inversely proportional to the temperature, while the current efficiency of the hydrogen is directly proportional to the temperature.

4. At higher temperatures, the color of the deposit is brighter than it is at lower temperatures.

5. The current efficiency is lower than Faraday's laws demand. The graph shows that the space between the curves for current efficiency of chromium deposit and that for the current efficiency of hydrogen liberated is the amount of current not accounted for.

A lead peroxide anode has been tried in place of steel. The results by analysis show that the concentration of the cathode solution decreases with each run, while the concentration of the anode portion is increased. This decrease of concentration means a decrease in the amount of chromium deposit. A study of the formation of the perchromic acid formed should be made.

The use of the above described apparatus is advisable only for the study of solutions with a temperature within two degrees of 23° C. due to the changes caused by radiation losses.

A new design is proposed. Preliminary experiments show very good results are obtained with it. (See figure 2.)

-11-

 $q_{1}=1$, $q_{2}=1$, $q_{2}=1$, $q_{3}=1$, $q_{3}=1$, $q_{4}=1$, $q_{4}=1$, $q_{4}=1$, $q_{4}=1$.

Procedure for operation of the apparatus shown in figure 2. Assemble the apparatus as shown in diagram. A solution of known density is placed in the flask S. The tube R is rubber, so the flask S can be raised or lowered. Gas flask A is surrounded by another flask which is filled with water for regulating the temperature of the gas in the flask A. The tube on the meter scale is for evaluating the atmospheric pressure of the solution.

Fill the vessel D with chromic acid solution to above the top of the funnel. Close the stop cock F and open the stop cocks E and B. Raise the flask S to force the solution toward the top of the flask A. Now close the stop cock B and open the stop cock F, draw up the solution from the vessel D to the top of the tube. The stop cook is closed again and the flask S raised until the flask A is filled. Close the stop cocks A and F. Open the stop cock F. Close the circuit now and let the gas form to replace the solution in the tube to F. Then open the cock B. adjust to a point so the solution will not siphon back. When the hydrogen is liberated in the flask to the calibrated point I. the current is broken. Get the solution level on the meter scale M and the atmospheric pressure on the point N. Take the difference on the scale reading and multiply by the density of the solution in the flask S. Divide by the density of mercury to get the decrease in pressure of the gas in the flask. Atmospheric pressure minus this decrease in pressure is the pressure of the gas in the flask.

The following data is typical of the results obtained from the above procedure.

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Amp.	Time Min.	Temp. C.	Gas CC.	Grams Depst.	I% on Cr.	I% of H.gas	Ampere x Minutes	
2.0	60-40	20-21	528	.1786	27.38	59.43	121.4	
	6 0-52	Ħ	5 29	.1797	27.41	59.14	121.8	
3.0	42-48	M	530	.2137	31.03	56.39	128.3	
	42-45		Ħ	.2134	31.01	56.47	128.25	

The described method, as shown by the above data, may obviously be used for other cases where greater accuracy is desired than may be obtained when the original apparatus is employed.

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