

(1) The mean value for the faraday, 96,538 coulombs, given in column XIII has a precision of 0.005%. The average deviation of the individual results from the mean is 0.010% and the maximum is only 0.012%. These deviations are caused by the silver coulometer, not by the iodine coulometer.

(2) The value 96,538 agrees astonishingly well with the value, 96,535, obtained by Richards with his copper coulometer (see Table I).

(3) The results with the iodine coulometer confirm the conclusion, already reached, that the silver deposit obtained in the silver coulometer, even under the best conditions, is greater than that required by the reaction, $\text{Ag}^+ + (-) = \text{Ag}$.

(4) The value 96,538 coulombs per equivalent corresponds to the value 1.1174 milligrams per coulomb for the *true* electrochemical equivalent of silver. This is 0.08% lower than the value obtained by Smith, Mather and Lowry and 0.05% lower than the recent result of Rosa, Vinal and McDaniel (see Table I).

(5) Although we have no reason to believe that our results are affected by any source of error amounting to 0.03%, they are, perhaps, too few in number to justify the conclusion that the value, 96,538 coulombs, is correct within this limit. We believe, however, that the evidence presented in the foregoing pages justifies the statement that the value of the faraday is certainly *greater than* 96,500 coulombs and that the *true* electrochemical of silver is certainly *less than* 1.1180 milligrams per coulomb. We hope to be in a position to make a more definite statement during the coming year.

URBANA, ILL., June 27, 1912.

PASSIVITY OF IRON UNDER BOILER CONDITIONS.

BY HORACE G. BYERS AND FLOYD T. VORIS.

Received August 10, 1912.

Introduction.

The use of substances which inhibit the rusting of iron in order to protect it from the action of corrosive agents was suggested by Cushman,¹ who says that "small quantities of inhibitive substances in boilers should be highly efficacious in preventing pitting." Wyatt² suggests the use of sodium bichromate in boilers to precipitate the scale-forming materials and states that the chromic acid formed does not attack the iron. On the other hand, Schoch and Randolph³ state that "the corrosive character of an aqueous solution cannot be extensively lessened by additions of certain electrolytes such as chromates, hydroxides, etc." Also it was shown by one of us⁴ that in many solutions, in which iron as an anode is

¹ Office Public Roads, U. S. Dept. Agric., *Bull.* 30, 29.

² *Eng. Min. J.*, 60, 220.

³ *J. Physic. Chem.*, 14, 719.

⁴ Byers, *THIS JOURNAL*, 30, 1718.

passive at ordinary temperatures, the passive state is destroyed at temperatures ranging from 60° to 80° , and that it is impossible to render iron passive in halogen salt solutions by the use of anodic current density alone. It therefore seemed to be of interest to determine which of these views, (Cushman *vs.* Schoch), neither of which is adequately supported, is verified experimentally. Since the work was begun two papers bearing on the problem have appeared. Dunstan and Hill,¹ have shown that the presence of salt solutions destroys the passive condition of metals and that on the other hand iron could be obtained in a passive state in boiling potassium bichromate, sodium carbonate and potassium hydroxide. J. L. R. Hayden² has shown that iron plates remain passive in the presence of 0.02% of ammonium chloride but corrode slightly in 0.04% of the same salt.

The present contribution is an effort to go into the subject more thoroughly and at temperatures approaching those prevailing under steam boiler conditions. After the details of the experimental conditions and results are presented, a summary will be offered.

Experimental.

Figs. 1 and 2 show the apparatus devised to determine at what temperatures iron can be kept passive as an anode in bichromate solutions of various concentrations and the arrangement of the coulometer, ammeter,

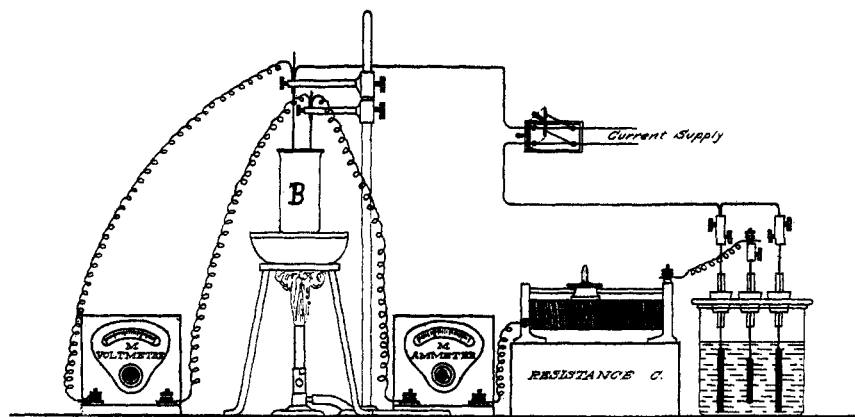


Fig. 1.

voltmeter, etc., to measure the anode loss and current used. In Fig. 2 is shown a boiler which consists of a heavily capped piece of gas pipe, the upper cover of which is pierced with two holes, $\frac{1}{2}$ inch in diameter, to carry the anode and cathode. The boiler also carries a pressure gauge and safety valve and a broad base in order that it may set securely in a

¹ *J. Chem. Soc.*, 99, 1835.

² *J. Frank. Inst.*, 172, 295.

large paraffin bath. The cathode and anode consist of standard iron wire (99.8%) of about 0.7 mm. diameter, sealed in glass tubes and passed through corks securely plugged into the cover of the boiler. The area of the anodes was calculated from the diameter of the wire and the length

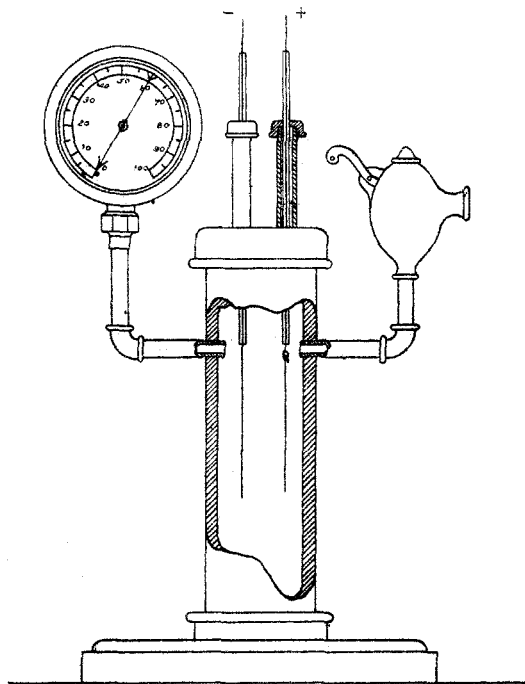


Fig. 2.

of the portion immersed, but because of the difficulty of exact determination of this latter quantity, the density per sq. cm. given in the tables is only approximate. The current used was determined approximately by means of a milliammeter graduated to read to tenths and the amount regulated by a slide wire resistance. To get exact values the current used was measured by means of a copper coulometer with a variable cathode. In conducting the experiments a voltmeter was connected with the electrodes and a key in order to determine when the anode was passive. The readings are not recorded since the voltages have no other significance than to indicate when the iron goes into the passive condition. When active the potential fall between the electrodes was below 2.5 v. and when passive upwards of 4 v., varying of course with the concentration of the electrolytes used and with the current strength employed. Where temperatures of less than 100° are involved the boiler was replaced by a porcelain beaker (B. Fig. 1) and when this was used at or near boiling temperature the level of the electrolyte was maintained as accurately as possible by means of a hot water bottle. Temperatures were determined by a thermometer immersed in the bath close to the boiler and, as the rise of temperature in heating the bath was very gradual, represent very accurately the temperature of the electrolyte. The electrolytes used were prepared in the form of 5% stock solutions of the salts used and the various concentrations employed were obtained by placing the required volumes of each in a 200 cc. flask and diluting to the mark with distilled water.

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TABLE I.

No.	Per cent of $K_2Cr_2O_7$.	Temperature.	Time in min.	Weight of copper deposited.	Weight of iron lost.	Current in milliamperes.	Milliamperes per sq. cm. anode.	Condition.
1....	2.5	80 to 113	39	0.03048	0.00048	39.57	52.9	Passive
2....	4.0	100 to 135	75	0.00810	0.00005	5.47	6.73	Passive
3....	2.0	112 to 146	91	0.00735	...	4.09	5.24	Passive
4....	1.0	103 to 151	116	0.09390	...	40.98	31.0	Passive
5....	0.50	106 to 147	82	0.07235	0.00024	44.67	40.6	Passive
6....	0.25	111 to 120	120	0.05142	0.00010	22.20	32.5	Passive
7....	0.125	122 to 160	107	0.04831	0.00018	22.86	31.48	Passive

Table I gives the results obtained for bichromate solutions of a concentration varying from 4% to 0.125%. The temperatures used varied from 80° to 160° and in all cases the iron is wholly passive, the minute losses and gain of weight being due to rusting above the area immersed in the electrolyte. In each case the iron was presumably active when immersed, being cleaned thoroughly either by pickling in dilute sulphuric acid or by scrubbing with fine emery paper. Temperatures above 160° were not reached because of softening of the cork and loss of steam. Having thus determined that the solutions keep the iron passive at temperatures at and above 100°, the next step was to determine what concentration of sodium chloride is sufficient to destroy the inhibiting influence of bichromate. The results obtained at room temperature are shown in Table II. At all ratios of concentration of less than 40% bichromate to 1 of salt the iron remained active, but the loss of weight of iron is not given because the pitting and rusting were so great as to render cleaning of the anode impracticable. In two cases, Nos. 11 and 12, the iron used was previously made passive by immersion in bichromate

TABLE II.

No.	Per cent of $K_2Cr_2O_7$.	Per cent NaCl.	Ratio of $K_2Cr_2O_7$ to NaCl.	Temperature.	Time in minutes.	Weight of copper deposited.	Current in milliamperes.	Milliamperes per sq. cm. of iron anode.	Condition of anode at close of experiment.
1....	1.0	0.5	2/1	21°	40	0.02565	32.53	52.8	Active
2....	1.0	0.25	4/1	18.5	31	0.02053	33.58	56.5	Active
3....	2.0	0.25	8/1	19.0	40	0.02584	32.88	55.3	Active
4....	4.0	0.25	16/1	19.5	40	0.02840	38.52	64.9	Active
5....	4.0	0.10	40/1	23	40	0.02618	41.68	70.0	Passive
6....	4.0	0.10	40/1	93	32	0.02032	32.15	48.7	Passive
7....	0.3125	0.025	12.5/1	16	8	0.00413	17.42	24.8	Active
8....	0.25	0.0225	20/1	14.5	11	0.00575	26.46	?	Active
9....	0.375	0.0125	30/1	17	11	0.00450	20.71	?	Active
10....	0.50	0.0125	40/1	15	47	0.02398	25.83	28.2	Passive
11....	0.3125	0.0125	25/1	19	12	Qual.	(20.0)	..	Active
12....	0.3125	0.0125	25/1	16	40	0.01518	19.21	26.4	Active
13....	0.3125	0.0125	25/1	21	40	0.01495	19.45	32.4	Active
14....	0.3125	0.0078	40/1	20.5	45	0.02404	27.04	30.2	Passive
15....	0.3125	0.0104	30/1	19	30	0.01633	27.06	29.9	Active

before beginning the experiment in the mixed electrolyte. These results are in accord with those obtained by Dunstan and Hill¹ and by Hayden.¹

The next step was to determine the ratio of bichromate required to keep iron passive in salt solution at about boiling temperature. The temperature registered was 93° as that was conveniently maintained without great loss of solution and without deposition of salts upon the wire outside the electrolyte. The fact previously shown (see introduction) that the general effect of elevation of temperature is to destroy passivity, naturally led us to expect that a larger ratio would be necessary. Quite the reverse was the case and the results given in Table III show that a ratio of 25 of bichromate to 1 of salt is sufficient to render the iron almost if not quite wholly inactive. In Nos. 12 and 13 a small degree of activity is observed but only a very small fraction of that demanded for accord with Faraday's law. In Nos. 4, 7 and 8, it is seen that even a ratio of 20 to 1 is practically effective. In No. 12 the solution used in No. 11 was poured into a flask, which was filled, allowed to cool and used with the same electrodes. The anode was almost theoretically active, probably wholly so if the adhering oxide could be quantitatively removed. In No. 13 a cold solution of the ratio 25 : 1 showed itself wholly active in spite of the anode being previously rendered passive in pure bichromate solution, and when used hot as in No. 14 was effective in producing the passive state.

The next step, the determination of the ratio at temperatures above 100°, was carried out with results as indicated in Table IV. Here again a somewhat surprising result is obtained. While a ratio of 40 : 1 (see Nos. 5, 7, 8) is absolutely effective in inhibiting the activity of the iron even where the concentration is so small as 0.1% to 0.025%, there is appreciable rusting at 35 to 1 and yet the anode loss is not at all equal to that which takes place when iron is wholly active. The exact amount of loss is not indicated by the loss of weight recorded, since much oxide adheres even to the carefully cleaned anode, as in Nos. 1 and 2. The variation in temperature noted in the table is as follows: The boiler was immersed in hot paraffin and when the temperature ceased to fall the current was allowed to pass through the electrodes. The higher temperatures were then gradually attained by continued heating and the apparatus kept at the highest mark for from fifteen minutes to half an hour, when leaks usually developed.

Since in the natural waters likely to be used for boiler purposes the only substances other than chlorides which would remain in solution after treatment with bichromates, are sulfates and carbonates of the alkalis,

¹ *Lec. cit.*

TABLE III.

No.	Per cent of $K_2Cr_2O_7$.	Per cent of NaCl.	Ratio of $K_2Cr_2O_7$ to NaCl.	Temperature.	Time in minutes.	Weight of copper deposited.	Current in milliamperes.	Milliamperes per sq. cm. of anode.	Weight of iron lost at anode.	Condition of anode at close of experiment.
1.....	1.0	0.025	40	93	48	0.03632	38.31	45.8	0.00007	Passive; bright, slight brass colored coating
2.....	0.50	0.0125	40	93	58	0.04224	36.87	44.1	...	Passive; bright, slight brass colored coating
3.....	0.375	0.0125	30	93	40	0.02920	35.69	34.5	0.00004	Passive; bright slight, brass colored coating
4.....	0.25	0.0125	20	93.5	50	0.02452	24.85	25.6	0.00002	Passive; bright
5.....	0.125	0.0125	10	93	54	0.02503	23.47	23.2	...	Active; parts of anode were bright, parts heavily rusted
6.....	0.1875	0.0125	15	93	15	Qual.	Active; heavily rusted
7.....	0.25	0.0125	20	93	30	0.01297	21.89	31.1	0.00066	Active in part, two small patches of rust near tip, otherwise bright
8.....	0.25	0.0125	20	93	45	0.03159	35.54	29.3	0.00010	Active in part, very small patch of rust near tip
9.....	0.3125	0.0125	25	93	50	0.03292	33.33	30.3	0.00012	Passive; bright, brass colored coating
10.....	0.3125	0.0125	25	93	39	0.02711	35.14	31.9	0.00026	Passive; (electrolyte, same as No. 11, Table II)
11.....	0.3125	0.0125	25	93	40	0.01490	18.86	28.6	0.00026	Passive (electrolyte, same as No. 12, Table II)
12.....	Same solution	..	18	45	0.01627	18.30	27.7	0.00707	Active	Active
13.....	0.3125	0.0125	25	21	40	0.01495	18.92	28.6	0.00812	Active
14.....	Same solution	..	93	37	0.01458	19.95	32.4	0.00024	Passive; bright	Passive; bright

TABLE IV.

No.	Per cent of $K_2Cr_2O_7$.	Per cent of NaCl.	Ratio of $K_2Cr_2O_7$ to NaCl.	Temperature.	Time in minutes.	Weight of copper deposited.	Current in milliamperes.	Milliamperes per sq. cm. of anode.	Weight of iron lost at anode.	Condition of anode at close of experiment.
1.....	0.125	0.0125	10	117	109	0.07162	33.27	31.5	0.00952	Active. Heavy coat of rust
2.....	0.125	0.025	5	125	105	0.07543	36.37	31.8	0.01028	Active. Heavy coat of rust
3.....	0.25	0.0125	20	126	67	0.05016	37.90	46.5	0.00228	Active. Partly covered with rust
4.....	0.375	0.0125	30	123	85	0.06510	38.77	38.2	0.00002	Active. Bright, except for few dark spots
5.....	0.437	0.0125	35	125	89	0.06877	38.93	..	0.00082	Active. Mostly bright; several large patches of rust
6.....	0.50	0.0125	40	123	108	0.08095	37.08	41.7	0.00013	Passive. Bright, brass colored coating
7.....	0.25	0.0061/4	40	124	93	0.03578	19.48	26.0	0.00002	Passive. Bright, brass colored coating
8.....	0.1	0.025	40	132	92	0.07065	38.88	46.5	0.00005	Passive. Bright, brass colored coating
				150.5						

a series of tests was made to determine the ratio of bichromate to sulfate which would keep iron passive.

Some additional interest attaches to these experiments since Dunstan and Hill,¹ whose paper appeared during the progress of the work, state that sulfates and nitrates as well as chlorides render iron active when added to solutions in which it is passive. That nitrates do not necessarily do so is shown sufficiently by the experiments of Hayden¹ when he shows that 1% of potassium nitrate will be sufficient to keep iron passive in 0.02% of ammonium chloride. He also shows that 0.5% of bichromate will keep iron passive in the presence of 1% of ammonium sulphate. Table V shows that with a ratio of 1 to 1, bichromate and sodium sulfate, the iron is always practically passive, not only at ordinary temperatures but at near the boiling point and at about 150°. When the concentration ratio is less than 1 : 1 the influence of current density in producing the passive state becomes evident as may be seen by reference to Nos. 6 and 7, and also to Nos. 18 and 19, where the only difference discernable is that of the density of the current employed.

Table VI contains the results obtained, at the temperatures indicated, with bichromate and various concentrations of sodium carbonate. It would not have been necessary to have performed these experiments in view of the results previously obtained by one of us² but for the work of Krassa,³ in which it was shown that iron is apparently active as an anode at elevated temperatures in hot, strong solutions of sodium hydroxide if the current density is not too great. It will be seen from the results that at all the temperatures and concentrations and variations of current density used the iron could not be made to rust, this passivity is produced despite the fact that the anodes were carefully made active by dipping in dilute sulfuric acid until hydrogen began to be liberated and then were washed and dried. Connections were also made by immersion of the cathode and closing the circuit by means of the anode. No. 12 of the table shows that iron is passive, even with the slight current employed, in a sodium hydrogen carbonate solution at 93°.

A few experiments were made to determine if iron is normally passive in water containing free carbonic acid. The results were negative. With current densities varying from 0.4 to 75 milliamperes per sq. cm. of anode the iron remained active throughout at room temperature. The statement of Dunstan and Hill¹ that iron does not rust in the absence of air even when immersed in sodium chloride solution, led to some successful experiments to determine if the anodic passivity could be established in a salt solution in the absence of air. It has already been shown by Byers¹

¹ *Loc. cit.*

² Byers, *Loc. cit.*

³ *Z. Elektrochem.*, 15, 490.

TABLE V.

No.	Per cent of $K_2Cr_2O_7$.	Per cent Na_2SO_4 .	Ratio of $K_2Cr_2O_7$ to Na_2SO_4 .	Temperature.	Time in minutes.	Grams of copper deposited.	Current in milliamperes.	Volts.	Grams of iron lost at anode.	Milliamperes per sq. cm.	Treatment of anode before use.	Condition at end of experiment.
1	0.25	0.0125	20/1	18	40	0.01609	22.33	5.8	...	33.8	Cleaned with H_2SO_4 and placed for few minutes in $K_2Cr_2O_7$	Bright; passive
2	0.25	0.25	1	16	40	0.01510	19.11	4.0	0.01282	28.9	Stood for some time in $K_2Cr_2O_7$	Covered with rust; active
3	0.25	0.25	1	15	40	0.02338	29.59	5.1	0.00024	44.8	Polished with emery paper and clean paper	Bright; passive
4	Same solution	93.5	44	0.02272	26.14	4.7	0.00032	51.6	Stood in $K_2Cr_2O_7$	Bright; passive
5	0.125	0.25	1/2	19	40	0.02362	29.90	5.8	0.00009	?	Stood in $K_2Cr_2O_7$	Bright; passive
6	Same solution	1/2	1/2	94	35	0.02350	34.00	4.7	0.00001	51.1	Stood in $K_2Cr_2O_7$	Orange coating; passive
7	Same solution	1/2	1/2	94	5	...	36	2	...	about 25	Stood in $K_2Cr_2O_7$	Covered with rust; active
8	0.125	0.375	66/100	15.4	37	0.02104	28.79	5.3+	0.00018	53.6	Stood in $K_2Cr_2O_7$	Bright; passive
9	Same solution	66/100	66/100	93	30	0.02014	33.99	2.3	0.01884	51.5	Stood in $K_2Cr_2O_7$	Heavily rusted; active
10	0.125	0.250	1/2	17.5	40	0.01992	25.86	5.7	0.00060	43.5	Polished with emery and clean paper	Bright except small spots and color at surface of liquid; active

11	Same solution	1/2	93	40	0.02490	31.52	3.7+	0.02080	49.4	Polished with emery and clean paper	Rusted; active	
12	0.25	0.125	2/1	93	40	0.02200	27.85	4.4	0.00008	42.2	Polished with emery and clean paper	Bright except coating at tip and surface; passive
13	0.125	0.125	1	93	40	0.02520	31.89	4.8	0.00011	51.7	Polished with emery and clean paper	Mostly bright, pitted in spots
14	0.250	0.125	2/1	113 to 155	120	0.07154	31.18	3.5	0.00070	42.9+	Polished and dipped in H ₂ SO ₄	Bright, orange coating; passive
15	0.125	0.125	1	128 to 156	60	0.03615	30.50	3.6	0.00035	42.0	Polished, tested in CuSO ₄ again polished	Bright, orange coating; passive
16	Same solution	1	128 to 156	67	0.02563	19.37	3.1	0.00104	27.0	Polished, tested in CuSO ₄ again polished	Very thickly coated with rust; active	
17	0.125	0.250	1/2	127 to 154	61	0.03580	29.71	Varied greatly	0.00720	45.0	Polished, tested in CuSO ₄ again polished	Heavily rusted; active
18	0.10	0.15	66/100	131 to 154.5	60	0.03480	29.35	Varied greatly	0.00898	47.0	Polished, tested in CuSO ₄ again polished	Heavily rusted; active
19	0.10	0.15	66/100	127	60	0.05996	49.65	4.7	0.00028	70.5	Polished, dipped in H ₂ SO ₄	Bright; passive

N. B.—Where the same concentration gives both active and passive condition the circuit was closed by means of anodes in the latter case, and the initial density was therefore probably sufficient to induce the passive state though the activity may be due partially to smaller current densities.

TABLE VI.

No.	Per cent of $K_2Cr_2O_7$.	Per cent of Na_2CO_3 .	Ratio of $K_2Cr_2O_7$ to Na_2CO_3 .	Temperature.	Time in minutes.	Weight of copper deposited.	Current in milliamperes.	Milliamperes per sq. cm. of anode.	Condition of anode at end of experiment.
1	0.125	0.125	1/1	18	30	0.01780	30.04	...	Passive
2	Same solution		1/1	93	35	0.02000	28.93	40.1	Passive
3	0.125	0.250	1/2	93.5	35	0.01996	28.87	41.0	Passive
4	0.125	0.50	1/4	93	35	0.01996	28.87	43.7	Passive
5	0.05	0.50	1/10	93	40	0.02258	28.58	38.3	Passive
6	0.05	0.75	1/15	93	40	0.02177	27.49	29.75	Passive
7	0.025	0.50	1/20	93	40	0.01138	14.40	18.19	Passive
8	0.015	0.50	1/33 $\frac{1}{3}$	93	98	0.00172	0.89	1.1	Passive
9	0.01	0.50	1/50	93	95	0.00115	0.61	0.79	Passive
10	...	0.50	...	93	100	0.00122	0.62	0.67	Passive
11	...	0.50	...	127 to 160	90	0.00730	4.11	0.49	Passive
NaHCO ₃									
12	...	0.50	...	93	90	0.0051	2.86	3.25	Passive

that a density of 3000 amperes per sq. cm. is not sufficient to render iron passive in such a solution. A tube was prepared in one end of which were sealed two electrodes, one of iron wire and one of platinum; the iron was then rendered passive by prolonged immersion in bichromate. The bichromate solution was then removed, the tube carefully rinsed and in the opposite end was placed a 1% solution of sodium chloride. The tube was then attached to a Gaede pump and carefully and completely evacuated. It was then reversed so as to bring the electrodes beneath the salt solution and a current of 40 to 44 milliamperes per sq. cm. was turned on. In a second series the current was connected before submerging the electrodes. No evidence of even temporary passivity could be obtained. No bubbles rose from the anode and an abundant greenish precipitate of ferrous hydroxide was formed. The only value of these experiments lies in further demonstration of the exceedingly destructive effect of halogen salts upon the passive state of iron.

Summary.

The results detailed in the experimental discussion and tables lead to the following conclusions:

1. Iron as an anode is rendered passive by bichromate solutions of small concentration, as low as 0.125%, and is kept passive even when the anodic current is very small, at temperatures ranging from room temperature to those approximating boiler conditions.

2. In the presence of moderate quantities of common salt the concentration of bichromate required to maintain the passive state is approximately 40 times greater at room temperature; 25 times greater at 93° and again 40 times greater at 125° to 150°. No explanation is apparent to the writers for this peculiar fact.

3. In the presence of sodium sulfate of moderate concentrations, an

equal concentration of bichromate is sufficient to *insure* passivity of the anode and an even smaller ratio is ordinarily effective even at temperatures as high as 150°.

4. The presence of carbonates and bicarbonates in water seems to have no destructive effect on the passivity induced by bichromate.

5. Since chlorides, sulfates and carbonates represent the common salts found in water, the general conclusion of Cushman seems to be verified at least so far as anodic conditions are concerned and the further fact is established that the suggestion of Wyatt (see introduction) is valuable. It seems probable also that since the percentage of chlorides in boiler water is usually small and easily determined that a valuable boiler preservative is provided by the addition of an amount of bichromate forty times that of the chlorides present, calculated as sodium chloride, plus that needed to precipitate the scale-forming factors. The cost of such preservative agent is not excessive. The doubtful factor in this case is the extent of the influence of the anodic current in producing the results above detailed. Experiments are at present under way to determine how long iron will remain unruined in such inhibitive solutions in the absence of electrical current.

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DETERMINATION OF MANGANESE AS SULFATE AND BY THE SODIUM BISMUTHATE METHOD.¹

BY WILLIAM BLUM.

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