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PART 3.

SOME INVESTIGATIONS RELATIVE TO THE DEPRECIATION OF ELECTROLYTICALLY PRODUCED SOLUTIONS OF SODIUM HYPOCHLORITE.

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(*A Paper read before the Faraday Society on Tuesday, November 13, 1906,
DR. F. MOLLWO PERKIN, TREASURER, in the Chair.*)

In a previous Paper read before the Faraday Society the writer alluded to the effect of instability on the efficiency of hypochlorite production, and cited, in one instance, depreciations of 0·20 to 0·45 grammes per litre in six hours, and in another instance of from 0·03 to 0·40 grammes per litre during a period of twelve hours. These depreciations referred only to the reaction or reversion to sodium chloride taking place during the process of manufacture, but did not concern solutions made under circumstances calculated to maintain their strength for fairly long periods, nor did they concern conditions of storage likely to affect this stability. The present note, therefore, contains some records of depreciations taking place over a long period, and also some records taking place over a short period under exceptional conditions of storage.

A.—GLASS BOTTLE TESTS.

These tests cover, firstly, a comparison between the effect of storing hypochlorite solution in bottles of dark and light amber colour, the first and last dates being over five years apart.

TABLE I.

Strength in Grammes of available Chlorine per Litre.	At Start.	After 31 Days.	After 212 Days.	After 689 Days.	After 750 Days.	After 1,358 Days.	After 1,817 Days.
Dark Amber Bottle ...	4·216	4·180	4·053	3·258	3·224	2·657	2·515
Light Amber Bottle ...	4·216	4·145	3·826	2·551	2·480	1·771	1·275

The initial strength in available chlorine being in each case 4·216 grammes per litre, the final strength after 1,817 days had fallen to 2·515 grammes per litre with the dark amber bottle, and to 1·275 grammes per litre with the light

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amber bottle, the average loss per diem in the first instance being practically 0·936 milligrammes, and in the second instance 1·619 milligrammes.

A second set of bottle tests covering a lesser period gives results concerning the relative value of dark and medium amber bottles, and contrasts these with the results obtained from transparent white glass bottles and dark blue glass bottles, the initial strength in available chlorine being :—

TABLE II.

Strength in Grammes of available Chlorine per Litre.	At Start.	After 61 Days.	After 122 Days.	After 365 Days.	After 730 Days.	After 1,187 Days.
Dark Amber Bottle ...	4·145	3·791	3·623	3·051	2·480	1·913
Medium Amber Bottle ...	4·145	3·791	3·623	3·051	2·480	1·878
White Glass Bottle ...	4·145	3·190	2·691	1·417	0·708	0·354
Dark Blue Glass Bottle ...	4·145	3·330	3·082	1·771	0·887	0·425

In each case initially 4·145 grammes per litre, the final strength after 1,187 days had fallen in the case of the dark amber bottles to 1·913 grammes per litre, in the case of the light amber bottles to 1·878 grammes per litre, in the case of the uncoloured glass to 0·354 grammes per litre, and in the case of the blue glass to 0·425 grammes per litre. The loss of available chlorine in milligrammes per day, therefore, works out as follows: Dark amber, 1·87; medium amber, 1·90; clear glass, 3·16; blue glass, 3·13.

The above tests are set out in Diagram 1.

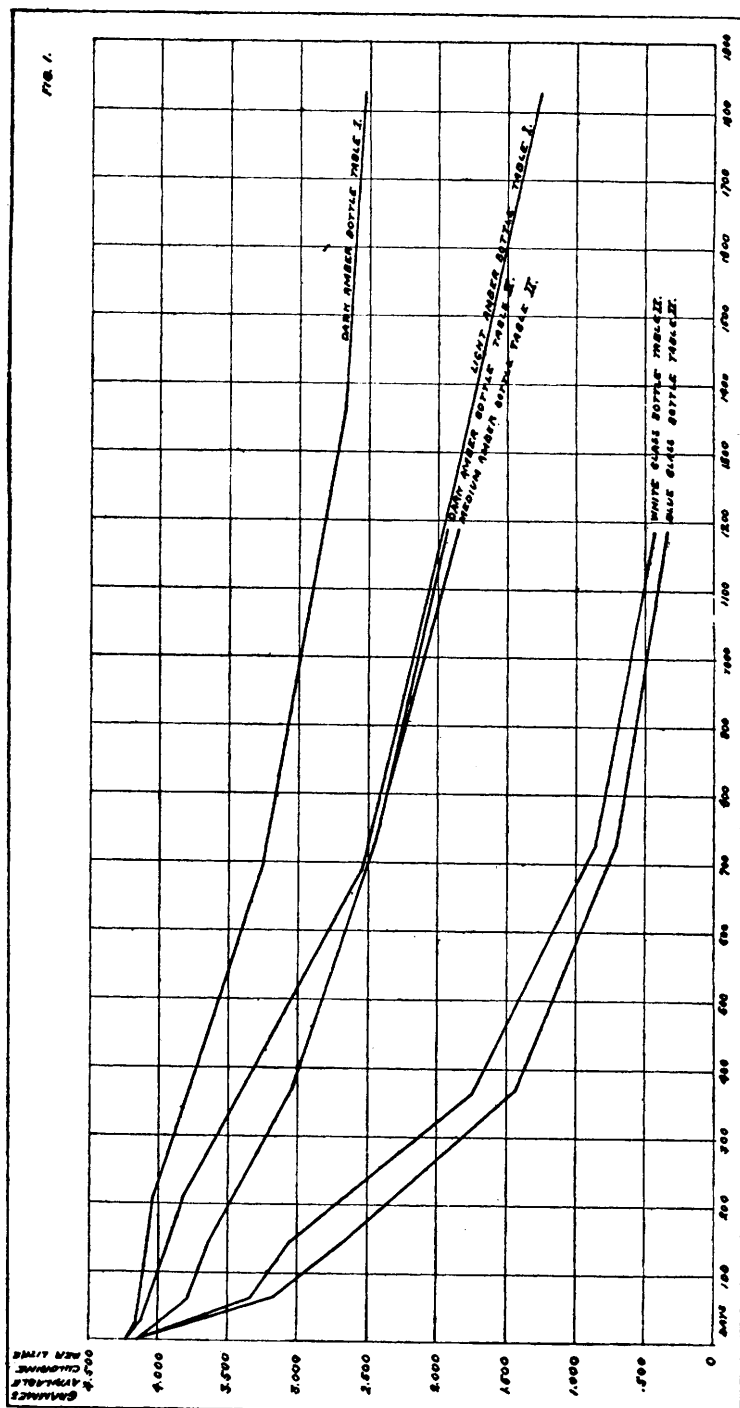
As regards the exposure of these bottles to the sunlight, an attempt was made to render the conditions as nearly as possible equal to those to which they would have been subjected in a chemist's shop. The bottles were placed on a shelf opposite a window facing due south, and received a full measure of sunlight, but practically no artificial light whatever. In order that every factor likely to bear upon the question might be available for future investigators of hypochlorite stability, the outside area of the bottles was measured, and the ratio of square centimetres of surface to cubic centimetres of contents was as follows :—

Dark Amber Bottles }	...	0·0153 sq. cm. per cub. cm. of contents.
Light Amber Bottles }	...	
Clear Bottle	0·325 " " "
Dark Blue Bottle	0·345 " " "

It is not, of course, any new discovery that the stability of hypochlorite solutions is affected prejudicially by sunlight. In regard to this, however, it must be pointed out that what takes place in dark amber bottles exposed to the light in the manner described, also takes place, but to a less degree, when the same bottles are placed in wooden boxes and nailed down. Deterioration due to light being eliminated, one can only blame the rubber stopper used—which contained a minimum of pure rubber—or the inherent instability of the substance of electrolytically produced hypochlorites.

B.—SINGLE METAL TESTS.

In the previous Paper it was pointed out that metallic impurities had a marked effect on the depreciation. The metallic fittings of the tanks were connected to the negative terminals of the generator, and therefore acted as subsidiary cathodes. When the plant was standing idle during the week-end, these would be liable to be attacked by the hypochlorite solution, and, for

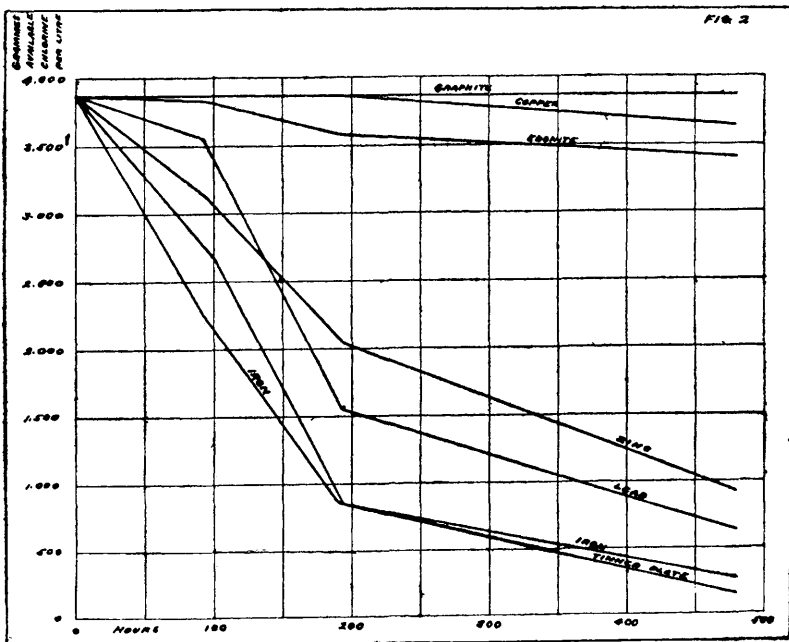


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example, ferric chloride might be formed then ; or else from rust brought in with the water used to make up the electrolyte. In order to ascertain how far single metals placed in open earthenware jars in hypochlorite solutions were attacked and what depreciation resulted, strips of metal foil, and also of ebonite, having a gross area of 100 square centimetres, were each separately immersed in 900 cubic centimetres of hypochlorite solution of 3·887 grammes of available chlorine per litre strength, and tests were taken at the end of four, eight, and twenty days' immersion.

TABLE III.

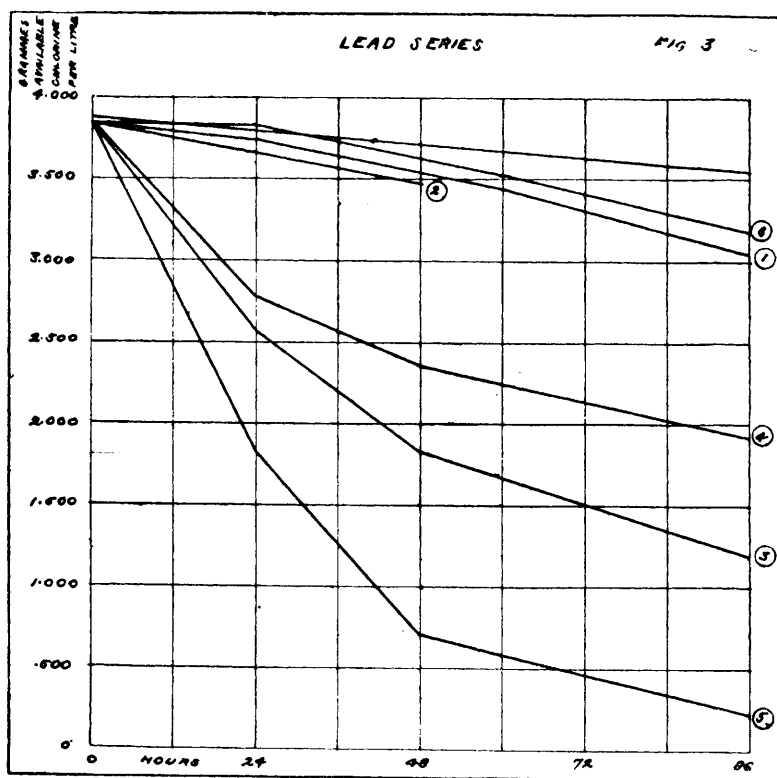
Time in Hours from Commencement.	96.	192.	480.	Remarks.
Graphite, Grammes av. Cl. per Litre...	3·887	3·887	3·887	No change whatsoever.
Copper, Do. ...	3·887	3·887	3·614	Very faint green deposit on plate. Depreciation of 0·273 grammes per litre.
Ebonite, Do. ...	3·826	3·580	3·401	Depreciation 0·486 grammes per litre.
Zinc, Do. ...	3·118	2·055	0·921	Heavy white deposit on plate, solution milky. Depreciation 2·966 grammes per litre.
Lead, Do. ...	3·542	1·560	0·636	Plate black. Depreciation 3·251 grammes per litre.
Iron, Do. ...	2·267	0·850	0·283	Heavy dark rusty deposit. Depreciation 3·604 grammes per litre.
Tin Plate, Do. ...	2·691	0·850	0·142	Heavy rusty deposit, light in colour. Depreciation 3·745 grammes per litre.



In regard to the last line of the above table, pure tin from some neighbouring engineering works was ordered, but the tinned plate of commerce supplied. As a result, in the early stages, while the coating remained intact, the tin-plate was superior to iron, but subsequently, owing to local galvanic action, the depreciation was more active, corresponding to that of the iron curve. With regard to the graphite used, it can only be observed that, while not a metal, it was included in this series in order to test the graphite for metallic impurities which might give rise to local action. That none occurred is a testimony to the purity of the material experimented with.

C.—METAL COUPLE TESTS.

A further series of tests was carried out in which, instead of using a single metal, two metals were used, as well as single metals and ebonite sheets.



Twenty-one sets were placed in open jars, the gross area of each metal in each unit being 100 sq. cm., and the volume of liquid 900 cub. cm. The initial strength in grammes of available chlorine per litre was 3.826.

The metals were joined together by short wires only a few centimetres in length, the wire used in each case being insulated throughout its length, and also at the joint, by Chatterton compound applied hot. For the purpose of comparison and discussion, diagrams Nos. 3 to 9 inclusive give the results of these tests under the headings of each metal. For instance, test No. 8 is to be found both under the Copper Series (Fig. 4), and under the Iron Series

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TABLE IV.
Grammes available Chlorine per Litre.

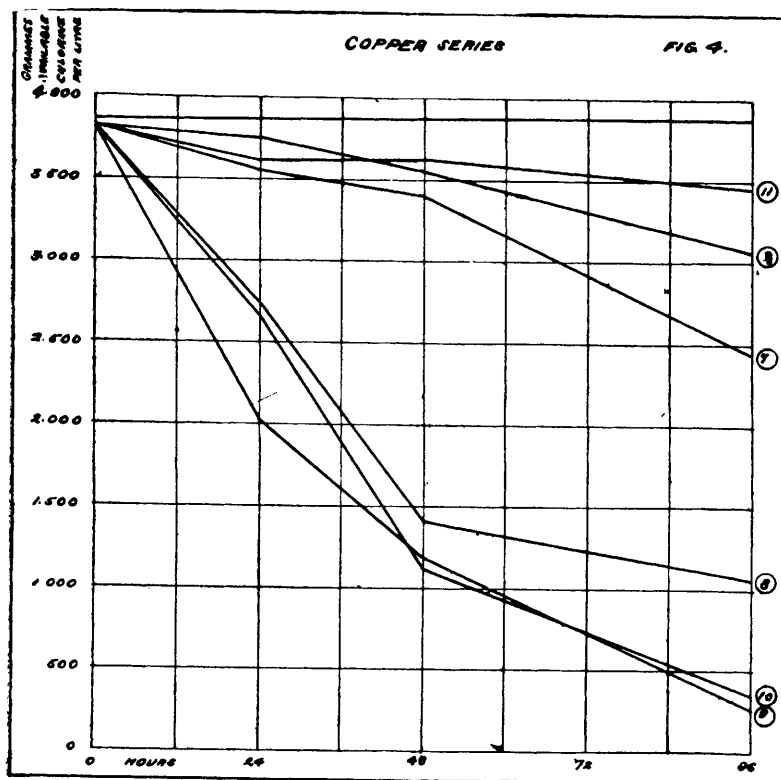
Test No.	Description of Couple.	At Start.	After 24 Hours.	After 48 Hours.	After 96 Hours.	Condition of Plates at End of Test.
1	Lead and copper with copper wire	3·826	3·744	3·542	3·407	No deposit, lead turning black.
2	Lead and graphite with lead wire	3·826	3·684	3·472	3·649*	No deposit, lead turning black.
3	Lead and iron with lead wire	3·826	2·551	1·842	1·204	Heavy deposit, light rusty colour on iron plate.
4	Lead and tinned plate with lead wire	3·826	2·602	2·338	1·913	Heavy deposit, light rusty colour on tinned plate.
5	Lead and zinc with lead wire	3·826	1·841	0·708	0·212	Heavy white deposit on zinc plate, solution milky.
6	Lead and ebonite with lead wire	3·826	3·826	3·614	2·692	No appreciable deposit, lead turning black.
7	Copper and graphite with copper wire	3·826	3·542	3·401	2·444	Slight green deposit on copper.
8	Copper and iron with copper wire	3·826	2·751	1·417	1·063	Heavy deposit, light rusty colour on iron plate.
9	Copper and tinned plate with copper wire	3·826	2·195	1·175	0·283	Heavy deposit, light rusty colour on tinned plate.
10	Copper and zinc with copper wire	3·826	2·602	1·134	0·354	Heavy white deposit on zinc plate, solution milky.
11	Copper and ebonite with copper wire	3·826	3·614	3·614	3·474	No deposit on copper plate.
12	Graphite and iron with tin wire	3·826	2·266	1·417	0·638	Heavy deposit, light rusty colour on iron plate.
13	Graphite and tinned plate with tin wire	3·826	2·910	1·771	0·921	Heavy deposit, light rusty colour on tinned plate.
14	Graphite and zinc with zinc wire	3·826	2·105	1·175	0·354	Heavy white deposit on zinc plate, solution milky.
15	Graphite and ebonite with tin wire	3·826	3·542	3·465	3·401	Slight rusty deposit, light rusty colour on both plates.
16	Iron and tinned plate with tin wire	3·826	2·480	1·204	0·738	{ Deposits of light rusty colour on both plates, heavy on iron plates.
17	Iron and zinc with zinc wire	3·826	2·107	0·780	0·212	Heavy white deposit on both plates, solution milky.
18	Iron and ebonite with tin wire	3·826	3·118	2·194	1·414	Slight deposit, light rusty colour on iron plate.
19	Tinned plate and zinc with zinc wire	3·826	2·779	1·346	0·921	Heavy white deposit on zinc plate, solution milky.
20	Tinned plate and ebonite with tin wire	3·826	2·901	2·409	1·842	Slight deposit on tinned plate, light rusty colour.
21	Zinc and ebonite with zinc wire	3·826	3·118	2·551	2·167	Slight white deposit on zinc plate, solution milky.

* Probable the previous titration (48 hours) gave too low a reading.

(Fig. 6). This, while in some respects redundant, permits of easier comparisons. Also in each diagram the curve for the single metal of the series is given for ninety-six hours.

Taking these diagrams in their order, the Lead Series (Fig. 3) shows that the galvanic action is greatest in the case of the lead and zinc couple, next greatest in the case of lead and iron, while the lead-graphite, lead-copper, and lead-ebonite couples show a depreciation rather greater than that due to the lead plate alone.

The Copper Series (Fig. 4) shows the greatest depreciation in the case of the copper-tinned plate couple, which agrees closely with the copper-zinc curve. The lead and copper couple stands out superior to the copper-



graphite. The copper-ebonite couple gives a greater depreciation than either copper or ebonite alone.

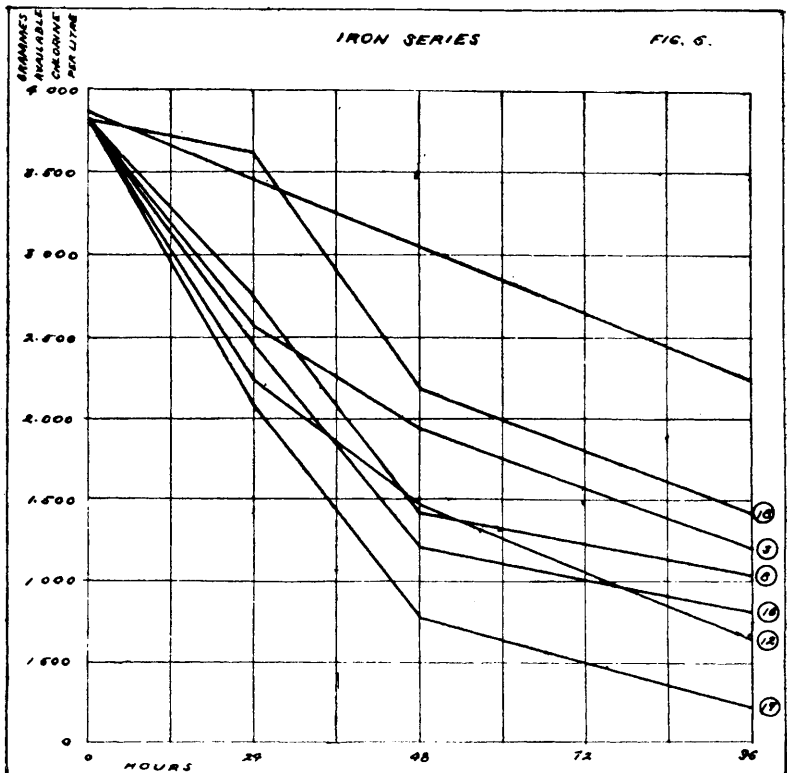
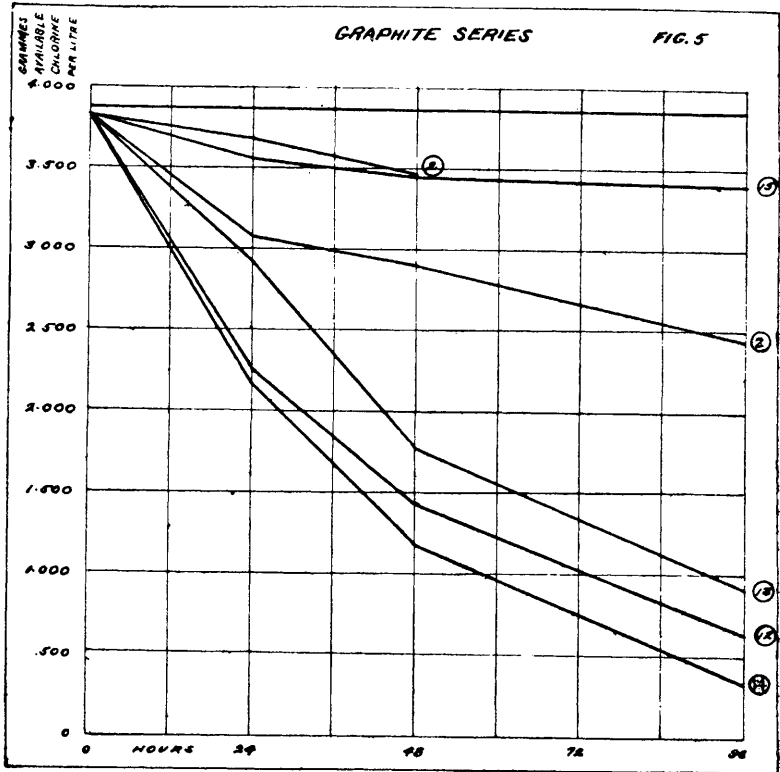
The Graphite Series (Fig. 5) is notable for the fact that the worst depreciations are due to couples of graphite-zinc, graphite-iron, and graphite-tinned plate, in the order named.

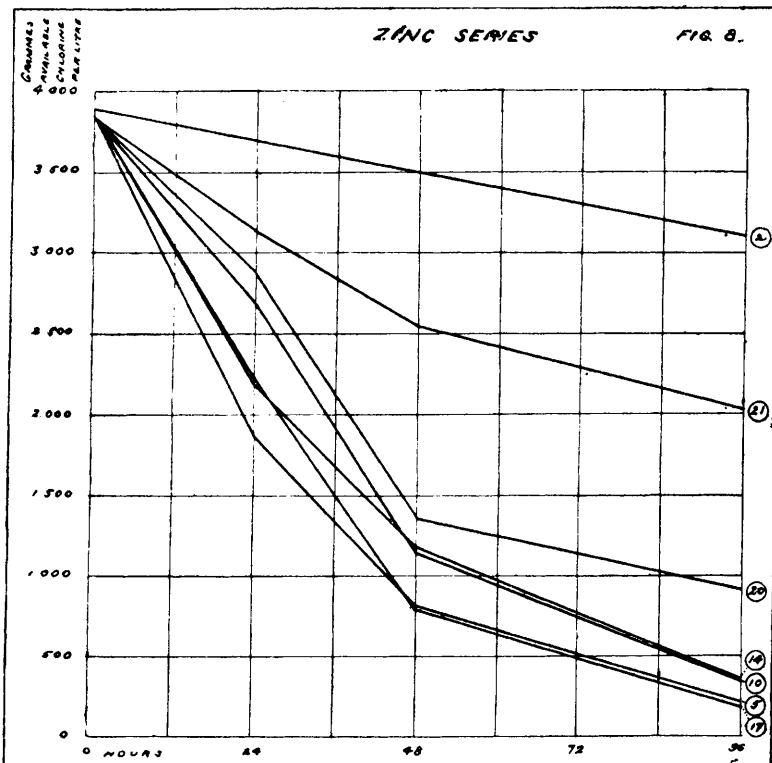
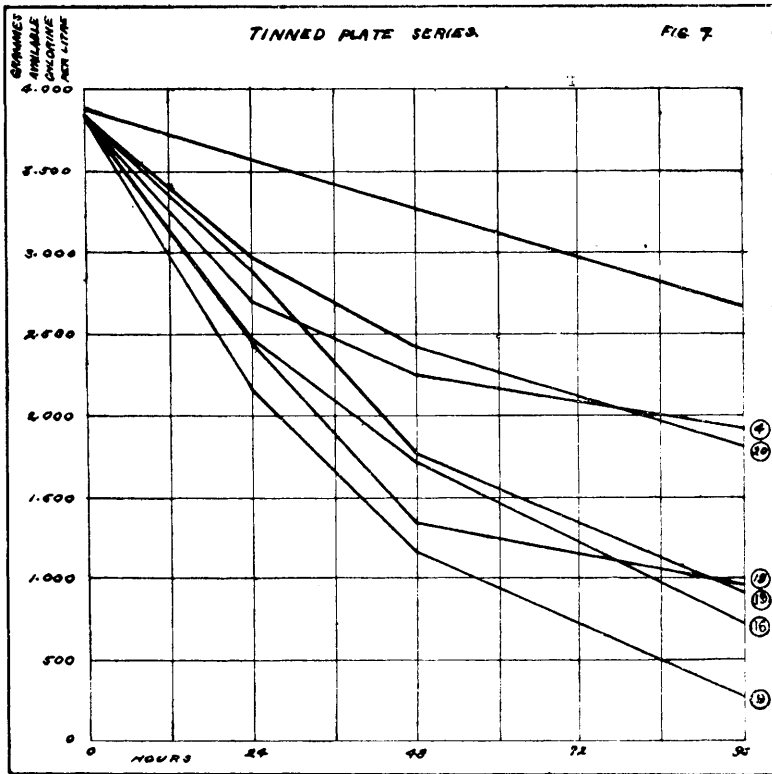
The Iron Series (Fig. 6) show heavy depreciations, the worst being that due to the iron-tinned plate couple. Probably the 24-hour reading on the iron-ebonite couple is incorrect.

The Tinned-plate Series (Fig. 7) is somewhat irregular, perchance owing to irregularities in the local action on the surface of the tinned plate.

The Zinc Series (Fig. 8) is also irregular. Table IV. shows what is difficult to depict on a small diagram, the final identical effect of the lead-

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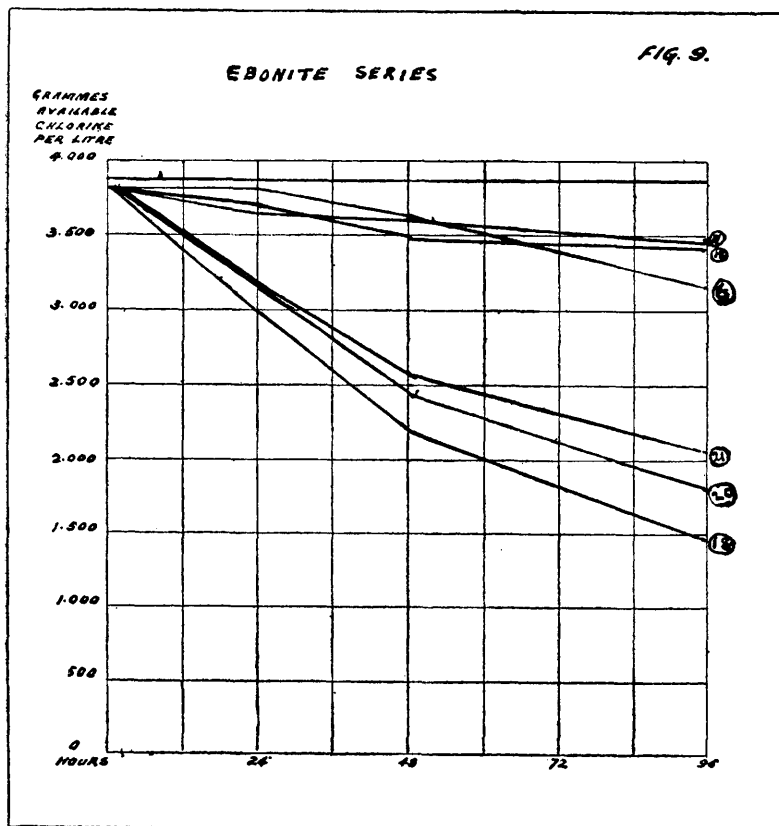
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zinc couple with the iron-zinc couple, and of the copper-zinc couple with the graphite-zinc,

The Ebonite Series (Fig. 9) is, of course, not a metal couple test. It is not easy to explain why the depreciation should in each case exceed that for the single metal plate of identical area.

D.—SINGLE METAL TESTS WITH INCREASED AREAS.

The effect of varying the exposed area of the metal immersed in the solution was also studied. The volume of the liquid was 900 cub. cm., tests



being taken at 24-hour intervals for eight days. The results are set out in Table V.

The general deductions from this set of experiments are that the amount of depreciation due to metallic contact and chemical reaction in any given time varies directly with the area of the exposed surface, for solutions of equal strength in available chlorine.

Figs. 10, 11, and 12 show the results of varying the area for iron, zinc, and tin respectively. No curve has been plotted for copper, which does not seem to cause corrosion to any material degree when the area is doubled. The figures given in Table V. represent but little more than might have been anticipated from exposure to air and light.

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TABLE V.
Grammes available Chlorine per Litre.

Test No.	Description, Metal and Exposed Area.	At Start.	After 24 Hours.	After 48 Hours.	After 72 Hours.	After 96 Hours.	After 120 Hours.	After 144 Hours.	After 168 Hours.	After 192 Hours.
22	Iron, 400 sq. cm. ...	3'614	1'452	0'425	0'010	0'006	No trace	No trace	No trace	No trace
23	" 300 sq. cm. ...	3'614	1'708	0'466	0'017	0'010	No trace	No trace	No trace	No trace
24	" 200 sq. cm. ...	3'614	1'984	1'063	0'815	0'425	0'354	0'177	0'010	0'007
25	" 100 sq. cm. ...	3'614	2'905	2'055	2'055	1'842	1'557	1'155	1'000	0'779
26	Zinc, 400 sq. cm. ...	3'614	3'224	2'691	2'480	1'842	1'523	1'155	0'850	0'674
27	" 300 sq. cm. ...	3'614	3'330	2'691	2'480	2'055	1'880	1'452	1'240	1'027
28	" 200 sq. cm. ...	3'614	3'401	3'224	3'082	2'657	2'480	1'913	1'842	1'275
29	" 100 sq. cm. ...	3'614	3'507	3'401	3'334	3'153	2'940	2'571	2'409	2'196
30	Tin, 400 sq. cm. ...	3'614	2'090	1'240	0'885	0'673	0'463	0'177	0'177	0'010
31	" 300 sq. cm. ...	3'614	2'090	1'559	1'134	0'885	0'638	0'425	0'354	0'212
32	" 200 sq. cm. ...	3'614	2'728	2'090	1'878	1'559	1'418	1'311	1'204	1'098
33	" 100 sq. cm. ...	3'614	2'829	2'303	2'196	1'948	1'842	1'878	1'55	1'418
34	Copper, 200 sq. cm. ...	3'614	3'554	3'507	3'452	3'437	3'437	3'401	3'354	3'354
35	" 100 sq. cm. ...	3'614	3'554	3'554	3'554	3'554	3'507	3'507	3'507	3'452

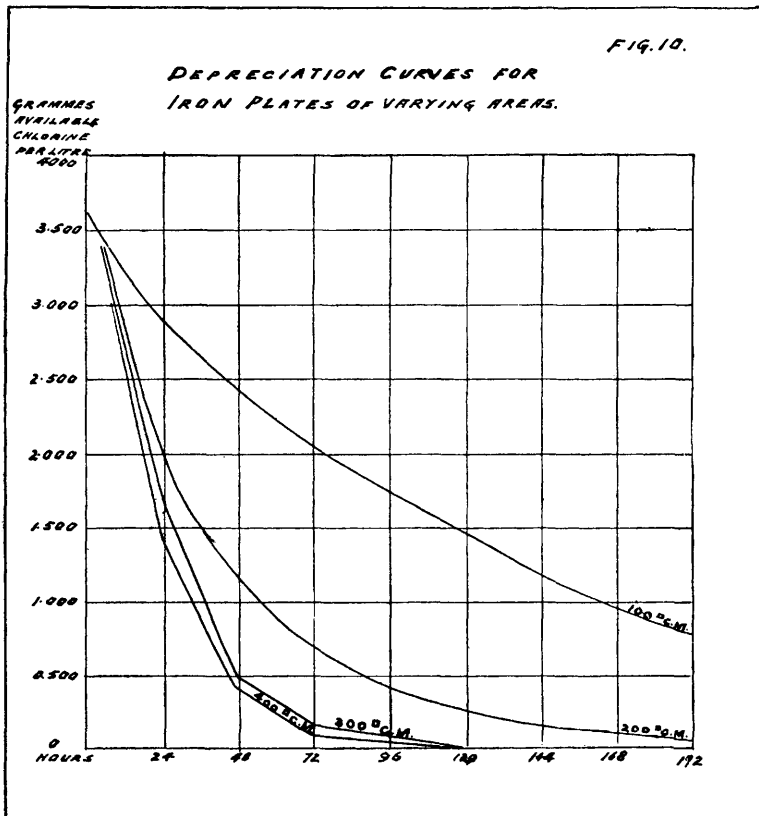
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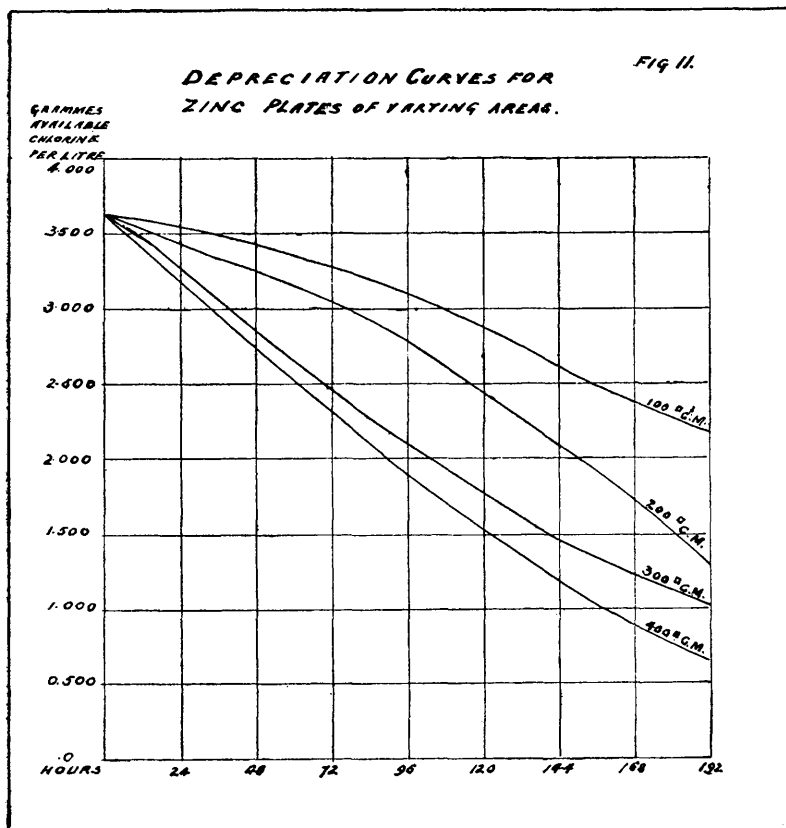
E.—VALUE OF PROTECTIVE COATINGS.

It has been shown above that if hypochlorite solutions are allowed to come into contact with single metals corrosion of the metal and depreciation of the available chlorine results. When two metals are present in electrical contact corrosion and depreciation are accentuated. A series of tests was therefore made with six metal couples and three single metals. Tests were taken every twenty-four hours for ten days. In each case 900 cc. of hypochlorite solution containing 3·614 grammes of available chlorine per litre was used. A "bitumastic" paint was applied to each plate. The following figures summarise the results obtained :—

TABLE VI.

Test No.	Description of Metal (exposed Area 100 sq. cm. for each Plate).	Final Strength at end of 240 Hours.	Actual Loss in Grammes during Period.	Daily Percentage Loss during Period.
36	Lead and zinc	3·507	0·0963	3·17
37	Copper and zinc	3·401	0·1877	5·89
38	Lead and iron	2·905	0·6381	19·34
39	Iron and tinned plate...	2·551	0·9567	27·86
40	Zinc and tinned plate...	3·437	0·1693	4·62
41	Tin	3·437	0·1693	4·62
42	Zinc	3·437	0·1693	4·62
43	Copper	3·507	0·0963	3·17
44	Iron	3·082	0·4788	14·72





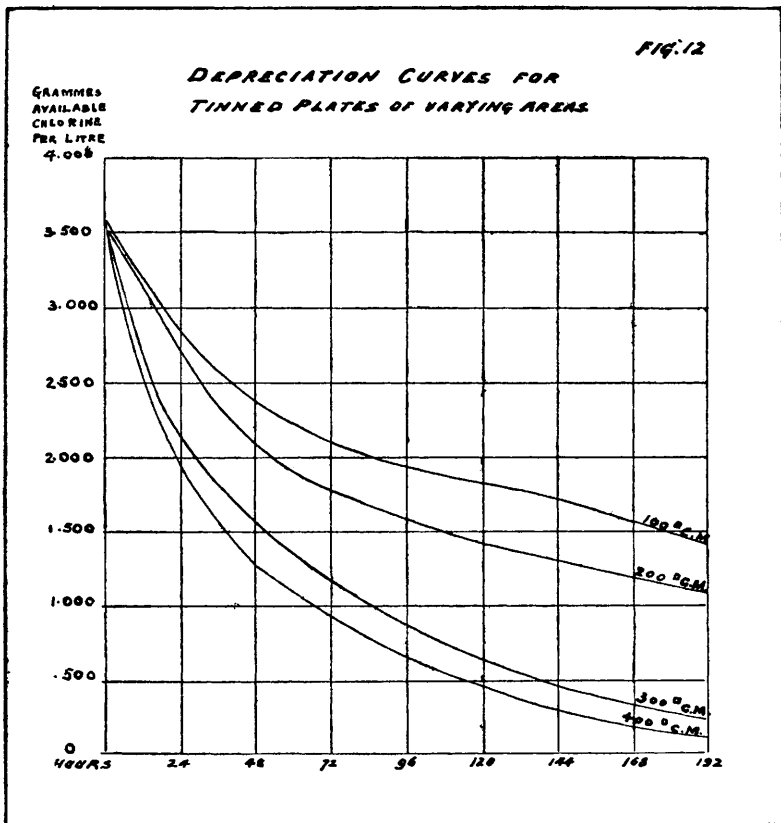
The above results must be regarded as bearing upon the effectiveness of applications only. Best results, for instance, were obtained in these protected metal tests from the lead-zinc couple, which, according to Table IV., test No. 5, should have been about the worst. As it is a matter of difficulty to paint the inside of small plates, and, still more, of pipes evenly, the writer deprecates reliance upon insulating materials for the protection of any vessel in which hypochlorite liquids are stored, or of any metallic piping in contact with hypochlorite liquids. When once the paint breaks down, corrosion of the metal will follow at a rapid rate.

Arising out of the above tests, it occurred to the writer that wood boiled in bitumen might be used as a substitute for slate electrolysing tanks, and perhaps as a substitute for ebonite in electrode construction. Messrs. Calender's Cable and Construction Company, Ltd., responded very promptly and courteously to a request for samples of wood which had been bitumenised. These samples had 200 square centimetres of their surface (not including the edges) immersed in vessels containing three litres of liquid of a strength of 3.153 grammes available chlorine per litre. The woods tested were oak, elm, and ash, each of which had been submitted to three different temperatures, viz., No. 1 "Low" temperature; No. 2 "Medium" temperature; and No. 3 "High" temperature. The experiments were continued for fifteen days, titrations being made at the end of each twenty-four hours. The final results are given in the following table, the interim depreciations being shown in Fig. 13:—

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TABLE VII.

Kind of Wood and Grade of Treatment.	Final Strength of Solution in Grammes of available Chlorine.	Loss in Grammes of available Chlorine during Period.	Average Loss in Grammes of available Chlorine per Day throughout Period per 100 sq. cm. of Exposed Surface.
Ash No. 1	1'524	1'629	0'0543
Ash No. 2	0'921	2'232	0'0744
Ash No. 3	0'815	2'338	0'0779
Elm No. 1	1'204	1'949	0'0649
Elm No. 2	0'815	2'338	0'0779
Elm No. 3	0'815	2'338	0'0779
Oak No. 1	1'807	1'346	0'0448
Oak No. 2	1'138	2'015	0'0672
Oak No. 3	0'389	2'761	0'0921



These final results show that the No. 1 series (submitted to low temperatures) have given the best results throughout, and that the Oak No. 2 sample ranks after these. The Ash and Elm samples (Nos. 2 and 3 in each case) are practically identical, Oak No. 3 coming last on the list. Examining

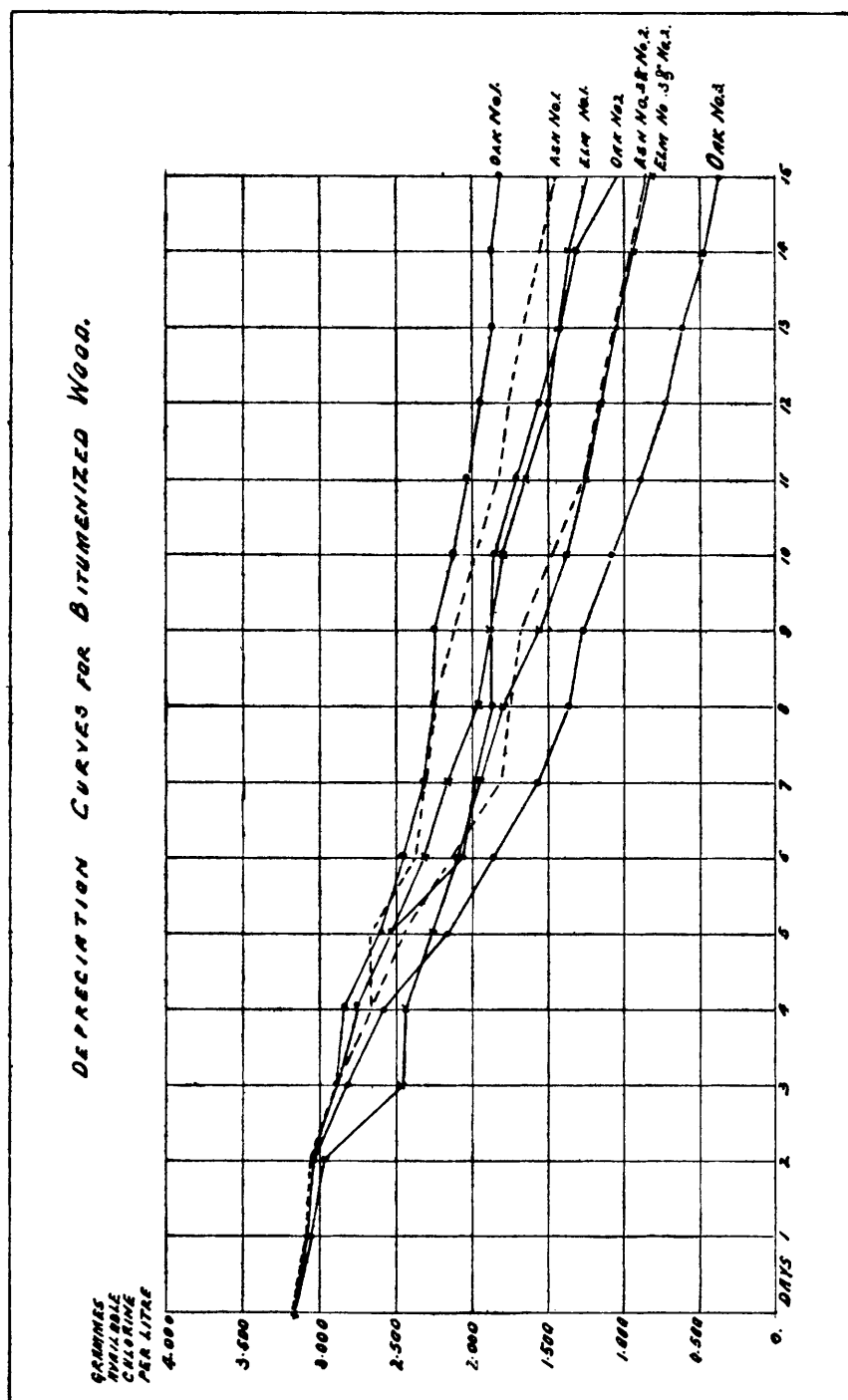


FIG. 13.

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the individual curves in Diagram 13, it will be seen that except for the Elm samples distinctive differences only began to be apparent after the fourth day. The laboratory records state on that occasion that "while it cannot be said that the hypochlorite solution has actually eaten off the bitumen, it has certainly changed it to a very light colour." An examination of the samples of wood at the end of the test certainly shows that ultimately the bitumen was eaten off.

From these tests it may be concluded that, while bitumenised wood resists disintegrating action while the coating is unimpaired, that coating has relatively a short life. It should not, therefore, be used in the construction of electrodes, nor of electrolysing tanks; but for temporary purposes it would be useful for the preservation of wooden troughing.

F.—CONCLUSION.

It may be thought by some that this account of some instances of the depreciation of electrolytic hypochlorite solution contains too much of relatively irrelevant detail. But the author having given a good part of over ten years to the making of hypochlorite solutions, realises that success is only obtained by infinite attention to minute details, and has found much of the detail here given of infinite value in the practical working of such processes. As regards methods of manufacture, these have nothing to do with the present Paper, which is wholly concerned with certain causes which may contribute towards the unsatisfactory operation of an installation. Storage, transport and methods of conveyance from place to place, or even from one part of a factory to another, are details meriting attention. Certain conditions of storage may clearly be regarded as fatal to stability, particularly those in which the galvanic action of dissimilar metals is likely to arise. These tests were all made with a solution produced at the works of a company in the north of England manufacturing electrolytic hypochlorites. While the relative order of values of different metals as occasioning depreciation is as stated, these figures must only be regarded as absolute in regard to the product of the factory in question. Tests with solutions produced by other processes, while agreeing in order of value with those recited, do not give identical analytical results, the rate of loss being accelerated (or retarded) according to method of manufacture. The discovery of this latter point has led the author to devise a galvanic couple test which, in a given time, for any solution, will indicate what may perhaps be called its "stability coefficient." Detailed tests are at present being carried out on various hypochlorite solutions, both chemical and electrolytic, with a view to simplifying the test methods. It is hoped that a Paper on this subject will be of interest to the Society.

The writer desires to express his thanks to Mr. F. T. Talmadge for valuable assistance rendered in carrying out these tests.