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No. 90

STRUCTURE OF THE COATING ON TINNED SHEET
COPPER IN RELATION TO A SPECIFIC
CASE OF CORROSION

BY

PAUL D. MERICA, Associate Physicist

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INTRODUCTION

There has recently come to the attention of the Bureau of Standards an instance of corrosion of tinned sheet copper, which presents some rather unusual and interesting features, in the investigation of which a study has been made of the structure and properties of tin coatings on copper, with particular reference to the influence of this structure on the resistance of this material to corrosion.

This question of the corrosion of such material is a fairly important one, although in comparison to the quantity of other coated materials, such as tin plate and galvanized iron, commercially used, that of tinned copper is small. It finds, however, fairly wide application, being used for roofing, for containing vessels such as milk cans, and for fittings, troughs, etc., for soda fountains and breweries. It may be noted that of the total amount of copper roofing used only a small proportion, perhaps 5 per cent, is tinned. In many cases the application of tin is made as much for the sake of the appearance of the article as for the protection afforded against corrosion.

I. PITTING OF TINNED COPPER ROOFING SHEET

The greater part of the roof of the Library of Congress, in Washington, is covered with tinned sheet copper material, all of which is from the same manufacturer, and which was installed at the time of the completion of the building, approximately 1893 to 1894.

This is 16-ounce sheet, tinned on both sides, and it lies on cement or terra cotta.

The lower or under side of this sheet has become but little altered in the course of time, except that it has become blackened at points where the sheet is perforated by the holes described below. The upper or exposed side has taken on, for the most part, a dark, slightly greenish patina, which is dense and coherent, although in some areas there is a whitish tinge, due to the tin or tin oxide. On this surface are found in fairly dense distribution small pits or furrows, of which the diameter or width varies from 0.5 to 1 mm, the furrows being sometimes as much as 5 cm long. The appearance of these pits and furrows is shown in Fig. 1. In many sheets there will be as many as 20 or 25 per square decimeter; in others much fewer. Often these extend completely through the sheet as perforations, through which leakage takes place. The edges of these pits are exceedingly sharp and well defined, much more so than the photograph indicates. Their inside surfaces are sometimes covered with a thin reddish or black layer of copper oxide, often also, with a thin green layer, which is probably basic carbonate of copper. It was stated that these pits had first been noticed some 8 or 10 years after completion of the roof.

Careful examination fails to relate the location or distribution of these pits to any features of service conditions, such as proximity to ventilators, chimneys, or to places where soot or cinders accumulate. They occur practically in all of the sheets, both in the gutters and on the slopes. They are much less serious in extent on north exposures and in areas within shadow; on the vertical surfaces where the sheets are joined by flanging they are practically absent. These pits are also not arranged in any manner symmetrical to the direction of rolling of the sheet.

It is to be noted that the Library of Congress is located in a section of Washington, itself uncommonly free from smoke, etc., which is not near power stations or factories producing smoke, such that the atmospheric conditions may be looked on as most unfavorable for corrosion.

The most striking feature about the pits is their distribution almost without exception along the line of surface scratches. This can be seen clearly in Fig. 1. They generally occur in groups, the scratch passing through the center of each pit, although some isolated pits are found through which no such scratches pass; these are, however, comparatively rare. It is really this peculiar

feature which has lent interest and also direction to the present work.

Pitting and other local corrosion of copper and other metals and alloys is unfortunately a well-known phenomenon. References on this topic will be found quite generally.[1] Such local corrosion is generally held to be electrolytic in origin, depending on the simultaneous presence of electronegative and electropositive areas, "hard" and "soft" areas, oxide inclusions, etc., or is due to the deposition of electronegative basic salt, such as that of zinc oxychloride on brass. In the case of tin plate, such pitting is held to be due to the presence of pinholes originating during the process of tinning, which allow access of the corroding liquid or water to the iron, which is in electric contact with the more electronegative tin. The author has found no reference to local corrosion of tinned copper such as has been described above.

II. MANUFACTURE OF TINNED SHEET COPPER

Copper sheets are generally tinned in the following manner: The tin mixture is melted up in a cast-iron pot; in the meantime the copper sheets, after having been cleaned and pickled are rubbed with a fluxing solution of zinc chloride and hydrochloric acid. They are, then, one by one, laid on an inclined plane adjacent to the pot; the operator takes a ladle full of molten tin and flows it over the sheet, the excess running back by troughs into the pot. Then, beginning with the top of the sheet, he wipes off the excess tin with a brush or bundle of tow. This produces a smooth even coating.

Another method of tinning is also used. The cleaned and pickled sheet is laid on a bench, which contains an inset gas grate, flush with the top. The sheet is passed over the grate and heated, while the operator takes small flat plates of tin, lays them on the sheet, and rubs them into the copper sheet when they have melted. Powdered ammonium chloride is used as a flux. The manufacturers claim that this method gives a more uniform coating than the first one.

A tinning mixture is often used containing a small amount of lead, as it is claimed that the latter increases the fluidity of the mixture and exerts no harmful effect, provided the material is not to be used in containers for foodstuffs or liquids for drinking purposes.

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[1] J. T. Corner, Some Practical Experiences with Corrosion, Jour. Inst. Metals, 5, p.. 115, 1911; T. A. Eastick, The Corrosion of Copper, Metal Industry, 11, p. 524, 1913; E. Johnson, Annealing and Diseases of Copper, Met. & Chem. Eng., 9, p. 87, 1911.

III. STRUCTURE OF TIN COATINGS ON COPPER

In order to make a study of the tin coating, other samples besides the one mentioned from the Library of Congress were obtained. Of these several were most kindly furnished by two manufacturers of this material; one was from the roof of the statehouse of Texas. These samples are described in the following table:

TABLE 1

Description of Samples Tested

B. S. No.	Sheet gage	Furnished by—	Description
1053	22	Library of Congress......................	New; tinned on one side.
1054	22	.....do.................................	Corroded and pitted in service; tinned on both sides.
1119	22	Manufacturer A.........................	New; tinned on both sides.
1120	18	.....do.................................	Do.
1241	20	Manufacturer B.........................	New; tinned on one side.
1242	17	.....do.................................	Do.
1243	14	.....do.................................	Do.
1244	22	Statehouse, Texas......................	Did not pit or corrode in service (30 years).

A chemical analysis was made of several of the tin coatings.

A sample of 1054, area 31 cm^2, was treated with strong hydrochloric acid. The solution resulting contained:

Grams

Tin... 0. 3050
Copper.. .2135
Lead.. .0269
Iron.. .0035
Zinc.. .0050

The coating was computed to contain: [2]

Per cent

Tin... 89. 5
Lead.. 8. 0
Iron.. 1. 0
Zinc.. 1. 5

A sample of 1242 was dissolved in 1:1 HCl with aid of the electric current (6 to 8 volts). The solution contained:

Grams

Tin... 0. 8320
Copper.. 6. 8725
Zinc.. .0150

Coating was computed to contain: [2]

Per cent

Tin... 98. 2
Zinc.. 1. 77
Lead.. Trace (0.1 per cent).
Iron.. Not detected.

[2] The copper found in the coating is due to alloying during the tinning operation and is not here included in the analysis of the tinning mixture.

The microstructure of a cross section of the base copper of the corroded sheet 1054 is shown in Fig. 2; the cuprous oxide is clearly seen.

Since the application of the coating has been made at a high temperature, above the melting point of tin, 232° C, it is to be expected that the tin will be found alloyed with the copper at the
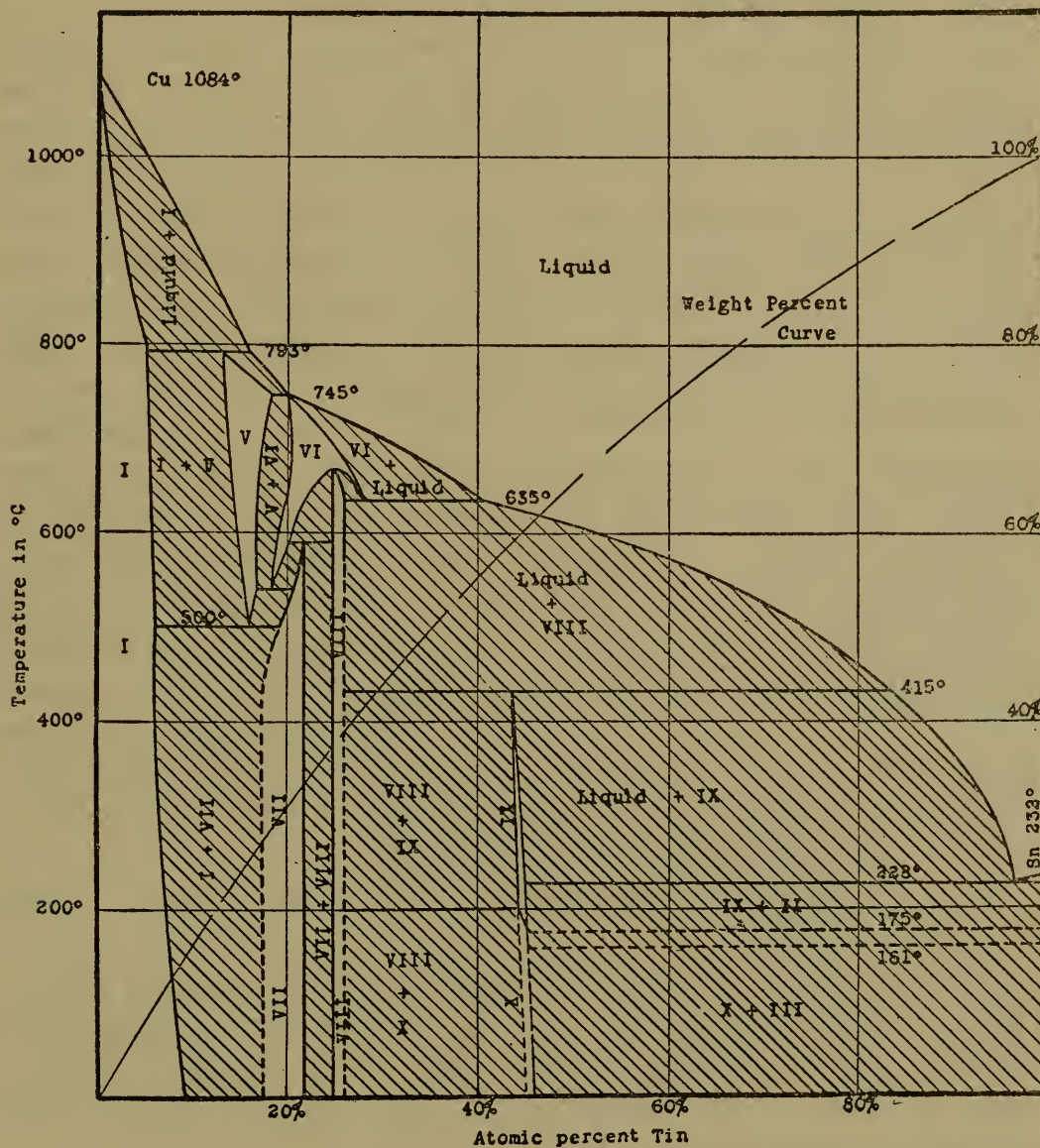

FIG. 3.—*Equilibrium diagram of copper-tin alloys*

juncture of copper and tin, the copper content of the alloy increasing from the outside to inside of the coating. The equilibrium or constitution diagram of the alloys of copper and tin is shown in Fig. 3 as given in Guertler's "Handbuch der Metallographie," 1912, largely from the work of Heycock and Neville, and modified slightly by Haughton.[3]

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[3] J. L. Haughton, The Constitution of the Alloys of Copper with Tin, Parts I and II, Jour. Inst. Metals, **13**, p. 222; 1915.

The ternary diagram of the copper-tin-lead alloys has not yet been worked out. It is most probable, judging from the very slight solubility of lead in copper and by the fact that in a mixture of lead and copper, practically the whole of the lead does not solidify above 386° C, that all of the lead in a ternary alloy, containing only a small percentage of it, will be found in the tin rich phase—that is, the eutectic of tin and the constituent *X*.

In studying the structure of the coating two methods of preparing the specimens were used. In order to observe it in cross section, samples of the sheet were carefully copperplated, and then mounted in ordinary solder, care being taken not to heat the solder much above its melting point. It was noticed, however, that sometimes, even with care, a certain amount of alloying took place at the copper surfaces during the mounting, and therefore control specimens were also mounted in plaster of Paris. This coating is very thin, and many features of its structure were not noticed until it was observed in oblique section. A specimen, sometimes, but not always previously copperplated, was bent slightly, and then ground and polished through the coating on the convex surface. In this way a magnified section of the coating was obtained, as it were, which will be hereafter referred to as an oblique surface section. This method has been used by Guertler [4] in studying the structure of zinc coatings on iron. It was found that etching to develop structure was best done by the successive application of (1) a concentrated solution of ammoniacal copper ammonium chloride (Cu-Am-OH–1), and (2) a dilute hydrochloric and solu'ion of ferric chloride ($FeCl_3.HCl$).

Fig. 4 shows a transverse section of the coating of 1054 (reverse or uncorroded side).[5]

There are clearly seen (1) the underlying sheet copper; (2) the bright, unetched alloy layer; (3) the ground mass of copper-tin eutectic, which probably contains also all of the lead, and in which crystals of the constituent *X* can be seen; and (4) the protecting layer of copper plate.

The same layers are also seen in an oblique surface section of 1054, in Fig. 5.

Further examination shows that this light, unetched layer next to the copper is in reality composed of two constituents. Immediately adjacent to the copper is found in it a bluish border, which

[4] W. Guertler, Die Struktur des verzinkten Eisens, Int. Zeitsch. Metallographie, 1, p. 352; 1911.

[5] Hereafter photomicrographs and description of the coating structure of 1054 refer, unless otherwise stated, to that of the uncorroded side.

can be readily seen under the microscope but is not easily photographed. In order to render it possible of reproduction, it is necessary to etch much more heavily with (FeCl$_3$.HCl), and until all of the eutectic has been attacked and removed. Then this blue border darkens and presents the appearance shown in Fig. 6.

The constituent which darkens very readily with (FeCl$_3$.HCl) is the eutectic of constituent *X* and tin, the constituent which remains light and unetched is *X*, the *H* of Heycock and Neville, containing about 60 per cent by weight of tin; the blue constituent is the *VIII*, the η of Heycock and Neville, and contains about 39 per cent by weight of tin.

It has not thus far been possible to isolate still further constituents of this coating, although there must be present still one more, namely, *VII*, between the copper and the *VIII*, and which escapes notice probably on account of its extreme thinness. It must be borne in mind that the whole coating is generally only about 0.01 mm thick.

The structures are here illustrated in a sample (1054) of which the coating contains about 8 per cent lead. This has, however, in no manner altered the type of structure; the other coatings, containing no lead, showed identically the same structures, as shown in Figs. 7 and 8. (The *VIII* constituent can be seen in Fig. 8.) In the lead bearing coating the lead simply forms part of the outer eutectic layer.

In tinning copper the excess tin runs back into the pot after each sheet is tinned. This, however, has dissolved some copper and carried it into the pot. In time, if the temperature is low enough—under 400° C—crystals are formed, probably of the *X* constituent. These are analogous to galvanizers' dross, the Zn$_7$Fe crystals, formed in galvanizing iron. When the tin bath becomes thus contaminated with copper there is danger of obtaining a brittle tin coating; that is, consisting wholly of intermediate alloy (*X*) with no ductile eutectic.

This coating, of such complicated structure, is not uniform in either thickness or structure. The molten tin has etched the copper, attacking certain groups of grains more readily than others, such that the surface of the copper, after stripping off the coating, presents a rippled appearance. This statement applies most particularly to 1054. In the "pockets" or "valleys" of this surface the excess tin or eutectic has remained, whereas the elevations have been wiped off, leaving only a thin coating. The thickness

of the coating of No. 1054 was, at maximum, about 0.03 mm; at minimum, about 0.006 mm; and in average, about 0.012 mm.

The structure of the coating of 1054 is also quite variable; this is illustrated by the Figs. 4, 9–12. The upper copper area is in each case the sheet copper, the lower the protecting copper plate, marked, respectively, (1) and (4). Fig. 4 shows a "pocket" or "valley" area with very thick coating, with continuous alloy layer and much eutectic; Fig. 9 shows the average appearance of the coating; Fig. 10 shows a break in the alloy layer, the eutectic being adjacent, apparently, to the copper; Fig. 11 shows an elevated area, at which the alloy layer extends through to the surface and is not covered by the eutectic; Fig. 12 shows breaks and irregularities in the coating. The constituent $VIII$ layer does not vary much in thickness; with the exception of a few complete breaks in it, it averages about 0.002 mm in thickness. The constituent X is more variable in thickness, varying from 0.002 mm to 0.006 mm; the eutectic layer is, however, the most variable in thickness, varying from 0 to 0.022 mm.

Fig. 13 shows the structure of the upper or corroded coating of 1054. The eutectic layer has been corroded away, leaving only the alloy layer, which is generally, but not always, continuous.

What has been said of the thickness of the constituent layers of the casting of 1054 applies generally to the other specimens examined, with the exception that the coating of 1054 seems to be much less uniform, both in thickness and structure than that of the others. Typical structures of the other samples are given in Figs. 7, 14, and 15.

IV. ELECTROLYTIC POTENTIAL AND CORRODIBILITY OF THE CONSTITUENTS OF THE TIN COATING

The properties of the alloys of copper and tin of high tin content have not been studied in great detail. Thurston, in a report [6] to the United States Board, account of which is also given in his book on the Materials of Engineering, 1890, gives results of physical tests of cast alloys throughout the whole range from 0 to 100 per cent copper. His results show that the alloys containing the constituent $VIII$ are hard and very brittle. As soon as this constituent disappears, the ductility increases. Apparently the constituent X is hard, but not particularly brittle. The eutectic of tin and X is, of course, soft and ductile.

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[6] Executive Doc. 98, 45th Cong.; 1878–1881.

The constituents X and *VIII* are not readily attacked by dilute acids, even in the presence of mild oxidizing agents such as ferric chloride. Campbell [7] states that "when from 1 to 8 per cent of copper is present, casting produces a fine network of bright crystallites throughout the eutectic. On treatment with 10 per cent nitric acid and washing with dilute hydrochloric, the eutectic is dissolved, and a fine dark-brown powder is left behind, which seems to be composed of very small shapeless plates. * * * The various residues after treatment with dilute nitric acid become more and more coherent" (as the copper content increases). Heycock and Neville [8] isolated these constituents, *VIII* and X, by treatment of alloys containing them with concentrated hydrochloric acid.

Experiments were carried out to determine the comparative corrodibility of the various constituents of the tin coating. These were of two groups: Those in which attempt was made to determine the electrolytic solution potential of the constituents and those in which actual, generally accelerated, corrosion tests were made.

The difficulty of measuring directly the electrolytic emf's is at once apparent, since in the coating itself the constituents are so close together that in making a measurement only the resultant of the individual values is obtained, and this is practically equal to that of the most electropositive. Measurements [9] of the emf of the coating against that of the base copper gave practically the emf of pure tin against copper; that is, from + 260 to + 460 millivolts, depending upon the electrolyte used.

Samples were tested from which the tin or eutectic layer had been removed by boiling for a few minutes with concentrated hydrochloric acid. After such treatment the alloy layer, constituents *VIII* + X, remain. The emf against the base copper of the same sample was tested in each case. The results of typical measurements of this kind are given in the Table 2. Indication is here given that the alloy layer is electronegative to the copper. A positive value indicates that some tin has still remained in the coating.

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[7] W. Campbell, The Microscopical Examination of the Alloys of Copper with Tin, Proc. Inst. Mech. Eng., 3–5, p. 1211; 1901.

[8] C. T. Heycock and F. H. Neville, The Constitution of the Copper-Tin Series of Alloys, Phil. Trans. Roy. Soc., 202, p. 1; 1902.

[9] In all of such measurements the entire surface, except that to be tested, was protected from the electrolyte by a layer of paraffin. Further, each electrode was paraffined above and below the surface of the electrolyte, such that during the measurements every portion of the surface tested was completely immersed.

TABLE 2

The Electrolytic EMF Values of the "Alloy" Layers of the Tin Coating Against the Base Copper

Time in minutes	EMF in millivolts [a]	Time in minutes	EMF in millivolts [a]	Time in minutes	EMF in millivolts [a]
1054 in 5 per cent H_2SO_4 solution		1054 against 4 A in tap water		1242 in dilute $SnCl_2$.HCl solution	
0	−9.0	0	>−80.0	0	−55.0
1	−4.5	36	−57.0	3	−15.0
5	+4.5	62	−62.0	8	− 2.0
8	[b]−8.0	103	−70.0	9	[d]−12.0
11	[c]+4.0			28	± 0
1054 in 5 per cent HCl solution		1054 in tap water to which has been added a few drops of $SnCl_2$.HCl solution		1243 in dilute $SnCl_2$.HCl solution	
0	−25.0			0	+50.0
1	−12.0			10	+60.0
7	+ 0.5	0	−35.0		
8	[d]−22.0	7	−50.0		
10	[c]+ 2.0	37	−67.0		
		51	−52.0		
1054 in 5 per cent HCl. $SnCl_2$ solution		1800	[e]+ 0.5		
0	−60.0	1241 in dilute $SnCl_2$.HCl solution			
5	−20.0				
18	− 9.0				
20	[d]−50.0	0	−15.0		
23	[c]−22.0	15	− 7.0		
65	[c]+25.0				
66	[d]− 8.0				

[a] A plus sign indicates that the alloy layer was electro-positive to the copper in solution.
[b] Solution slightly stirred.
[c] Solution quiet again.
[d] Solution stirred.
[e] A precipitate of basic tin chloride has been formed.

In order to obtain a clearer indication of this, alloys were cast, using Banca tin and electrolytic copper, to have as nearly as possible the compositions of the constituents *VIII* and *X*, alloys 1124 (38 per cent Sn) and 1125 (59 per cent Sn), respectively. Since these alloys as cast do not consist wholly of these constituents, they were homogenized by annealing for from 50 to 100 hours just below 400° C. This produced two alloys, one of which consisted largely of *VIII* with traces of *X* and the eutectic; the other consisted largely of *X* with small grains of *VIII* and traces of eutectic. It may be mentioned that in such alloys there is considerable difficulty in getting rid by annealing of the eutectic, since it is absorbed in a peritectic reaction, which takes place very slowly.

TABLE 3

EMF of Cast and Homogenized Copper-Tin Alloys to Copper

[1125, 5₉ per cent; Sn, constituent X. 1124, 38 per cent; Sn, constituent VIII.]

Time in minutes	EMF in millivolts a	Time in minutes	EMF in millivolts a	Time in minutes	EMF in millivolts a
1125 against annealed copper wire in dilute SnCl₂.HCl solution; surface completely paraffined		1125 against electrolytic copper in N/10 SnCl₂. N HCl; surface completely paraffined		1125 against electrolytic copper in N H₂SO₄; surface completely paraffined	
	b +.260	0	g —59	0	i +26
		37	—97	6	—13
1125 against annealed copper wire in 0.27 N SnCl₂.N HCl				11	—23
		1125 against electrolytic copper in N H₂SO₄; surface completely paraffined		49	—12
0	c —67			1124 against electrolytic copper in N H₂SO₄; surface completely paraffined	
1	—73				
5	—64	0	h —67		
31	—76	260	—40		
1125 against electrolytic copper in 0.27 N SnCl₂. N HCl; surface completely paraffined		1124 against electrolytic copper in N/10 SnCl₂. N/10 CuSO₄. N HCl; surface completely paraffined		0	j + 4
				5	— 6
				10	— 8
0	d — 9			12	k —12
2	e —32				
17	—46	0	+9	1125 against 1241 copper base in tap water	
34	—48	3	—2		
		22	—5	0	l +37
1125 against electrolytic copper in 0.27 N SnCl₂. N HCl; surface completely paraffined		27	—5	12	+46
				24	+ 8
		1125 against electrolytic copper in N/10 SnCl₂. N/10 CuSO₄. N HCl			
0	f —17			1124 against electrolytic copper in N/1000 SnCl₂. N/100 HCl; surface completely paraffined	
4	—30				
25	—35	0	i —17		
53	—42	9	—14		
		34	— 9	0	+ 8
1124 against electrolytic copper in 0.27 N SnCl₂. N HCl; surface only ground and not paraffined				480	—45
		1124 against electrolytic copper in N/1000 SnCl₂. N/1000 CuSO₄. N/100 HCl; surface completely paraffined			
0	—34				
5	—24				
22	—10	0	j ± 0		
24	—14	6	+17		
30	—17	19	+12		

a A plus sign indicates that the electrode first named is electropositive to the second one.
b Opening made to the eutectic.
c Opening made by the VIII constituent.
d Opening to X constituent.
e Stirred solution.
f Several openings made, including grains of both VIII and X.

g Opening to VIII only.
h Several openings made, including VIII and X.
i Opening to VIII and X.
j Opening to VIII.
k Stirred solution.
l VIII+X.

The emf of these alloys was then measured against annealed copper wire or against electrolytic copper. A surface was prepared either by grinding alone, by grinding and polishing, or by grinding, polishing, and etching away the polished layer. In some cases the resultant emf of a portion of this surface was determined; in others the whole surface was covered with paraffin, and then an opening was made with a sharp needle, exposing one or the other constituents only. This could be done under the microscope, as the grains of the constituent were relatively quite large. Typical results of such measurements are shown in Table 3. The measurements were made by potentiometer.

The results indicate that the *VIII* and *X* constituents are both in general electronegative both to electrolytic copper and to remelted and worked copper, although when the concentration of Sn ions is very low they may give positive values. One set of tests made to determine the emf's of the individual constituents in the same alloy, 1125, showed that the *VIII* was about 80 millivolts and the *X* about 40 millivolts electronegative to copper. However, the variation in actual values obtained, not surprising in view of the difficult circumstances under which the tests were made, does not admit of any value being chosen for the emf of these constituents. Their values both lie close to that of copper, and in general below it by from 5 to 50 millivolts.

This fact has remained hitherto unnoticed, although emf measurements of the copper-tin alloys have been made.[10] This is due to the fact that these measurements were carried out only on cast alloys, not subsequently homogenized by annealing. In such alloys containing between 36 and 100 atomic per cent tin, there remain always portions of the tin containing eutectic. The emf value obtained is therefore that of the tin; the electronegative values of the constituents *VIII* and *X* present are completely masked.

The significance of the negative emf of these two constituents toward copper is realized when samples of tinned copper are exposed to corrosion. Two solutions and tap water were used in these tests, a solution of

30 cc conc. HCl

20 cc $FeCl_3.HCl$ solution,

and a dilute solution of $HNO_3 + HCl$. Oblique surface sections were prepared of the samples 1054 and 1241, one in which the tin

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[10] N. Puschin, Das Potential und die Chemische Konstitution der Metalllegierungen, Zeit. Anorg. Chem., 56, p. 1, 1908; M. Herrschkowitsch, Beitrag zur Kenntniss der Metalllegierungen, Zeit. Anorg. Chem., 27, p. 123, 1898.

coating contains lead and one in which it did not, either as received or copper-plated. At first upon immersion in the $FeCl_3.HCl$ solution, and for about 15 minutes, the eutectic and tin layers were attacked and dissolved, bubbles of gas (hydrogen) forming on the exposed copper layers which remained perfectly bright and unattacked. As soon as the eutectic was dissolved the copper layers were quite suddenly attacked and darkened within three or four seconds, leaving the alloy layers bright and unetched. The appearance of specimen 1054 is shown in Fig. 16. The islands of alloy containing black eutectic at the center are seen in a ground mass of heavily etched copper. The alloy layer will remain quite bright in such a solution for hours after both the tin and the copper have been heavily attacked. In $HCl + HNO_3$ the alloy layer is attacked before the copper.

A specimen of 1054 which had been plated was bent and polished through to the base copper and put in ordinary tap water for about 24 hours. Both the eutectic layer and the copper were attacked, leaving the alloy layer bright as before. This is true also of other specimens treated for 200 or more hours. The appearance of the coating and adjacent copper of the 24-hour specimen is shown in the Fig. 17. The same was true of other samples, 1241 and 1120, tested.

V. DISCUSSION AND CONCLUSIONS

It has been shown that the tin coating on copper consists of three well-defined layers—first and next to the copper a layer of the constituent *VIII*, probably the compound Cu_3Sn, then of the constituent *X*, an alloy of approximately 60 per cent (by weight) of tin, and finally a layer of quite variable thickness, a eutectic of copper and tin (and probably also lead when this metal is used in the tinning mixture), in which are found crystals of the constituent *X*. Etching experiments and measurements of electrolytic emf have indicated that these intermediate layers are electronegative to both the outer tin (eutectic) and the underlying copper itself (by from 5 to 50 miliovolts), and less readily attacked by water and dilute acids (also alkalies). This is true also of tin coatings containing lead, and holds not only for the corroded sheet examined, 1054, but for all others examined, including several direct from the manufacturers.

These results explain at once the local character and type of corrosion exhibited by the sample 1054, from the roof of the Library of Congress. The coating is very thin and also quite variable in

thickness and structure. The surface scratches have exposed the copper at various points. This exposure of the copper along these scratches is aided by the fact that the adjacent alloy layer is extremely brittle and readily torn or crumbled out. As long as the tin eutectic layer was present it has owing to its greater corrodibility and electropotential been first attacked, thus protecting the copper. Finally, however, after several years this layer has been almost wholly removed, and at those points where the copper is exposed the attack has set in, the copper, forming with the adjacent electronegative alloy layer a galvanic couple, of which the copper is attacked and eaten away, forming the pits as described above. The same thing happens at the points where, as has been shown, there is a break in the continuity of the alloy layer. Here the eutectic layer is corroded off exposing the copper at once, the latter being corroded in similar manner as above described.

Attention may be called here to the possible effect of the presence of the small amounts of iron and zinc found in the coating. These metals are both electropositive to tin and do not dissolve appreciably in solid tin, must therefore be present in the coating as segregated particles. These must, in the case of the iron, at least, be very small since tests with a solution of dilute acid and $K_3FeC_6N_6$, by which the presence of discrete particles of iron in a manganese bronze containing about 1 per cent of iron can be readily shown, fail to reveal them.

It would thus appear that whenever the outer tin or eutectic layer of a tin coating on copper is removed the alloy layer remaining gives only a mechanical protection from corrosion—that is, it does not protect the underlying copper electrochemically, as does zinc, iron in galvanized products. Corrosion of the type described, therefore, should be possible in any tinned copper material. Yet instances are known of tinned copper roofs, which have stood up for 20 to 25 years under apparently more severe service conditions without showing sign of any such pitting as has been described.

For the variation in resistance to corrosion of different samples of this material many factors might be responsible. First and foremost is the question of the mechanical abuses received, such as scratching and indenting. This has been shown to be the determining factor in the case described. A sample of the roof from the Statehouse in Texas showed absolutely no scratches; this roof has resisted corrosion for 20 or more years.

The other principal factor is undoubtedly that of the thickness and uniformity in structure of the coating. This varied quite noticeably in the various samples examined. The corroded sample, 1054, showed perhaps the greatest degree of nonuniformity in this respect.

A third factor which must not be lost sight of in this connection is that of the electrolytic solution potential of the base copper itself. Experiments have shown that this may vary for different samples within several millivolts, a range which is of the same order of magnitude as that of the difference in electromotive force between the copper and the tin-copper alloy.

The author wishes to express his appreciation to the Librarian of Congress, who brought the matter to the attention of the Director, Dr. Stratton, and to other officials of the Library of Congress for their cooperation in furnishing information and material, as well as to two manufacturers of this material, who have also furnished material of this type and information concerning it. Dr. Burgess, at whose direction the work was undertaken, has as usual been most ready with suggestion and helpful criticism, and to him and to Messrs. A. N. Finn and L. J. Gurevich, of this Bureau, who carried out the chemical analyses, the author's appreciation is expressed.

WASHINGTON, July 12, 1916.

Photomicrographs

[In the photomicrographs the bare copper area is marked (1), the electroplated copper (4)]

Fig.	Material	Etching	Magnification	Description
2	1054	$NH_4OH+H_2O_2$.......	100	Cross section of base copper.
4	1054	$FeCl_3.HCl+Cu-Am-OH-1.$	500	Transverse section of tin coating.
5	1054	.....do................	100	Oblique surface section.
6	1054	.....do................	500	Do.
7	1241	.....do................	100	Do.
8	1243	.....do................	500	Do.
9–12	1054	.....do................	500	Transverse sections showing irregularity in thickness and structure of coating.
13	1054	.....do................	500	Transverse section through coating remaining on corroded exposed side.
14	1242	.....do................	100	Oblique surface section.
15	1120	.....do................	100	Do.
16	1054	$FeCl_3HCl$.............	100	Do.
17	1054	Tap water.............	100	Do.

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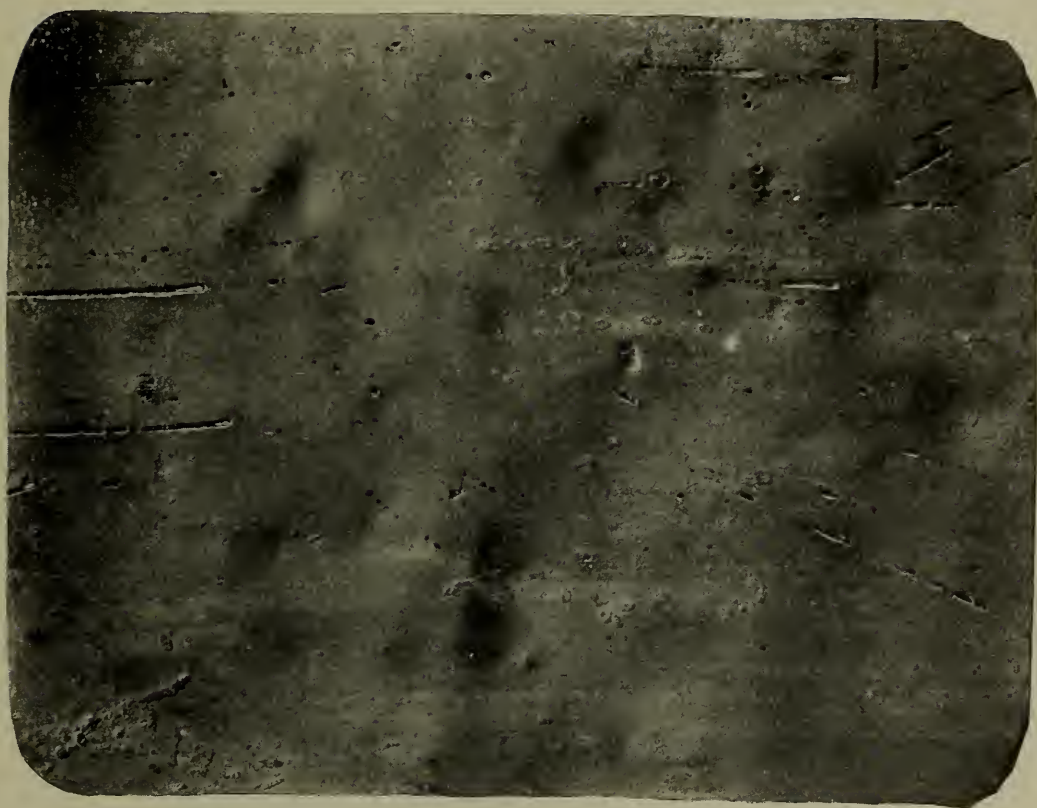
FIG. 1.—*Appearance of corroded tinned sheet copper roof*
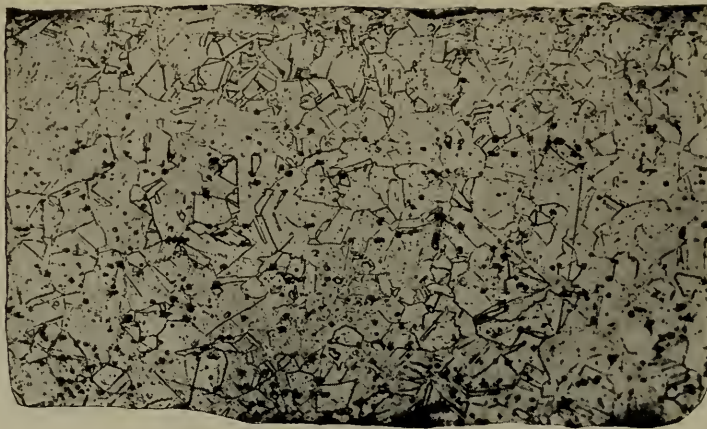
FIG. 2.—*Microstructure of base copper of 1054.* $\times$ *100*
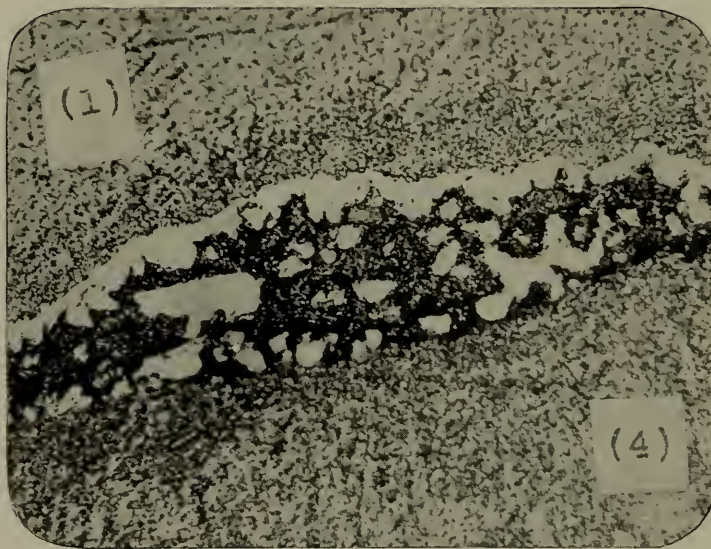
FIG. 4.—*Material 1054.* $\times$ *500*
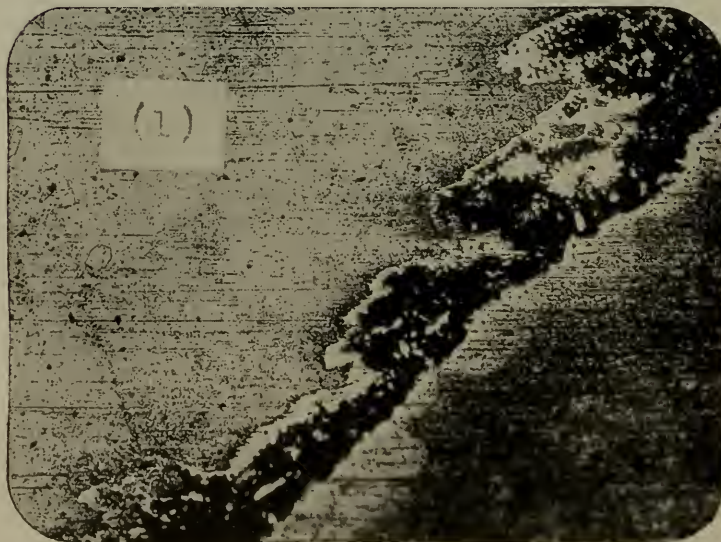
FIG. 5.—*Material 1054.* $\times$ *100*
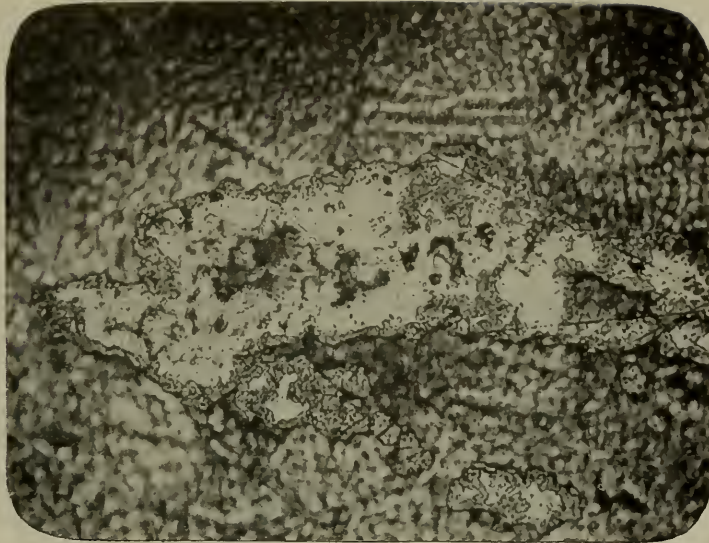
FIG. 6.—*Material 1054.*   × *500*
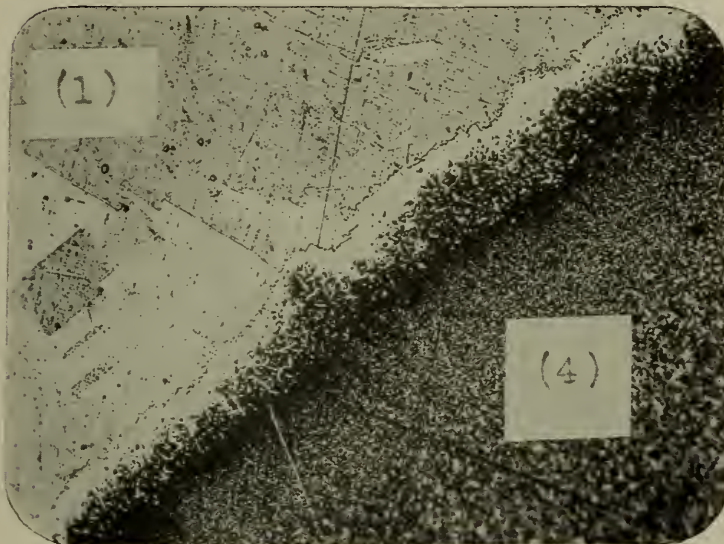
FIG. 7.—*Material 1241.*   × *100*
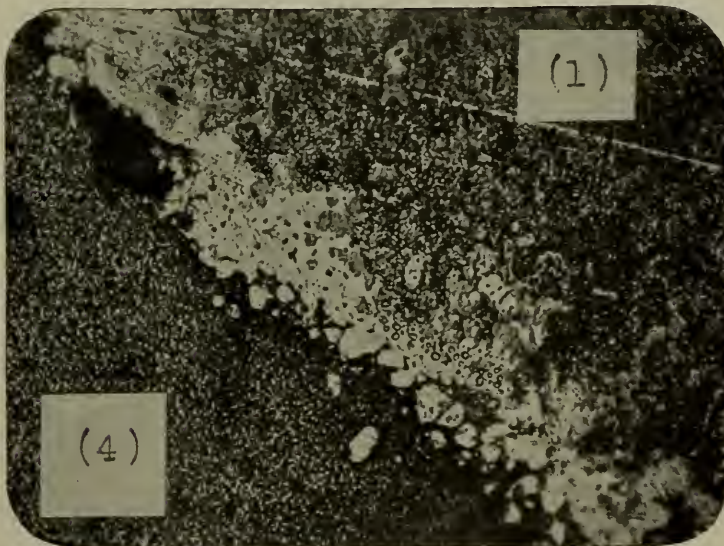
FIG. 8.—*Material 1243.*   × *500*
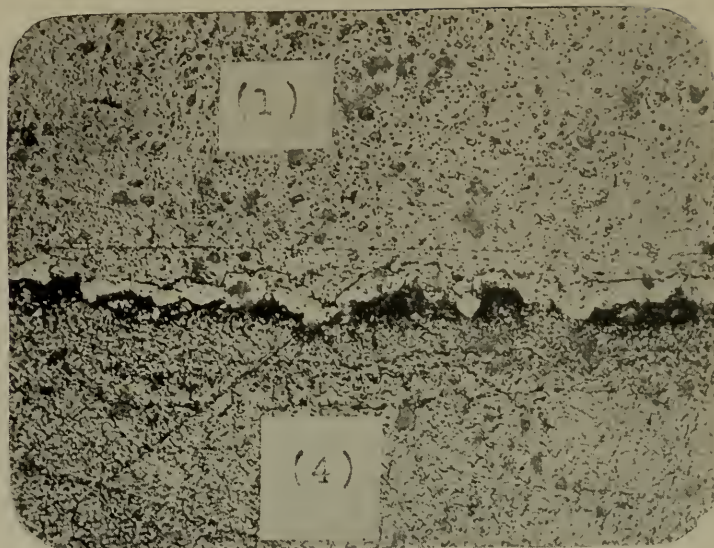
FIG. 9.—*Material 1054.* × *500*
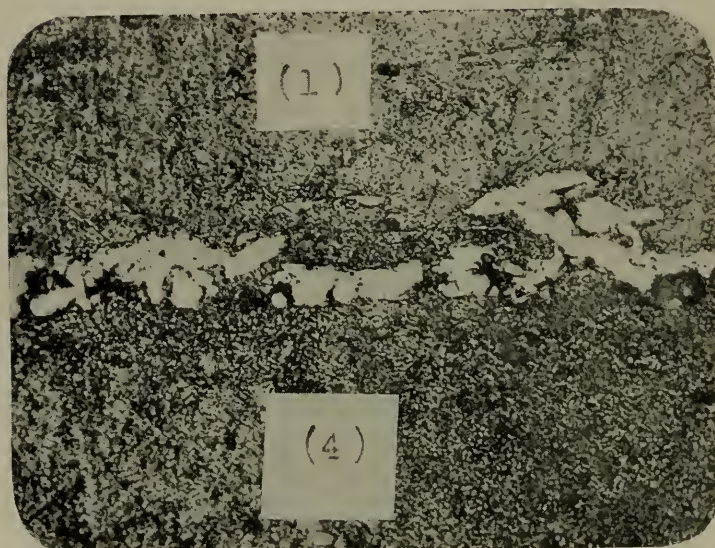
FIG. 10.—*Material 1054.* × *500*
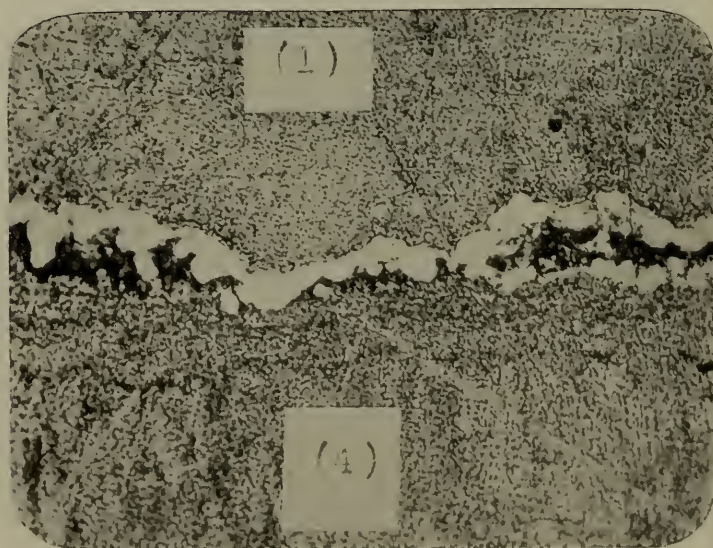
FIG. 11.—*Material 1054.* × *500*
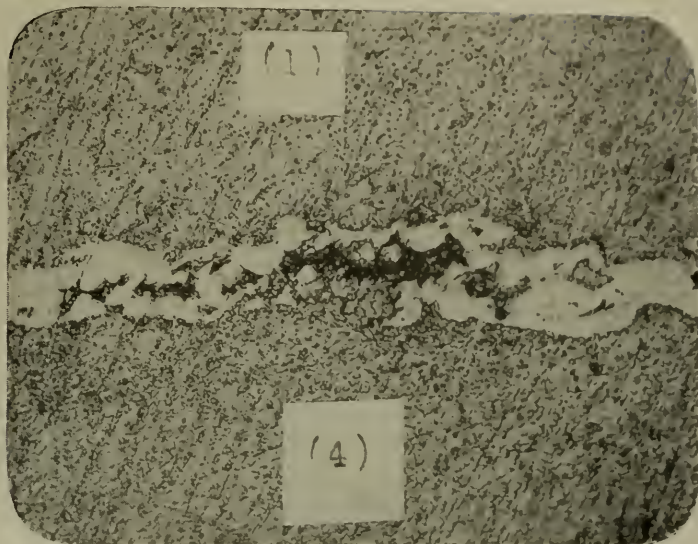
FIG. 12.—*Material 1054.* × *500*

FIG. 13.—*Material 1054.* × *500*
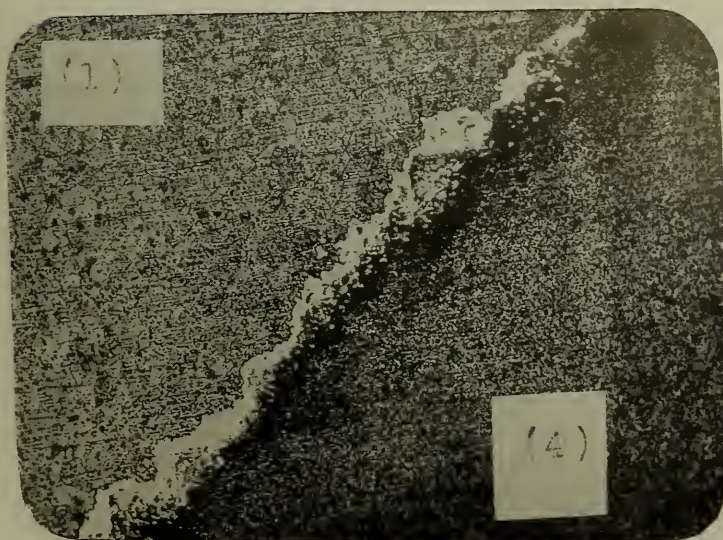
FIG. 14.—*Material 1242.* × *100*
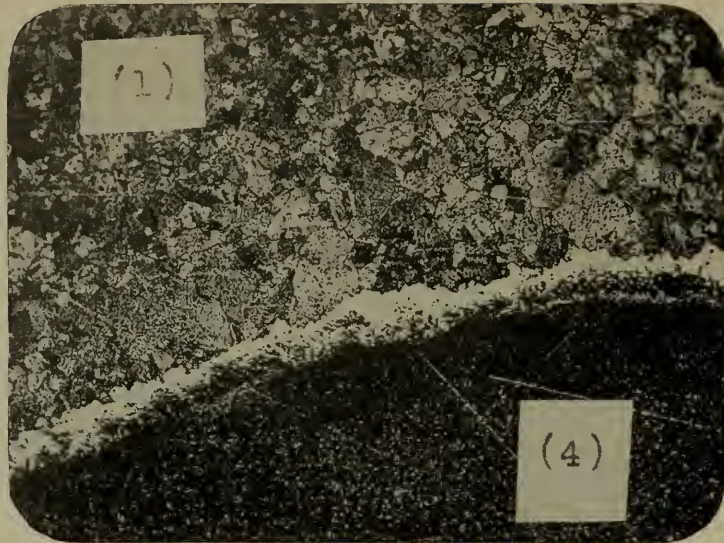
FIG. 15.—*Material 1120.* × *100*
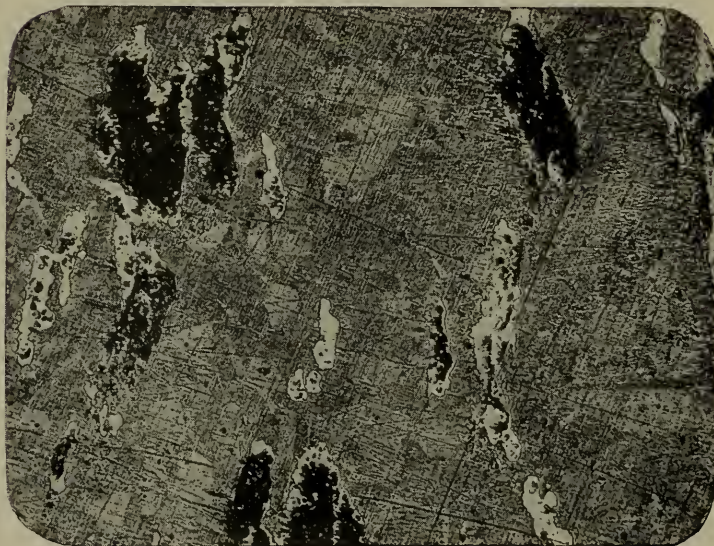
FIG. 16.—*Material 1054.* × *100*

FIG. 17.—*Material 1054.* × *100*