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MATERIALS IN THE NATIONAL BUREAU OF STANDARDS

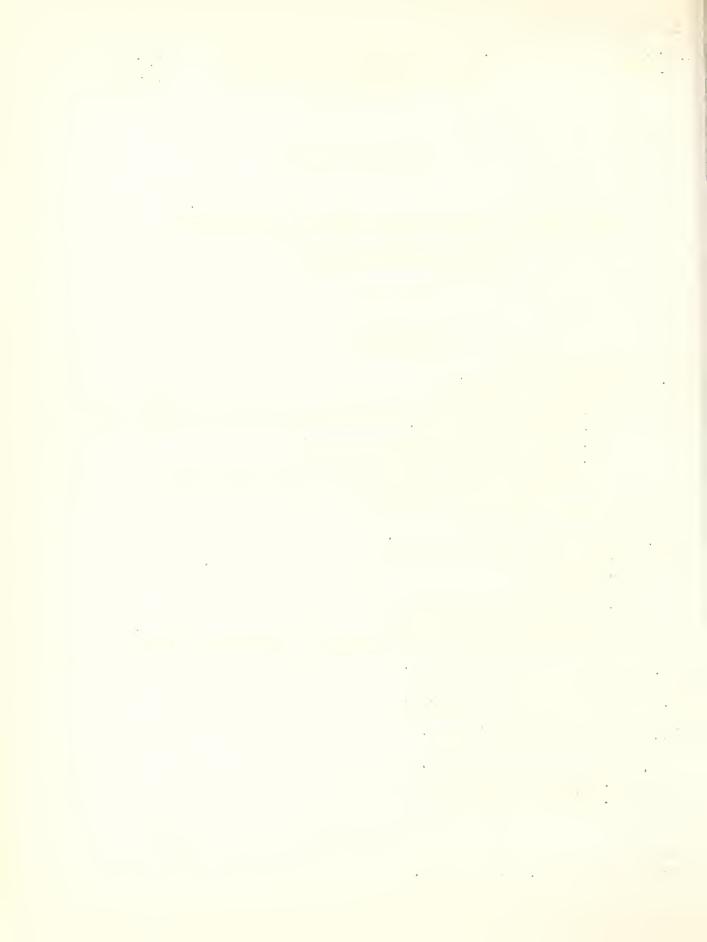
SOIL-CORROSION TESTS

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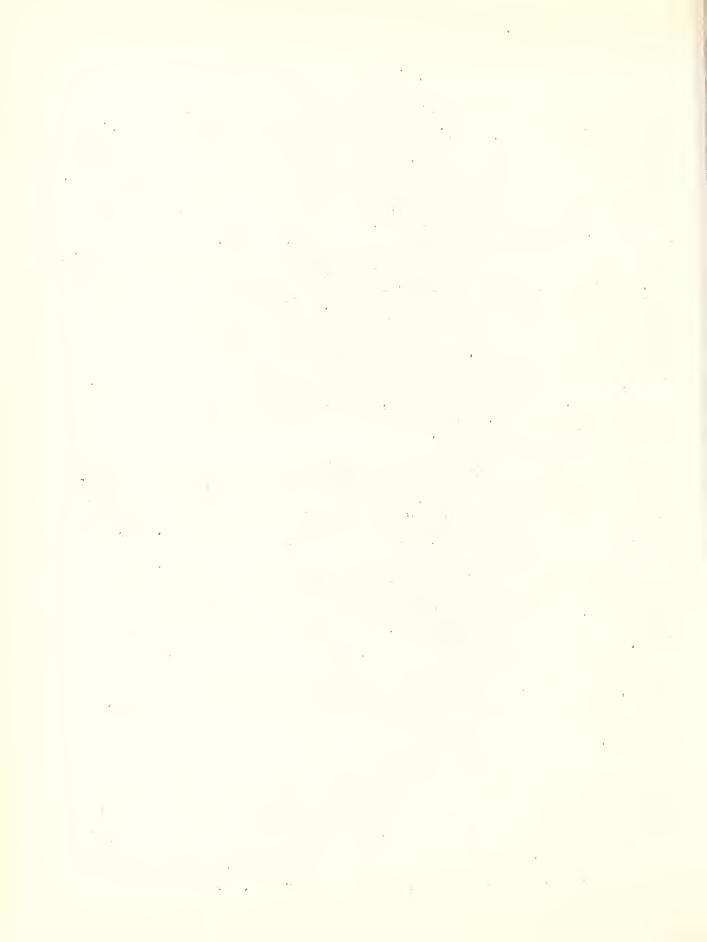


I. INTRODUCTION

The soil-corrosion investigation of the National Bureau of Standards, begun in 1922, was devised for the purpose of estimating the corrosive action of various soils toward the commonly used ferrous pipe materials. For this study 47 test sites were carefully selected to represent a wide range of soil conditions. Because of the severe corrosiveness shown by certain soils, corrosion-resistant materials, such as lead, copper, high and low copper brasses, and a number of metallic and nonmetallic coatings were later included in the field tests. The recent extensive development of low-alloy steels of high yield strength made available a large number of materials some of which might be selected for service underground if their resistance to corrosion in soils could be established. In 1932 specimens of a variety of these materials were buried at 15 additional test sites selected to represent different soil conditions and degree of corrosiveness. In 1937 and in 1939 additional specimens of newly developed materials were buried at these test sites. In order that the tests might be made as comprehensive as possible, nonferrous metals, steels coated with experimental protective coatings, and miscellaneous materials were also buried on these occasions.

At approximately two-year intervals two specimens of each material are removed from each of the test sites, the corrosion products carefully removed, and except in the case of certain classes of materials, the loss of weight is determined and the depth of the deepest pit on each specimen is measured. Since previous studies have shown that the corrosion-time relation is different for different materials and environments, it was considered necessary to conduct the test for at least 10 years before drawing final conclusions relative to the merits of the materials. Several progress reports on the conditions of the specimens have been published, the latest report appearing in The reader is referred to these reports for details of the corrosion tests, for descriptions of the test sites, and for data on the behavior of the materials in the various soils. 1-10 Corrosion rates for materials which are seldom used in soils and for which limited data are available, such as aluminum and its alloys, will be found in certain of these reports.

For the majority of the materials to be considered, a discussion of resistance to corrosion in the various soil environments would be premature at this stage of the investigation. Nevertheless, it is desirable to indicate the behavior of the materials toward those corrosive factors in the atmosphere, in natural waters, and in solutions, which are also present in soils, so far as these effects can be judged from the results of corrosion tests and experience in service. An advantage to



to be derived from such a consideration is that significant trends in the effect of alloying elements on corrodibility may be utilized in the interpretation of the results of the field tests. At the same time those interested in the production of alloys resistant to underground corrosion may be assisted in deciding whether specimens of their materials should be offered in the event of extension of the field tests in the future.

Although a discussion of the corrosion resistance of most of the specimens in the various soils must be deferred until more complete data are available, some information on the behavior of the materials buried in 1932 may be obtained by referring to the most recent progress report. A report on the first and third inspections of the materials buried in 1937 and in 1932, respectively, is being prepared for publication.

II. FERROUS MATERIALS

1. Wrought Materials.

The compositions of the wrought ferrous materials which have been buried at the various test sites are given in table 1. Where there is a possibility of confusion in referring to these and other specimens which have been assigned the same letter symbol, the symbol has been followed in the text by the year of burial.

a. Carbon Steels, Wrought Iron, and Open-Hearth Iron.The ordinary wrought materials represented in the tests are open-hearth iron, hand-puddled and mechanically-puddled wrought iron (Roe process), open-hearth steel and Bessemer steel.

In the manufacture of open-hearth iron (known commercially as ingot iron), carbon, silicon, phosphorus and manganese are held to the lowest possible point, the sum of these impurities usually not exceeding 0.15 percent. The relatively high degree of purity so obtained has no marked advantage with respect to corrosion in soils, however, since the potentials which result from differences in aeration, for example, are usually much greater than those that might arise from lack of homogeneity of the metal. Open-hearth iron is used largely in sheet form for galvanizing, tinning, enameling, etc. for wire and for other purposes.



TABLE 1 .- COMPOSITION OF WROUGHT FERROUS MATERIALS

	= = =	Copper	steel	Low alloy irons Copper-bearing	Carbon st Open-hear " Bessemer " Low carbo	Wrough Hand-r	Waterial
		Copper-molybdenum -Open hearth iron		lloy in	n st	Wrought iron Hand-puddled " " Roe process	ia1
	= = =	odenum i iron	open-meat on	and steel	is, wrought iron steel gel steel	, <u>, , , , , , , , , , , , , , , , , , </u>	
	HMO	MM	A	steels	iron a A A K K N N N N N N N N N N N N N N N N	្ឋា ភ្នំ ភូមិ	Iden- tifi- cation
	1937 1932	1939	1937	1922	and pure 1922 1922 1922 1922 1922 1932	1922	Year buried
	plate pipe	pipe	plate	pipe	open pipe	= = 	Form
	n n n	2.5	2.5	N	hearth i	7131 3	Nomin- al width or dia- meter in.
	12 12	12	12	σ	iron 66 66	1266	Length in.
	1255 5055 5055 5055 5055 5055 5055 5055	25	.250	.216	1011001	241 241 212 242	Thick-ness
	200 000 000	40,	.033	.07	.02	.03 .02 .016	,3 _C C
	.003		,002		.09	125	3. F.
	.098 .32	.16	.029	.24	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	trace .033 .029	Mn %
	.032	.027	.017	.032	000000 0000000000000000000000000000000	.023 .018	Ω P ₆
	.007	800	.006	. 000 Sa	.0013 .0043 .0043	106	<i>,9</i> , †⊎
	.02	404	.049				a C
	15	14	.034				Mi
	55 F5	.051	.052	.22	,014	.02	g Cu
	13	.07					Mo
		(SN)				Ox ide	
\		002				+ + •	Other elemen
1	\					ag 2.56 2.681	er

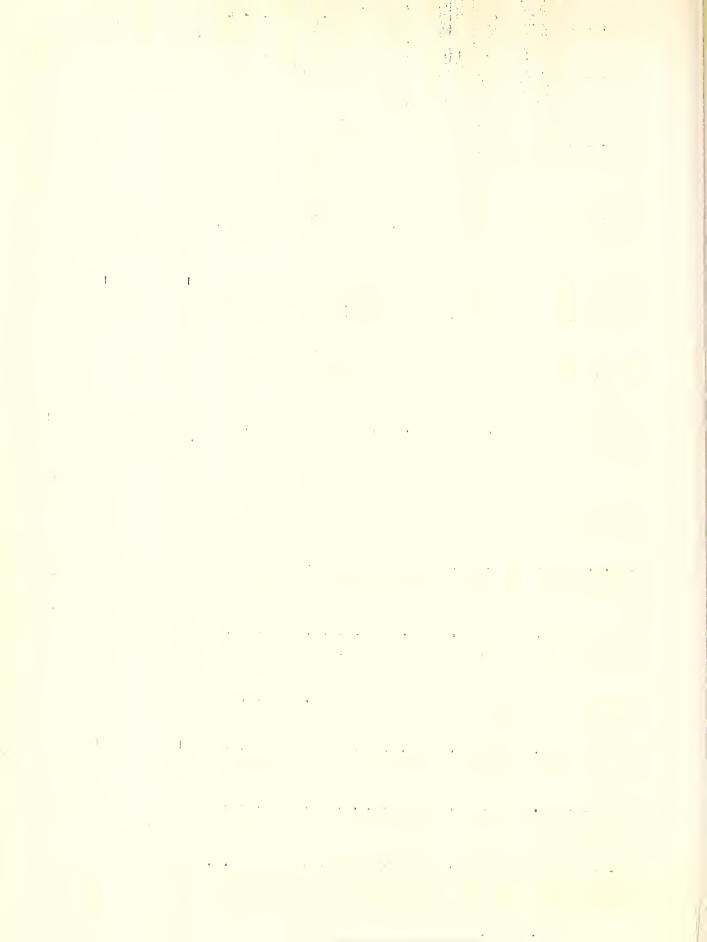


TABLE 1 - COMPOSITION OF WROUGHT FERROUS MATERIALS (continued)

		Year		Nomin-	Length	n Thick-										
Waterial	tifi- l	buried	Form	al width		ness										
				or dia-												Other
				meter			Q	Si	Mn	<u>ca</u>	ħ	Cr	Ni	Ou.	Mo	elements
				in.	in.	in.	150	53	<i>%</i>	%	6	9	200	69	%	<i>%</i>
Low alloy irons and st	steels (co	continued)	<u>a</u>)									٠				
per-nickel steel		1937	plate	2°5	12	.25	.06	,047	.49	.025	<u>.</u> 095			.95		
	ᅜ		==	2.5	12	125	.07	. 14	14	022	010		96	1.01		
## ## ## ## ## ## ## ## ## ## ## ## ##	ũ	1932	pipe	1.5	12	.145	. 14	.19	.21				2.47	1.08		
Chromium-silicon-copper	r															
phosphorus steel	Q	1937	plate	2.5	12	.25	.075	420	.20	.018	.124	1.02	.22	428		
olybdenum	NN	1939	pipe	1.5	14.5	5 . 145	.09	25	46	010	.015	1.96			.49	
2%chromium steel with																
3	KK	1937	plate	2.5	12	•25	.082	.51	94.	*015	-017	2.01	.07	+004	-57	
4-6% chromium steels																
6% chromium	ᅥ		pipe	2.0	10	.154	.13		94.	.025	.012	5.05				
	J	1937	plate	2.5	12	.25	.077	.43	.37	.005	.015	5.02	.09	800		
n molybdenum	[F]	1937	=	2.5	12	-25	.074	141	•32	.006	.013	4.67	.09	.004	•51	(Ti .022
with molybdenum	H	1937	=	5	72	N	.060	. 39	.40	410	.021	5.5%	.17	·004	.43	Al 0.27
12% chromium steel	đ	1932	=	t	0	.063		200	•38	.017	.011		182	.025		
chromium	V	32	=	+	0	.063	.070	.34	•36	.015	.014	17.08	002	.021		
	2 ×	1932	pipe	1.5	12	.145		.277	.42	.017	.016	17.72	.287			
20% curomium	C	0	=	-	0	.250						0				

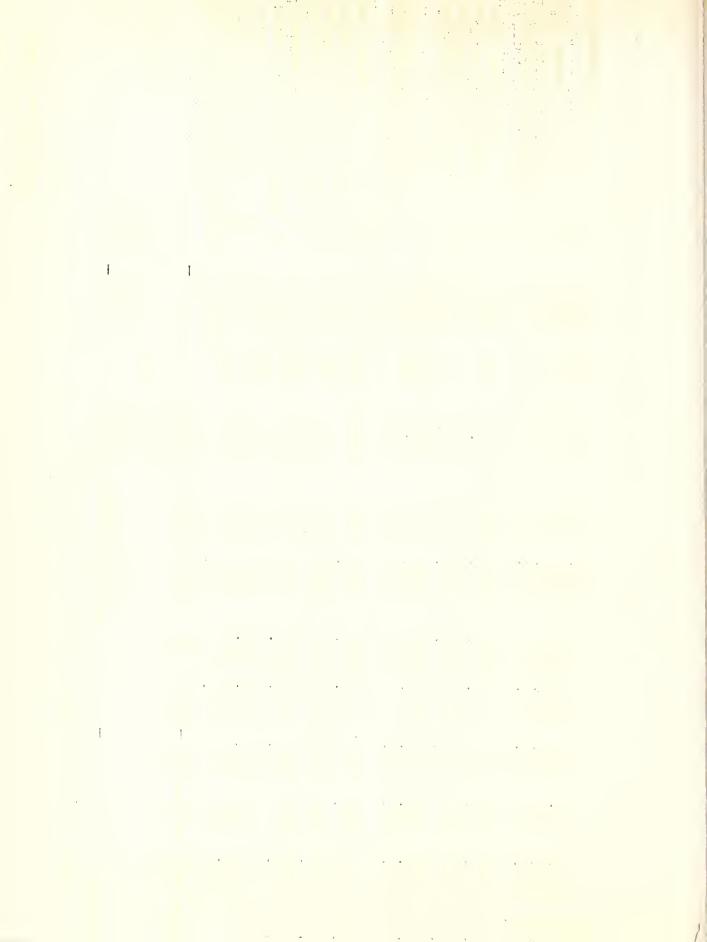
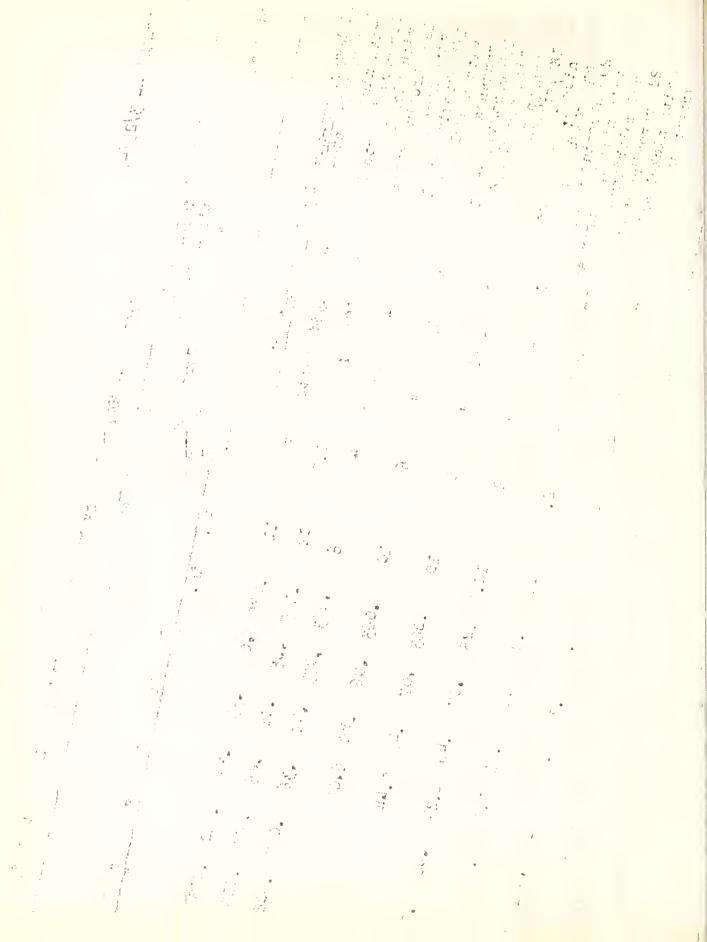


TABLE 1 - COMPOSITION OF WROUGHT FERROUS MATERIALS (continued)

	<pre>with nickel, manganese and molybdenum 22% chromium steel</pre>	<pre>nickel, manganese and molybdenum 20% chromium steel</pre>	with nickel and manganese 18%981891 unith	<pre>with nickel and manganese 18% chromium steel</pre>	, , ,	th nickel	1	High-chromium-nickel	Waterial
Y	se DT	CM	Ø	Н	AL	T,		and man	Iden- tifi- cation
1932	1939	1939	1932	1932	1932	1932	1932	mangangse	Year buried
3	#	ort Må	=	a	plate	pipe	plate	8 1 8 1 8	d Form
ŧ	2 3	N	0,	6	F	1.5	S	,	Nomin- al width or dia- meter in.
6	12	12.5	10	10	σ	12	,		Length
.063	25	.25	. 063	.063	*063	2145	.025	,	Thick-ness
. 144	.07	.07	.07	,06	,093	205	© ⊗		340
• 59	91	.40	18	04.	27	° ∞ ∞	*33		3 S.
1.80	1.99	1,24	444.6	6:09	36	94.	4440		u yi
.011	,012	800			.017	011	£022		n es
,015	.01 ⁴	.016			\$00	.015	.015		2 P
22.68 12.94	19.27	17.78	17.78	17.76	18,69	17.52	17:20		Cr
12.94	22,12	10.96		3.83	9.18	80.5	18,95		Ni
.021	1.07		.74	•95	.016		ra .		cu Cu
	3.52	2.63							o Mo
									Other elements



Wrought iron is distinguished from other irons by the fact that in the process of manufacture a certain amount of slag is incorporated mechanically in the molten iron. It is the existence of this slag, intermingled and dispersed among the crystals of iron which gives to wrought iron its characteristic properties. The superior corrosion-resistance claimed for wrought iron is often attributed to the action of the slag flakes in diverting attack which has started locally into the plane of rolling, obstructing it from advancing at right angles to the surface. In other words, the slag flakes are considered to divert pitting into general corrosion.

In the manufacture of wrought iron the slag is incorporated and distributed in the metal by the process of puddling and by the "work" that is performed in the later rolling operations. Fuddling is either by hand or machine. As the quality of wrought iron depends largely on the puddling operation, it was considered desirable to include in the soil-corrosion tests specimens of both hand- and machine-puddled wrought iron (materials A and B (1932), respectively).

The machine-puddled specimens were made by the Roe process. In this process puddling is accomplished by a specially designed furnace which is oscillated at different speeds as desired. This process, however, is no longer used commercially.

Comparison of the rates of corrosion of specimens of hand-puddled wrought iron, steel, and open-hearth iron in soils does not indicate significant differences in the behavior of the three kinds of materials underground. However, a number of examples of the superior performance of wrought iron pipe lines have been reported in the literature. Possible explanations for this behavior have been advanced by Ewing. 12

b. Low-alloy Steels. - Low-alloy steels are characterized by much greater resistance to atmospheric corrosion than is shown by ordinary steels. Although these steels corrode readily initially, the rust coating formed is very adherent and relatively impermeable and thus serves as a protective coating. Certain of these steels are used extensively for general structural purposes, in the manufacture of railway equipment, and generally where high strength and resistance to corrosive atmospheres are especially important. Corrosion resistance in these materials is obtained mainly by the addition of small amounts of chromium, nickel, copper, silicon, phosphorus or molybdenum. To the extent that the soil environment approaches the conditions of atmospheric corrosion, as in well aerated soils, certain low-alloy steels might be expected to prove superior to ordinary steels. However, as local differences in potential are probably considerably greater in soils than in the atmosphere, the protec-



tive film on the alloy steels is likely to be subjected to more severe attack when exposed to the soil.

The beneficial effect of small amounts of copper on the corrosion resistance of steel in the atmosphere has long been known. A few tenths of a percent of copper is sufficient to double or triple the resistance to steel to atmospheric corrosion. However, if certain other elements are elso present in the steel, the life of copper-bearing steel is greatly increased. For example, Kendall and Taylerson , in their analysis of the A.S.T.M. tests of the corrosion of steel sheets in the atmosphere, showed that at Pittsburgh the life of steel sheets containing from 0.15 to 0.40 percent Cu increased from 1500 days with 0.01 to 0.03 percent P to over 2500 days with 0.10 percent P, whereas the presence of phosphorus in noncopper steels had no beneficial effect on such material, at this test site. The high copper contents of the low-alloy steels as a class (Table 1) indicate the extent to which copper is being used along with other alloying elements in enhancing the corrosion resistances of this class of materials. Copper either alone or combined with phosphorus apparently has not improved the performance of steels in submerged corrosion tests to date. In the soil-corrosion tests carried out by the National Bureau of Standards no benefit has resulted from the presence of 0.2 percent Cu in open-hearth steel.

Phosphorus either singly or combined with copper has been shown to increase the corrosion resistance of steels in various atmospheres. While the benefit of small amounts of phosphorus apparently does not apply to total immersion, Ewing was able to correlate the phosphorus content of the eight kinds of wrought materials buried in 1922 at the Bureau soil-corrosion test sites with the average depth of the deepest pits on the specimens after 12 years exposure. The shallowest pits were observed on the specimens containing the highest content of phosphorus.

For submerged conditions low-alloy steels as a class do not appear to offer any appreciable advantage over low-carbon steels, although certain compositions are used to advantage in connection with specific corrosives. For example, nickel-molybdenum steels are used to gain improved resistance to corrosion and corrosion fatigue in oil well brines containing hydrogen sulfide. 16

c. 4-6 Percent Chromium Steels. - Steels containing intermediate percentages of chromium are widely used in oil refineries to resist the corrosive action of sour crudes containing hydrogen sulfide. However, as the operating temperatures are well above the dew point, the behavior of these alloys gives



no indication of their probable behavior in poorly drained organic soils in which hydrogen sulfide is present.

Molybdenum is incorporated in the 4-6 percent chromium steels principally to improve their mechanical properties at and after their exposure to elevated temperatures.

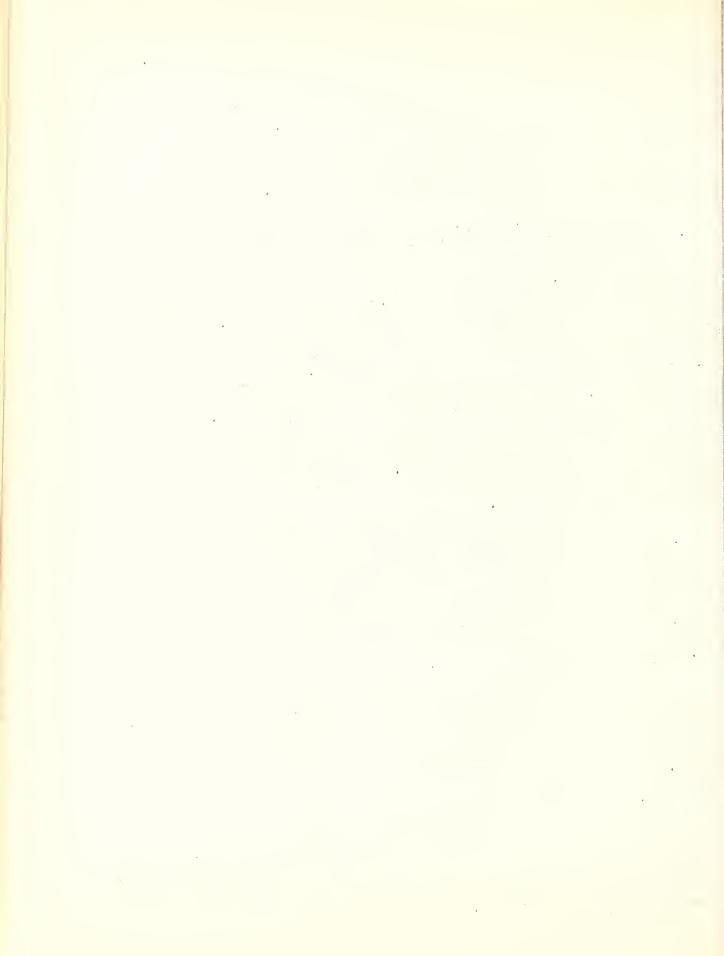
d. High-Chromium Steels. The high resistance to corrosion by the high-chromium alloys results from the capacity of these materials to assume and maintain the passive state in many corrosive environments. With most metals a change in the intensity of a corrosive factor leads to a more or less proportionate change in the rate of corrosion, but with the stainless steels, a slight change in environmental conditions may be sufficient to throw the material from the passive into the active condition. An increase in the chromium content and the addition of certain alloying elements, such as nickel, broadens the passivity range. Specimens containing 26 percent Cm (material C) after exposure for 8 years, were pitted deeply in several soils which were extremely corrosive to ordinary steel.

High-chromium alloys are resistant to attack by sea water, many salts, and non-oxidizing acids. Molybdenum is commonly used as an addition element in these alloys, and to a lesser extent silicon and copper.

e. High-Chromium Steels with Nickel and Other Alloying Elements.— The principal contribution of nickel to the corrosion resistance of the 18-8 alloy steels is its effect in expanding the passivity limits although nickel does have other specific effects on the corrosion resistance of the high nickel alloys. Nickel itself has a very high resistance to neutral chloride solutions and to acid solutions of low oxidizing capacity. These are conditions which for the 18-8 steels lie at the passivity-activity boundary.

Manganese contributes to stainless steel the property of resisting corrosive attack by sulfurous gases. Whether this effect also applies to reducing acids in solution is uncertain. Material S is representative of the 15-5 chromium-manganese steels. Material T may be regarded as an 15-5 chromium-nickel steel in which only a part of the nickel has been replaced by manganese.

Molybdenum added to 15-5 tends to expand the passivity range with respect to salt water. It also is stated to be notably successful in resisting the effects of sulfur compounds. Material CM resembles closely in composition the material known as 16-13-3, (nominal composition 15-17 percent Cr, 12-14 percent Ni and 2.5-3.5 percent Mo). This steel shows a somewhat lesser



tendency toward pitting and contact corresion in brines and sea water than the usual varieties of 18-8.18,19

With increase in the number and amount of alloying elements in stainless steel, increased corrosion resistance to a larger variety of soil conditions is to be expected.

2. Cast Materials.

Specimens of cast iron pipe made by sand casting (materials L and Z, 1922) and by the de Lavaud centrifugal process (material C, 1922) were included in the field tests. The compositions of these and other cast materials are given in table 2. In the de Lavaud process the metal is cast in a rotating horizontal metal mold. The material has a dense, fine-grained structure.

Corrosion-resistant cast irons have been developed in much the same way as corrosion-resistant steels, that is, by the addition of such elements as chromium, nickel, molybdenum, manganese and copper. However, in the group of low-alloy cast irons the influence of the alloying elements seems to consist rather in improvement in the structure of the iron rather than in specific effects on corrosion resistance. The indirect effects of the alloying elements are greater uniformity, denser structure of the casting and the finer subdivision of the graphite flakes.

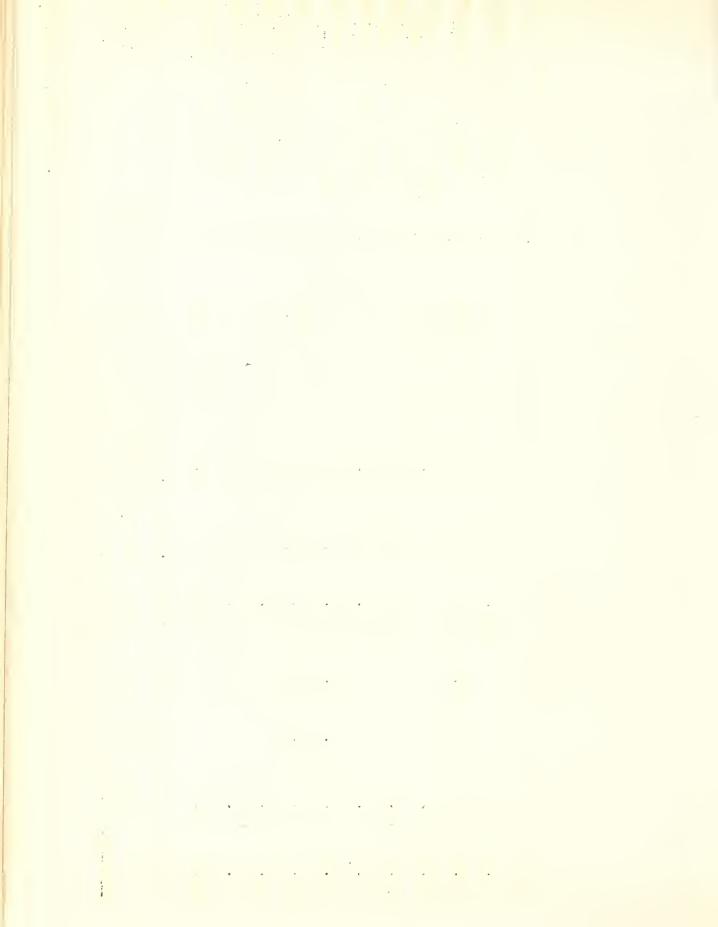
The specific effect of silicon on the corrodibility of cast iron in soils is exhibited by the behavior in the field tests of specimens of a cast iron containing about 13 percent of silicon (material D). After 8 years' exposure the loss in weight of the specimens was significant at only three of the 47 locations and only one of these specimens showed definite evidence of pitting. High-silicon cast irons are hard, brittle, and non-machinable.

Improvement in the structure of cast iron brought about by alloy additions or by other modifications in the manufacturing process apparently has the effect of reducing graphitic corrosion, 20 a type of corrosion to which cast iron is subject. By graphitic corrosion is understood that form of corrosion which results from electrolytic action between ferrite and graphite, the former constituting the anode and the latter the cathode of galvanic cells within the corroding iron. Graphitization may decrease or accelerate the normal rate of corrosion depending upon the tendency of corrosion products to deposit within the pores of the casting as determined by the nature of the environment. Donoho and MacKenzie in correlating the behavior of cast iron specimens in the National Bureau of Standards soil-corrosion tests with the properties of the soils at the test sites, pointed out that in poorly drained acid soils, and



TABLE 2.- COMPOSITION OF CAST FERROUS MATERIALS

Material	Identi- Year fication buried	Year buried	Form	Nominal width or diameter	Length	Thick- ness	Ö	led.	Total	Si	Mn	y y	ਾਹ	O.F.	Νί	Cu
				in.	in.	in.	% %	07	%	%	29	%	,9	59	19	%
PeLavaud cast iron	Ω	1922	pipe	5.0	0	++			3.56	2.34	.73	.083	.77			
	ᆫ	=	=	6.0	6	. 444			3.45	1.55	.56	.075	.55			
Sand mold cast iron	Z	=	=	6.0	0	44			3.40	1.61	.43	.083	<u>\$</u>			
Rattled cast iron	Ω	1932	=	1.5	12	.250	2.94 0	0.64	3.58	1.64	\$\$\frac{\pi}{4}\$.074	.79			
Sand-coated cast iron	'퍽	=	=	1.5	12	.250	2.94	+20.	3.50	1.64	\$ ±8	.074	.70			
Special process cast	н	=	s	1.5	12	. 350			2.53	1.43	22	.077	.128			.51
Special process cast	Сų	=	=	1.5	12	.350			2.90	2.04	83	.060	.248			. 62
High-silicon cast iron	ם	1922	=	3.0	97				.72	13.44	.26	.123	1			
Low-alloy cast iron	Ω	1932	=	1.5	12	.250	3.00	•50	3.50	2.50	.70	-050	.400	0.30	0.15	
High-alloy cast iron	ㅂ	=	=	1.50	12	. 250			2.98	2.13 1.00	1.00			2,61	2,61 15.00	6.58



neutral and alkaline soils high in soluble salts, cast iron may corrode at a somewhat higher rate than rolled ferrous products because of graphitic corrosion. On the other hand, in well aerated soils low in soluble salts, cast iron is less severely attacked, according to these investigators, than are rolled materials. It would seem, therefore, that improvement in cast iron from the standpoint of corrosion resistance is largely a matter of producing castings resistant to graphitization, However, in those soil environments where alloying elements are able to exert their specific effects in reducing corrodibility, it would be reasonable to expect that the presence of alloying elements in cast iron would be at least as beneficial as in steel.

Although a large variety of special cast irons are available, relatively few have been included for study in the field tests. Cast irons of compositions other than those given in table 2 are in use for types of service which suggest that these irons might be successfully employed for underground service. For example, Dieffenbach²² has reported that a copper-molybdenum cast iron has shown no noticeable corrosion in more than two years' service as lock gate valves under conditions for which protective coatings were unsuitable. Cast irons containing small percentages of nickel, chromium, and molybdenum are understood to be used also for similar purposes.

III. COPPER AND COPPER ALLOYS

Copper and alloys high in copper are generally resistant to corrosion in soils. Although severe corrosion of copper has been observed, no actual failures have occurred in the Bureau of Standards soil corrosion tests. Like certain other metals, the resistance of copper to corrosion depends on the maintenance of a protective oxide film. Wherever this film cannot be maintained intact, as in alkali soils high in chlorides and carbonates, poorly drained organic soils, such as tidal marsh, peat, and muck, and in cinders, corrosion results. The specimens of copper and copper alloys under test are listed in table 3.

1. Copper

Tough-pitch copper (material C) normally contains from 0.03 to 0.05 percent oxygen or 0.27 to 0.45 percent cuprous oxide. By treatment with phosphorus even this small amount of oxygen may almost completely be removed, the resulting product having superior ductility and toughness (material A, 1932). Copper specimens with soldered fittings (material M) were included in the test in order to determine the extent of galvanic action at the point of contact of the copper with solder. Laboratory tests with circulating water have not shown evidence of galvanic corrosion on this type of fitting.



TABLE 3 .- COPPER AND COPPER ALLOYS

Bronze Bronze Aluminum bronze	Brass Muntz metal " " " Acception Muntz metal with arsenic	Red brass Admiralty metal Two and one leaded	pper oxidi pper pper fitti	Material
보면	88 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	र धम	E ZUDO	Identi- fication
1932 1926	1926	= ==	1932 1926 1926 1932	Year buried
pipe rod	ell sheet	= = =	pipe	Form
1.7	2 0 1 1 i	• •	in. 1.7 1.7 0.9	Width or diameter
12 12	12251	12 12	in.	Length
.141	2563		in.	Wall thick-
97.15 87.00	55 55 50 50 50 50 50 50 50 50 50 50 50 5	85.18 71.28	99.97 99.94 99.93	Cu
	380 50 50 50 50 50 50 50 50 50 50 50 50 50		53	Zn
1.00		1.30	2	Sn
	2.50	n 01	$\mathcal{E}_{\mathcal{E}}$	Pb
			Ž	Ni
3.50	.02 trace	.01 .02	<i>,</i> 20	म ೧
1.04	•	7 -07	2,	St.
			5	Mn
			018	P !
	• О О		5	As
9.50			8	Al

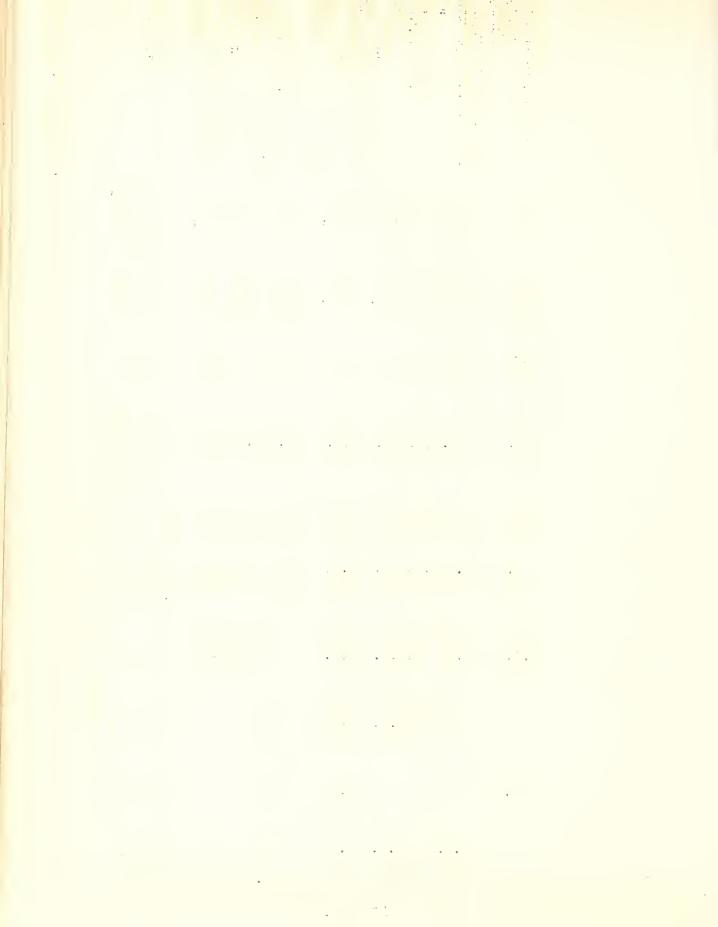
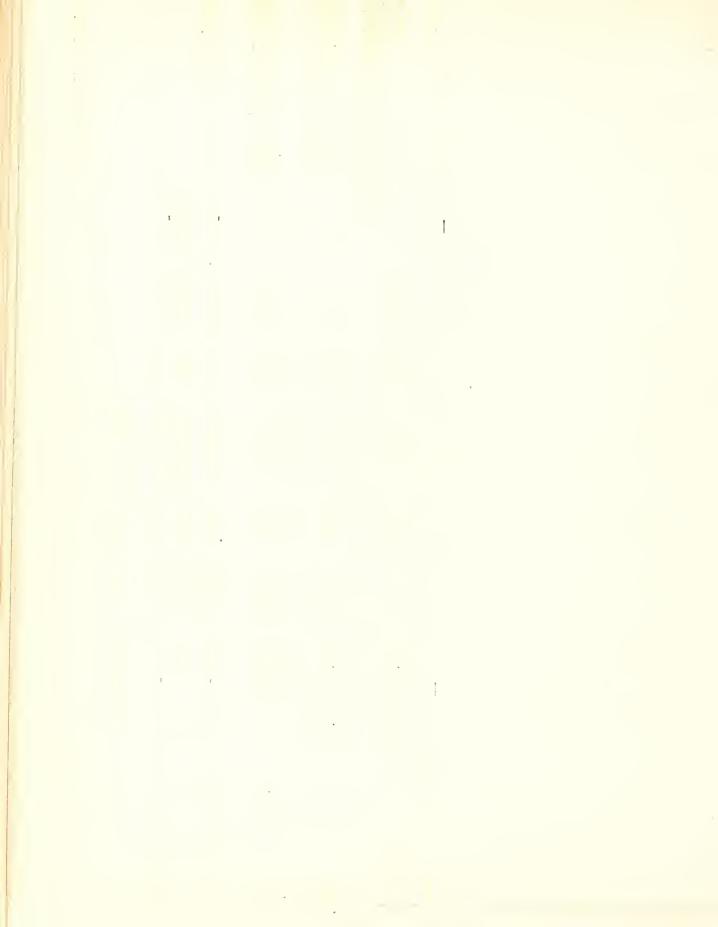


TABLE 3. - COPPER AND COPPER ALLOYS (continued)

	Identi- Year fication buried	Year buried	Form	Width or Wall diameter Length thick-	Length	Wall thick-	Ou	Zn	Sn	વવ	Ni	ĦО	S.	Mn	ਖ	AS	Al
Material				n.	in.	in.	29	%	3	%	200	53	69	8	<i>53</i>	%	8
Copper-silicon alloy Copper-silicon alloy	UZ	1932 pipe	pipe	1.7	12	·145	95.46 95.11		-14		080	11	3.19 3.19	1.05			
Copper-nickel alloy Copper-nickel alloy	Ç	=	=	1.7	12	.145	74.45 4.99	4.99		D 2	20.04			-52			
Copper-zinc-nickel alloy Copper-zinc-nickel alloy alloy	110 <u>y</u> A	1926	rod	0 4	12		47.00 40.50	40.50		2.50 10.00	10,00						



2. Brasses

Brasses containing high percentages of zinc are in general much less resistant to corrosion in soils than copper or high copper alloys. An exception, however, is to be noted in the case of marsh soils in which 60/40 brass (material L) corrodes at a considerably lower rate than copper. A probable explanation for this difference is the greater resistance of low-copper brasses to sulfides. The corrosion resistance of low-copper brasses to sulfur and sulfur compounds has been previously observed. 24

Corrosion of the higher zinc brasses under certain conditions results in dezincification. The addition, in small amounts, of several metals has been employed to inhibit this form of corrosion. Admiralty metal (material H), in which I percent of tin is substituted for an equal amount of zinc in 70/30 brass, appears to be effective in reducing dezincification under the conditions for which this alloy is generally used. Arsenic in fractional percentages is also said to be effective in repressing or inhibiting dezincification. Material B (1939) which contains 0.05 arsenic has been included in the test for comparison with the same material without arsenic (material L). Various investigators have found that antimony in amounts up to 0.10 percent is particularly effective in combating dezincification. Brasses of this type have not as yet been included in the soil-corrosion tests. Recently, the addition of phosphorus has been advocated as a means of preventing dezincification of Admiralty metal.

In general, soils which are corrosive to copper are relatively noncorrosive to lead. Hence it would be reasonable to expect that an alloy of copper containing lead as an addition element would be more resistant to corrosion than the same alloy low in lead. This has been confirmed in some degree by the results obtained in the soil-corrosion tests. Material K, known as two-and-one leaded brass, appears to corrode at a slightly slower rate than material J which contains a smaller quantity of lead. On this basis, a brass having a relatively high lead content might prove considerably more corrosion-resistant than a brass of the same copper content but low in lead.

3. Bronzes.

The term, bronze, which primarily connotes an alloy of copper and tin, is also applied to alloys of copper with aluminum, nickel and silicon. In an early test an aluminum bronze, containing 87 percent copper, 9.5 aluminum, and 3.5 percent iron (material N, 1926), corroded slightly slower than copper. The aluminum bronze, however, showed evidence of attack similar to dezincification in soils which were corrosive to copper. Other investigators have observed the same phenomenon.



A recently developed alloy having the composition 96 percent copper, 2.25 percent aluminum, and 1.75 percent tin is said to have proved very resistant to the corrosive action of locomotive fumes, salt fogs and spray and other corrosive conditions encountered along railroad rights-of-way. On this basis, some of the new nickel-aluminum bronzes might prove highly resistant to soil corrosion.

4. Copper-Silicon Alloys

Two copper-silicon alloys, materials N and D, containing 1.49 and 3.19 percent silicon, respectively, are represented in the field tests.

Copper-silicon alloys are said to be highly resistant to corrosion by sea water, corrosive natural and industrial waters a variety of salts, and to organic compounds and organic acids. 23

5. Copper-Nickel Alloys

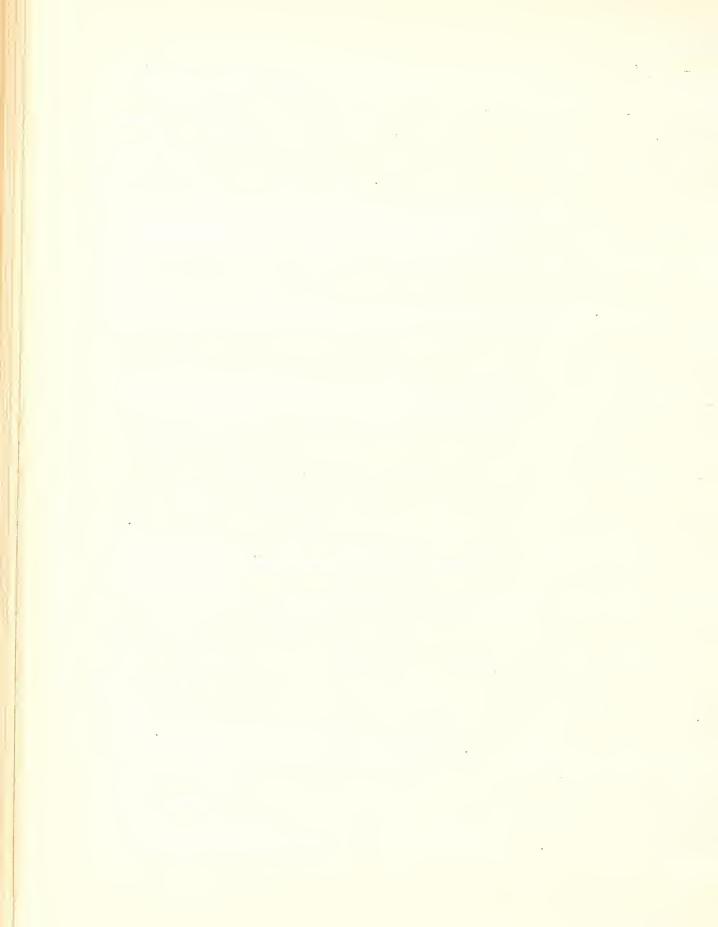
Specimens of a copper-nickel alloy containing 75 percent Cu, 20 percent Ni, and 5 percent Zn were buried at the test sites in 1932. The standard 70-30 copper-nickel alloy, in which the maximum zinc content is 1 percent has not as yet been included in the field tests. While the beneficial effect of zinc is open to question, there is no evidence that it has a deleterious effect. Copper-nickel alloys are used for condensers on ships and oil refineries and for piping salt water on board ship.

6. Metallic Coatings with Copper as the Base Metal.

Since copper is corroded appreciably in certain soil environments, the protection of copper by some type of metallic coating deserves consideration. Since tin is probably anodic to copper under all soil conditions, corrosion of tin would be expected to protect copper cathodically in the same manner that the corrosion of zinc protects the underlying steel in galvanized materials. Data on the thickness of the tin coating on the test specimens, which is of course a very important consideration, are not available at present.

Aside from the question of the minimum thickness required for protection, another possible cause of failure of tinned copper in soils is the formation of tin-copper alloys. These alloys have been shown under certain conditions to be more cathodic than copper.²⁹

In considering the effect of zinc on the corrosion resistance of brasses in soils, it was noted that both copper and



lead are apparently not appreciably corroded in the same environment. Advantage might be taken of this observation by using in corrosive soils copper coated with lead. In soils corrosive to lead but not to copper, no protection of the copper is needed. However, in soils corrosive to copper but relatively noncorrosive to lead, the copper would probably be protected cathodically. Lead-coated copper sheet is used as a roofing material. Copper can be coated with pure lead only with difficulty. A copper alloy containing a little tin gives a good bond with lead and greater freedom from pinholes. 24

IV. ZINC AND ZINC COATINGS

The chief use for zinc underground is in the form of coatings for iron and steel pipe. Results from an early study have shown that zinc coatings having a weight of 2.82 oz/sq ft of exposed area prevented the formation of pits in all but one of a group of 47 soils over a period of 10 years. In order to test further the protective action of zinc coatings in soils, this study was extended to include a second group of 15 corrosive soils. For this purpose specimens of galvanized iron pipe having a nominal weight of coating of 3 oz/sq ft were buried in 1937 in the special group of soils.

The protective action of zinc as a coating on iron and steel depends chiefly on the fact that it is anodic with respect to ferrous metals. However, as zinc is corroded relatively slowly under many soil conditions, it is difficult to determine whether the protective action is chiefly electrolytic or whether it results largely by shielding ferrous metals mechanically from the environment. In order to obtain experimental evidence on this point, specimens of bare iron pipe and two varieties of zinc were buried in 1937 in addition to the specimens of galvanized iron previously mentioned. The compositions of the zinc specimens are given in table 4.

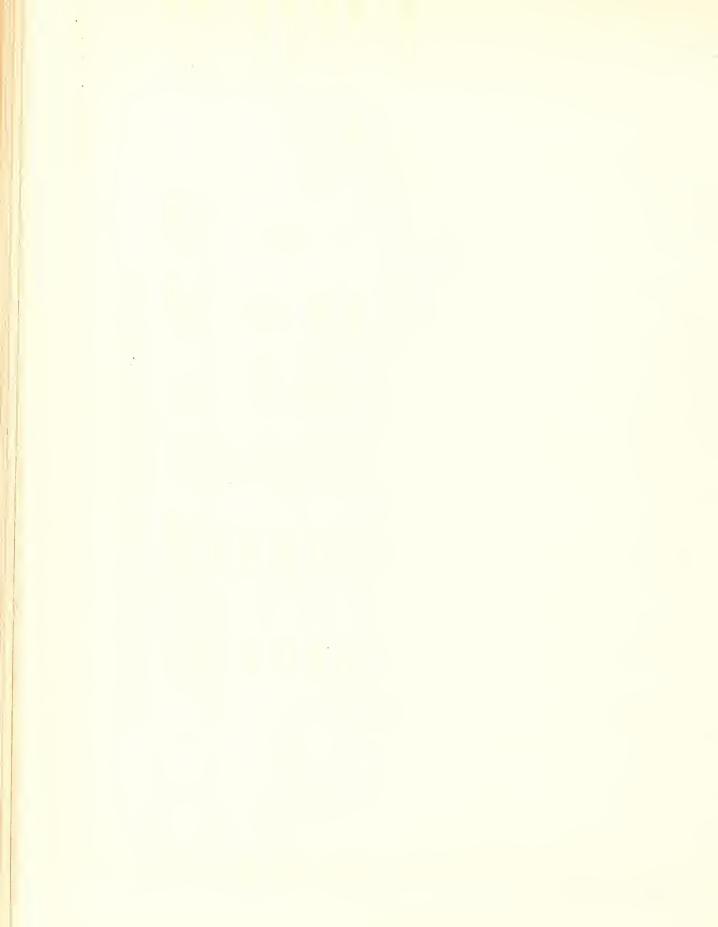
The behavior of zinc in electrolytic contact with ferrous metals in soils assumes special importance from the standpoint of the cathodic protection of pipe lines. In one type of installation the corrosion of zinc anodes distributed along a coated pipe line to which the anodes are connected at intervals by insulated wires provides the current required for protection of the line cathodically. In order to determine the conditions under which this type of protection is effective, plans are in progress for the burial at the 15 test sites of zinc-iron couples in various area ratios. These plans call for the use of zinc of different degrees of purity and for measurement at intervals of the electrode potentials and the galvanic current.



TARLT 4. - COMPOSITION OF ZING AND ZING GOATINGS

Material Rolled zinc	Identi- fication Z	vear buried	Form Plate	Length in. 12 6.81	width or diameter in. 2.3	Thickness of plate or coating in23	A1	7u	Fe .009	.0201	Pb 7d .095 .0038 .05 <.003	.003	38 03 <. 001	Zn		Al
				ıı.	in.	in.										
Rolled zinc	Z	1937	plate	12	2.3	.23			.009		.095	.00	38			
Die casting zinc	CZ	=	100 108	6.81		.125	4.00	1.05	.018	.020	05 K.003	3 (.00	4.00 1.05 .018 .0205 ~.003 <.001			
Galvanized iron steel	eel A	1924	pipe	17	3.0	.005										
Galvanized steel*	Н	1937	=	12	1.5	.00517			.07		.78			99	بآ	99,10 .008 nor

^{*}analysis of spelter



V. LEAD AND LEAD COATINGS

The compositions of the varieties of lead which are exposed at test sites are given in table 5. The samples of "chemical lead" contain 0.02 percent of bismuth, which is not present except as a trace in the standard grade of chemical lead. Lead of this composition is claimed to have certain advantages in mechanical properties over the A.S.T.M. standard "chemical" lead.

To improve the mechanical properties and to reduce corrosion of lead, it is commonly alloyed with small amounts of other metals, namely, antimony, tin, tellurium and calcium. Since these elements, as well as those normally present as impurities, such as bismuth, are in certain environments cathodic to lead, possibility of the development of local corrosion cells must be considered when lead is exposed to soils. In the corrosion tests extending over a lo-year period, lead containing 1 percent of antimony corroded at a slightly higher rate than commercial lead. Hiers, on the other hand, has reported that lead containing up to 3 percent of tin has shown best resistance on exposure to wet atmospheric conditions, water and some soils. Similarly, the introduction of approximately 0.05 percent of tellurium in commercially pure lead (material T) is said to result in a considerable increase in corrosion resistance.

Since lead in electrolytic contact with iron functions as a cathode, lead as a coating can not protect a ferrous metal electrolytically in the manner that zinc does. Hence, the protective value of a lead coating on steel is dependent entirely on continuity of the coating. In the case of sheets pinholes can be removed by rolling after the coating has been applied. Lead applied as a coating to copper would of course function anodically in an aqueous environment.

VI. ASBESTOS-CEMENT PIPE.

Specimens of asbestos-cement pressure pipe manufactured by different processes were buried at 15 test sites in 1939. Specimens of flue pipe were buried in 1932.

In the manufacture of asbestos-cement pipe a mixture of asbestos fiber and portland cement is built up by a continuous process on a revolving steel mandrel which is rotated under pressure until the required wall thickness is obtained. In at least one process of manufacture the pipe is cured in water for 7 days and then cured in air for a minimum of 21 days.

Since cement-asbestos pipe is nonmetallic, it is of course not subject to soil corrosion, tuberculation or electrolysis.

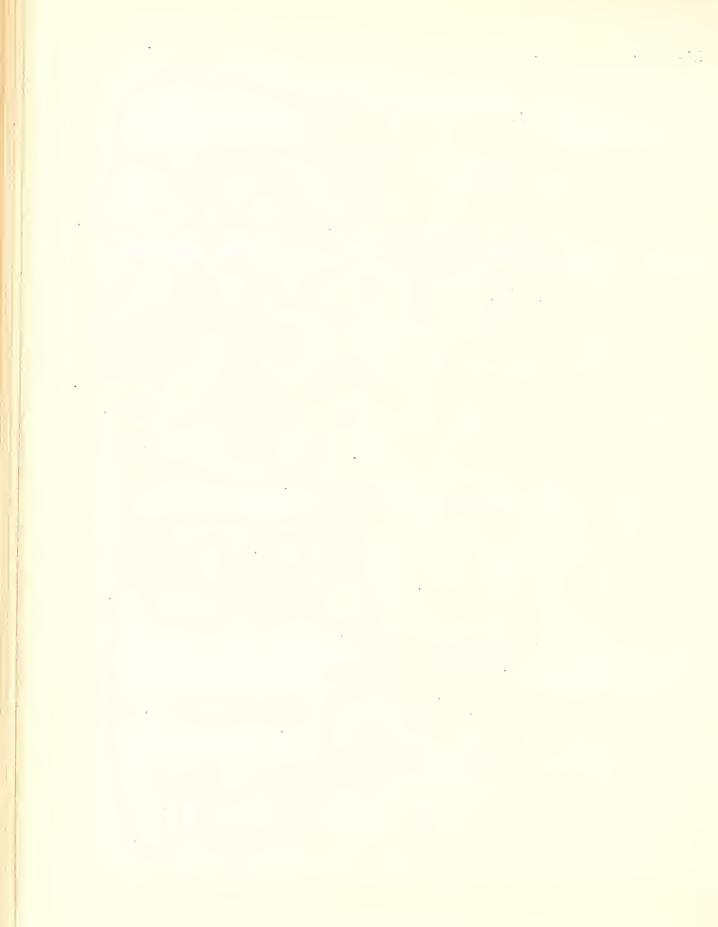
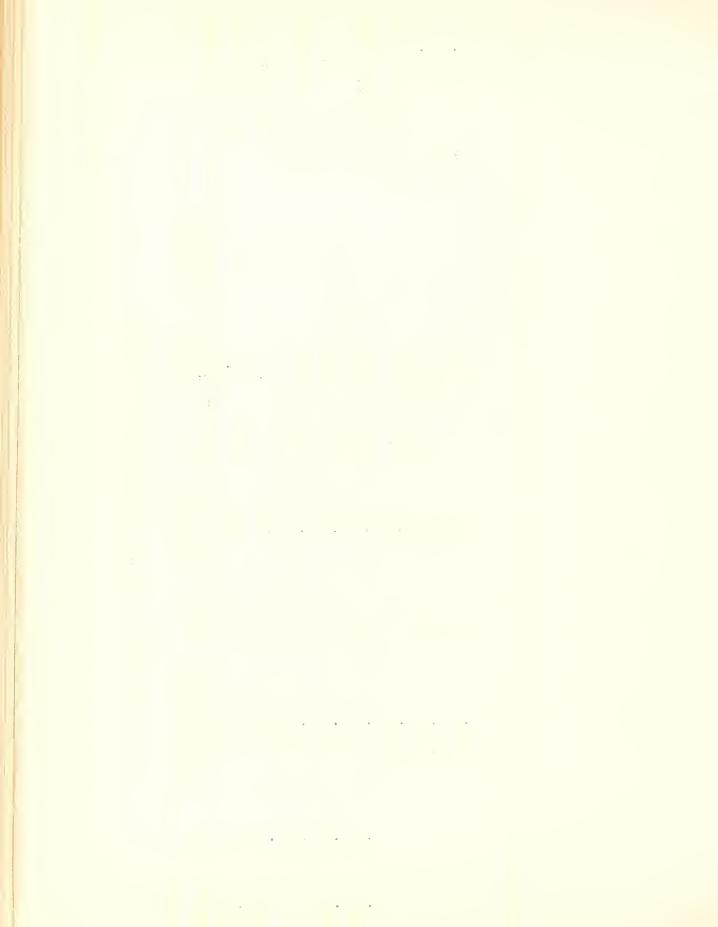


TABLE 5. -COMPOSITION OF LEAD AND LEAD COATINGS

# # # # # # # # # # # # # # # # # # #	\$ \$ \$ \$	Lead coated steel	Commercial lead		Antimonial lead	Tellurium lead	Chemical lead	Waterial
		901		ᅜ	*A	Н	0	Identi- fication
1932	1926	1924	1922	1937	1922	***	1937	Year buried
*** ****	=	pipe	sheet	pipe	sheet	=	pipe	Form
7 7	2.0	1.5	3.5	1.5	о 5	1.5	1.5	Width or diameter
13	17	0,	22	12	22	12	12	Length
.00297	.00196	.0025	,11	.177	.12	.177	in. .677	Wall or coat- ing thickness
			.013	.036	.062	.082	.056	Cu
			.013 .037	.016	=	none	002	81
				5-31	02 22	.0011	.0011	dS d
1.00				ц.	33	none	none	Sn
						.043		Te



Whether it is subject to deterioration under certain soil conditions will be indicated by examination of specimens after removal from the test sites.

VII. NONMETALLIC COATINGS

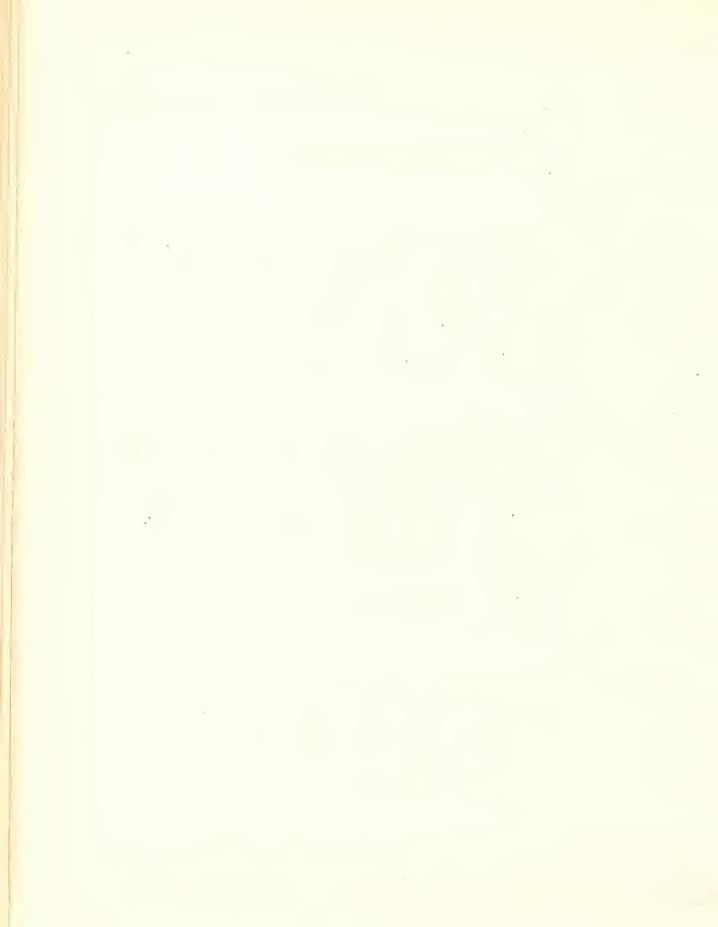
1. Organic Coatings.

Synthetic resins are used in the protection of steel structures such as locks and dams subject to submerged corrosion, and in the protection of freight and refrigerator cars which are subject to condensation of moisture containing dissolved sulfur compounds and to contact with brines and fruit acids. The resistance offered by synthetic resins to the rather severe conditions mentioned suggested the possible use of those materials in the protection of metal underground. The important classes of resins or plastics proposed for use as protective coatings on metals will be described briefly. However, not all of the classes to be mentioned are represented as yet by specimens in the field tests.

Phenolic Aldehyde Resins. The basic materials in the manufacture of this group of resins are phenol or cresol and formaldehyde. One type of coating included in the field tests consists of several coats of different resins with intermediate baking. In another type two coats of phenolic resin in which aluminum powder had been incorporated were applied to the primed surface, each coat being air-dried. A third type consists of two layers of asbestos tape impregnated with phenolic resin. Phenolic coatings are characterized by durability under conditions of exposure in which resistance to high humidity, water, and strong chemical reagents is necessary. The film has been described as being smooth, glossy, non-porous, hard and tough enough to withstand distortion produced in railway tank cars in service.

Hydroxy-carboxylic Resins. The hydroxy-carboxylic type of resin includes a wide variety of materials produced by the esterification of polybasic acids with polyhydric alcohols. They are often called alkyd resins (from alkyl-acid). Their principal use is as the resinous constituent of varnishes and lacquers. These finishes are said to be characterized by good durability out of doors, excellent flexibility, tenacious adhesion, and good electrical insulating properties. Coatings of this type are not at present under test.

Vinyl Resins. - Vinyl resins made by the polymerization of organic compounds having the vinyl group CH2=CH-. Dissolved in suitable solvent mixtures, these resins form lacquers which are claimed to be resistant to water, acids, alkalies, oxidizing agents and corroding materials in general. A coating consisting



of polyvinyl chloride is included in the field tests. Vinyl resin coatings are used in the chemical and electrochemical industries, as for example, as a lining material in chromium plating baths. A resin composed of a mixture of vinyl chloride and acetate is considered to have exceptional merit as a protective coating, 35 but this type of coating has not yet been included in the field tests.

Acrylate Resins. - Acrylate resins are polymers of the esters of acrylic acid. This group includes the well-known methacrylate resins which are finding application as protective coatings. The polymeric ester coatings may be applied either as a solution in a solvent or in the molten state by extrusion. High resistance to various chemicals and water and to other desirable physical properties are claimed for them. Coatings of this type are not under test at present.

Resins Derived from Rubber. - Chlorinated rubber is usually made by passing chlorine into a solution of rubber in chloroform, benzene or other solvent. The most important application of coatings of chlorinated rubber is in preventing corrosion of industrial equipment. These coatings are said to be characterized by unusual resistance to acids and alkalies. Specimens coated with chlorinated rubber are under test.

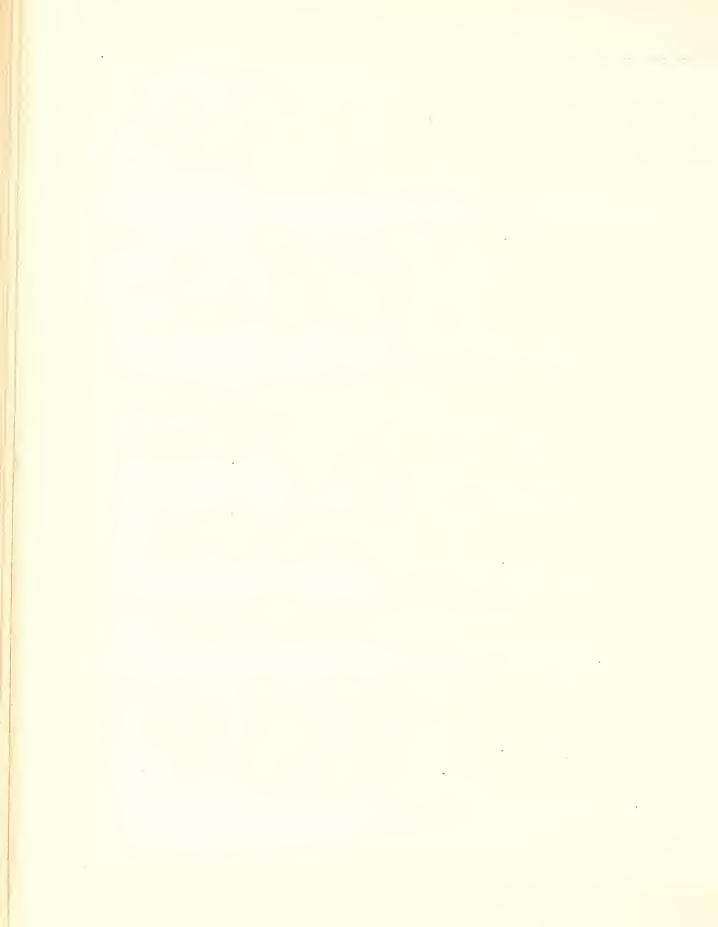
Another type of coating derived from rubber, which is included in the field tests, is made by reaction of rubber and chlorostannic acid, H₂SnCl₆, which gives a chloro derivative of isomerized rubber. It is considered to have many potential applications as a protective coating.

Synthetic Rubber. - In addition to the synthetic resin coatings which have been described, coatings composed of several varieties of hard rubber and a variety of natural resins are under test.

The particular synthetic rubber included both as a material and as a protective coating in the field tests is made from reaction of various dihalogenated organic compounds with alkaline polysulfides. The product is cured at an elevated temperature in a manner similar to the vulcanization of rubber, a rubberlike material being formed. Among its other applications, this material is used as a protective sheathing for electric cables.

2. <u>Vitreous Enamel.</u>

Vitreous enamel consists of a mixture of grit, clay, borax, feldspar, and water which is usually sprayed on the pickled or sand-blasted metal surface. The coating is then dried and heated

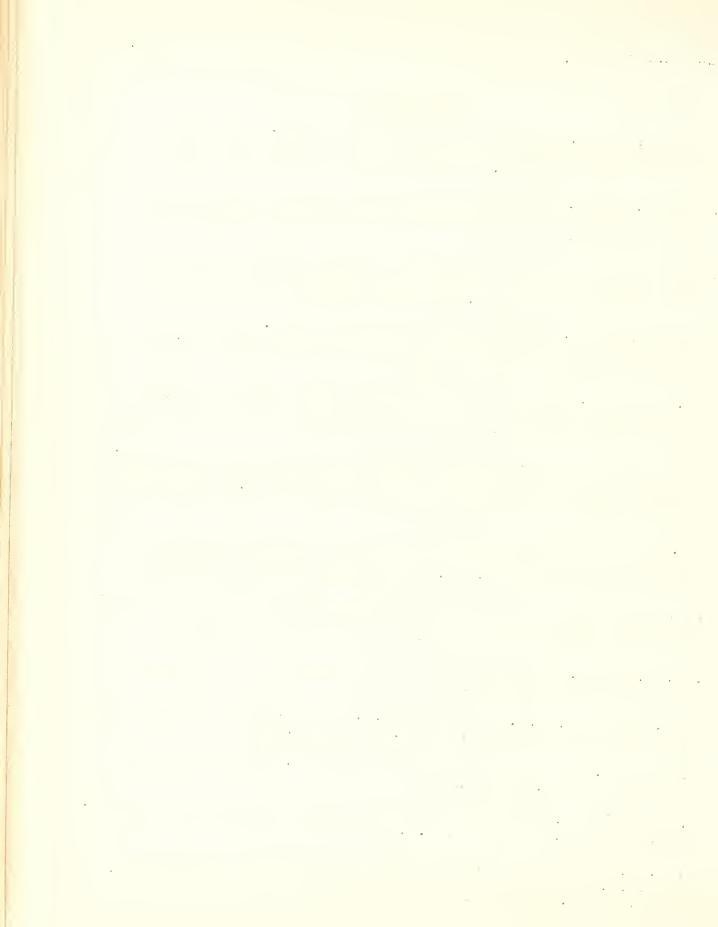


until the material is fused. Although coatings of this type submitted foff the field tests contained pinholes before burial, the specimens after five years' exposure showed no definite evidence of rust in any of the soils to which they were exposed, nor was there evidence of pitting except where the coating had been injured in handling.

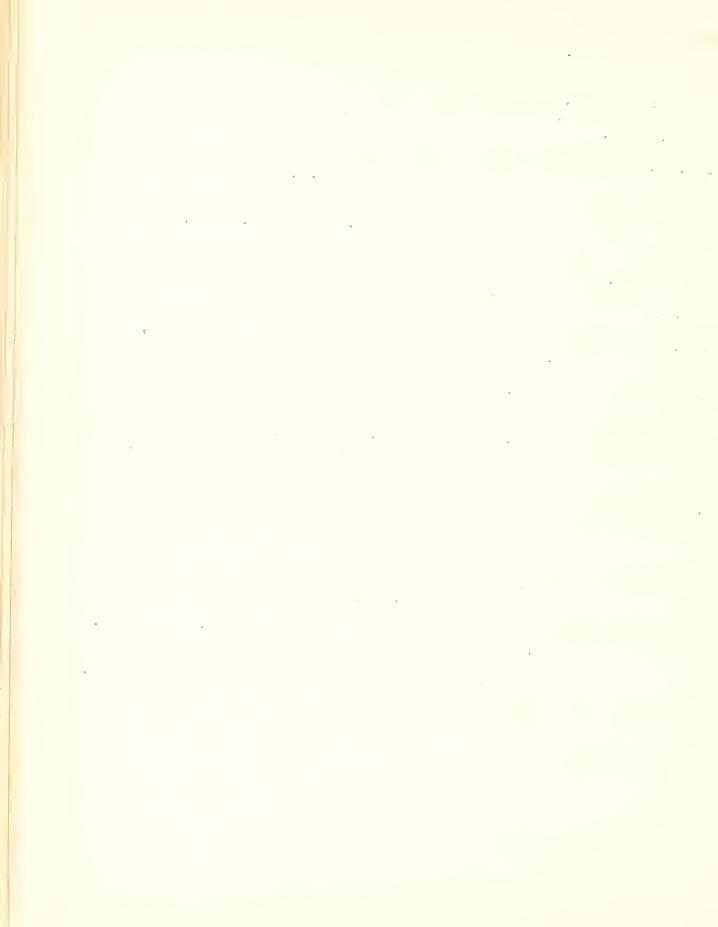


REFERENCES

- 1. Kirk H. Logan. Soil-corrosion studies, 1937. Corrosion-resistant materials and special tests. J. Research NBS 23, 515 (1939) RP1250.
- 2. Kirk H. Logan. Soil-corrosion studies, 1934. Bituminous coatings for underground service. J. Research NBS 19, 695 (1937) RP1058.
- 3. Kirk H. Logan and Scott P. Ewing. Soil-corrosion studies, 1934. Field tests of nonbituminous coatings for underground use. J. Research NBS 18, 361 (1937) RP982.
- 4. Kirk H. Logan. Soil-corrosion studies, 1934. Rates of loss of weight and penetration of nonferrous materials. J. Research NBS 17, 781 (1936) RP945.
- 5. K. H. Logan. Soil-corrosion studies, 1934. Rates of loss of weight and pitting of ferrous specimens. J. Research NBS 16, 432 (1936) RPSS3.
- 6. K. H. Logan and R. H. Taylor. Soil-corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and nonferrous specimens and metallic protective coatings. J. Research NBS 12, 120 (1934).
- 7. K. H. Logan. Soil corrosion studies. Nonferrous metals and alloys, metallic coatings, and specially prepared ferrous pipes removed in 1930. J. Research NBS 7, 585 (1931) RP359.
- 8. K. H. Logan and V. A. Grodsky. Soil-corrosion studies, 1930.
 Rates of corrosion and pitting of bare ferrous specimens.
 J. Research NBS 7, 1 (1931).
- 9. K. H. Logan. Soil-corrosion studies, 1927-28. J. Research NBS 3, 275 (1929) RP95.
- 10. K. H. Logan, S.P. Ewing, and C.D.Yeomans. Bureau of Standards soil corrosion studies. Tech. Paper 368, 1928.
- 11. James P. Roe. The Roe puddling machine. Yearbook Am. Iron and Steel Inst. (1925).
- 12. Scott Ewing. Soil corrosion and pipe line protection. 1938. Am. Gas Assn., New York, N.Y.
- 13. V. V. Kendall and E. S. Taylerson. A critical study of the A.S.T.M. data on uncoated commercial iron and steel sheets. Proc. A.S.T.M. 29, Pt. 2, 204 (1929).



- 14. H. W. Gillett. Phosphorus as an alloying element in steel 1. Metals and Alloys 6, 280, 1935; 2. Metals and Alloys 6, 307, 1935.
- 15. N. B. Pilling and W. A. Wesley, Atmospheric durability of steels containing nickel and copper. A.S.T.M. Preprint 1940,
- 16. L. W. Vollmer and Blaine B. Westcott. Discussion of new ferrous alloys for the oil industry. Ind. Eng. Chem. 28, 1379 (1936).
- 17. Robert J. McKay and Robert Worthington. Corrosion resistance of metals and alloys. Reinhold Publishing Corp., New York, N.Y. (1936).
- 18. J. H. Critchett. Stainless steels and irons. Mech. Eng. 58, 823 (1936).
- 19. Walter M. Mitchell. "18 and 8" and related stainless steels. IV. Metals and Alloys, <u>11</u>, 118 (1940).
- 20. W. A. Wesley, H. R. Copson and F. L. LaQue. Some consequences of graphitic corrosion of cast iron. Metals and Alloys 7, 325 (1936).
- 21. C. K. Donoho and J. T. MacKenzie. Soil corrosion of cast iron in the Bureau of Standards tests on ferrous metals. Presented at National Bureau of Standards Soil Corrosion Conference 1937 (unpublished).
- 22. Ferd Dieffenbach. Corrosion and erosion in river and harbor structures. Ind. & Eng. Chem. 30, 1014 (1938).
- 23. D. K. Crampton. Wrought copper-base alloys. Ind. Eng. Chem. 28, 1397 (1936).
- 24. Metals Handbook. Am. Soc. for Metals, Cleveland, Ohio (1939).
- 25. C. A. Gleason. Phosphorized Admiralty condenser tubes. Power Plant Eng. 44, 96 (1940).
- 26. R. A. Wilkins. Copper and copper-base alloys. Mech. Eng. 58, 809 (1936).
- 27. W. H. Bassett Jr. Discussion. Ind. Eng. Chem. 28, 1400 (1936).
- 28. Navy Department Specification 44T40, March 1940. Bureau of Supplies and Accounts, Navy Department, Washington, D.C.



@

- 29. P. D. Merica. Structure of the coating on tinned sheet copper in relation to a specific cause of corrosion. B.S.Tech.Paper 90 (1917).
- 30. George I. Rhodes. Cathodic protection or electric drainage of bare pipe lines. Proc. Natural Gas Dept., Am. Gas Assn., New York, N.Y. (1935).
- 31. George O. Hiers. Corrosion-resistant lead equipment. Mech. Eng. 58, 793 (1936).
- 32. George O. Hiers. New metals and alloys from lead, tin, zinc, and antimony. Ind. & Eng. Chem. 28, 1406 (1936).
- 33. Archie J. Weith. Plastics fortify against corrosion. Ind. Eng. Chem. Ind. Ed. 29, 380 (1937).
- 34. Gordon M. Kline. The classification and chemical genetics of organic plastics. Trans. Electrochem. Soc. 74, 23 (1936).
- 35. S. D. Douglas. Properties and applications of some of the vinyl resins. Trans. Electrochem. Soc. 74, 83 (1938).
- 36. H. R. Dittmar, D. E. Strain, and R. Grice Kennelly. The methacrylic ester resins. Trans. Electrochem. Soc. 74, 181 (1938).