The Corrosion of Certain Metals by Carbon Tetrachloride[1]

By F. H. Rhodes and J. T. Carty

CORNELL UNIVERSITY, ITHACA, N. Y.

Of the various metals tested, nickel is the most resistant to cold carbon tetrachloride, either wet or dry, and to the dry vapor of carbon tetrachloride; and tin is the most resistant to the action of the wet vapor. Some interesting phenomena in connection with the corrosion of aluminium and brass are observed.

MOST of the work on the corrosion of metals has been concerned primarily with corrosion by moist air, by water, or by aqueous solutions of electrolytes, and but comparatively little attention has been paid to the action of nonaqueous liquids on metals. That this latter phase of the general problem of corrosion has attracted so little attention is quite natural, since most of the common nonaqueous liquids are without pronounced action on most metals under ordinary conditions. Carbon tetrachloride, however, has been found to attack certain metals to a considerable extent, so that the study of the action of this liquid on metals might be expected to afford interesting information on the general subject of corrosion. Furthermore, such an investigation should furnish data that would be of value in the selection of materials for use in the construction of containers for this liquid and of apparatus used in extraction processes in which carbon tetrachloride is the solvent. Such data should also bear upon the suggested application of carbon tetrachloride as a liquid for use in transformers and electrical switches.

Previous Work

Some work on the action of carbon tetrachloride on metals has already been done, but unfortunately the published data are rather fragmentary and inconclusive and to some extent contradictory. Crocker[2] discusses the use of carbon tetrachloride as a solvent in commercial extraction processes and points out that this solvent may corrode the apparatus used in the extraction plant. He makes the rather confusing statement that—

> Steel, cast iron, and wrought iron are only slightly affected by carbon tetrachloride; but the presence of moisture causes decomposition, especially where the solution is in rapid circulation, and if, with rapid circulation there is an increase of heat, the decomposition takes the form of oxide of iron and a ferric chloride. This is quite marked if the moisture is excessive; but to exclude all moisture is practically impossible.* * * Lead, lead-antimony alloys, and tin resist carbon tetrachloride under varying conditions. Copper and its alloys and bronzes, German silver, and gun metal stand the action of carbon tetrachloride, but if the temperature is high the action is marked. Zinc and aluminium will stand fairly well, nickel about the same as copper; but the presence of moisture, especially if at a high temperature, is most deteriorating to these metals.

Crocker gives no more detailed data and no experimental results to support his statements.

Zappi[3] found that aluminium is uncorroded even after 4 months' exposure to carbon tetrachloride at room temperature, but that when heated with carbon tetrachloride in a closed tube to a temperature of 100° to 120° C. aluminium reacts rapidly to form aluminium chloride, hexachloroethane, and other higher chlorides of carbon and a resinous product of undetermined composition. Iron powder did not react in the cold and was only slightly attacked in the hot.

Sastry[4] reports that carbon tetrachloride vapor at its boiling point showed no action on steel, wrought iron, nickel, or aluminium, and only very slight action on copper and lead. As the period of exposure was only 10 hours the results are hardly conclusive.

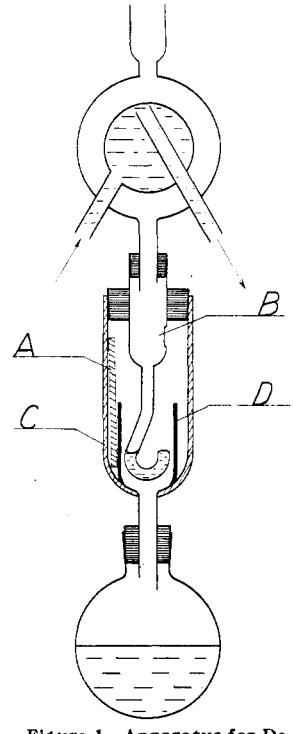

Figure 1—Apparatus for Determining Corrosion by Carbon Tetrachloride Vapor

Scope of Present Work

In the present investigation we have studied the action, upon a number of metals and alloys, of (*a*) dry carbon tetrachloride at room temperature, (*b*) carbon tetrachloride and water at room temperature, (*c*) the vapor of dry carbon tetrachloride at its boiling point (76° to 77° C.), and (*d*) the wet vapor from a boiling mixture of water and carbon tetrachloride at about 67° C.

Materials Used

The carbon tetrachloride was prepared from presumably pure carbon tetrachloride by agitating first with a 5 per cent

[1] Received May 27, 1925.

[2] *Electrochem. Met. Ind.*, **5**, 259 (1907).

[3] *Ann. soc. quim. Argentina*, **2**, 217 (1914); *C. A.*, **9**, 3001 (1915).

[4] *J. Soc. Chem. (London)*, **35**, 94 (1916).

Table I—Analyses of Metals and Alloys

METALS	Cu	Zn	Sn	Mn	Ni	Pb	Fe	S	Si	P	C
Steel	...	...	...	0.912	...	...	...	...	0.2546	...	0.114
Aluminium	...	...	...	0.00	...	...	0.496	...	0.80	...	...
Copper	99.52	...	...	...	...	...	...	...	...	...	...
"Ambrac"	74.21	5.60	...	...	20.05	...	...	...	...	...	...
Monel	29.98	...	...	0.32	66.75	...	1.61	0.022	0.20	...	0.14
Phosphor bronze	95.33	...	4.47	...	...	...	...	...	...	0.18	...
Manganese bronze	59.20	39.82	0.49	0.09	...	0.26	...	...	...	...	...
Tobin bronze	56.49	42.64	0.45	...	...	Trace	0.42	...	...	...	...
Brass No. 1	90.08	9.92[a]	...	...	...	...	...	...	...	...	...
Brass No. 2	78.90	21.10[a]	...	...	...	...	...	...	...	...	...
Brass No. 3	70.27	29.73[a]	...	...	...	...	...	...	...	...	...
Brass No. 4	59.73	40.27[a]	...	...	...	...	...	...	...	...	...
Nickel	0.250	...	...	0.066	...	...	0.59	0.019	0.210	...	0.0798
Tin	...	...	99+	...	...	...	...	...	...	...	...
Lead	...	...	...	...	...	99+	...	...	...	...	...

[a] By difference.

solution of silver nitrate, then with a 2 per cent solution of sodium hydroxide, and finally with distilled water. The washed material was dried over anhydrous sodium sulfate and redistilled fractionally, the first and last fractions being discarded and only the middle fraction that passed over at constant boiling point being collected for use. The metals used in the corrosion experiments were commercial sheet aluminium, block tin, chemical sheet lead, copper, malleable nickel, mild steel, monel metal, phosphor bronze, Tobin bronze, manganese bronze, "Ambrac" (copper-nickel-zinc alloy), and various brasses ranging from 60 per cent copper to 90 per cent copper.[5] The block tin and the sheet lead were not analyzed. The analyses of the other metals and alloys are shown in Table I.

Procedure

In the experiments made at room temperature the test pieces were simply immersed in carbon tetrachloride or in a mixture of carbon tetrachloride and water and allowed to stand.

In the tests made with carbon tetrachloride vapor the apparatus used in Figure 1 was used. A glass tube, *C*, approximately 5 cm. in diameter was connected with a reflux condenser and with the flask containing the boiling carbon tetrachloride or mixture of tetrachloride and water. A return tube, *B*, with a vapor inlet near the top and with a trapped outlet for the condensed liquid at the bottom was attached to the end of the reflux condenser. The bottom of

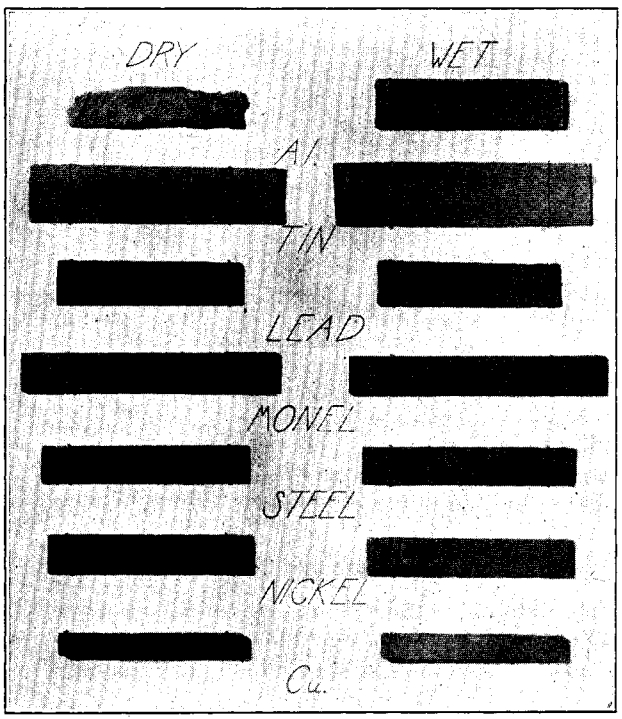

Figure 2—Appearance of Test Pieces after Exposure to Wet and Dry Vapors

the return tube was surrounded by a guard tube, *D*, so that the refluxed liquid from the condenser did not come in direct contact with the metal test piece, *A*, in the outer tube. The entire tube was surrounded with a layer of asbestos insulation to minimize the condensation within the tube. The period of exposure in these tests was 100 hours.

[5] The brasses, bronzes, and "Ambrac" metal were obtained through the courtesy of the American Brass Company division of the Anaconda Copper Co.; the malleable nickel through the courtesy of the International Nickel Company.

Results

Of the metals exposed to the action of the dry liquid carbon tetrachloride at room temperature the only one to show appreciable attack was steel, which became covered with a uniformly thin, adherent, brown film. On each of the test pieces of copper, bronze, and brass a very thin, iridescent, brownish film was formed, but no appreciable corrosion or pitting took place. All the other metals and alloys remained bright and unattacked, even after 6 months' exposure.

The results obtained in the tests made with liquid carbon tetrachloride and water at room temperature are presented in Table II. The period of exposure in these tests was approximately 6 months.

Table II—Corrosion by Carbon Tetrachloride and Water at Room Temperature

Metal	Loss in weight[a] Mg./sq. dm./24 hours	Remarks
Aluminium	7.715	Test piece covered with white crust interspersed with black resinous deposit and gelatinous masses of hydrated Al_2O_3
Tin	0.738	Yellow powdery deposit, marked pitting at boundary between CCl_4 and water
Lead	0.147	Slight white film
Monel	0.229	Rather marked pitting, some parts of surface not attacked
Steel	6.640	Marked corrosion and slight pitting, metal covered with heavy deposit of Fe_2O_3 and Fe_3O_4
Nickel	0.028	No corrosion, very faint blue or yellow spots on surface of bright metal
Copper	0.774	Dark purple film, few localized green deposits
Phosphor bronze	3.48	Rather marked superficial corrosion, metal covered with greenish crust
Manganese bronze	1.187	Brown film
Tobin bronze	0.340	Brown film, with localized green patches
Brass, 60–40	0.342	Slight uniform brown film
Brass, 70–30	1.07	Brown film with green spots
Brass, 80–20	1.69	Uniform brown film
Brass, 90–10	0.618	Iridescent purple film with few green spots
"Ambrac"	0.229	Metal covered with grayish green scale and slightly pitted

[a] Before weighing the test pieces after corrosion they were scrubbed thoroughly to remove any adhering deposit of oxide or basic salt.

In every case the water layer acquired an acid reaction although with the test made with the metallic nickel the acidity was very faint. With the 60–40, 70–30, and 80–20 brasses the aqueous layer assumed a distinct green color. Inasmuch as dry carbon tetrachloride has no appreciable effect upon the metals, it is probable that the corrosive action of wet tetrachloride is due largely to the hydrochloric acid formed by the interaction of carbon tetrachloride and water. The observed differences in the rates of corrosion of the various metals may be due either to differences in susceptibility to the action of hydrochloric acid under the conditions of the experiment or to differences in the effects of the metals in promoting the decomposition of carbon tetrachloride by water.

Nickel, lead, "Ambrac," and the various brasses and bronzes were not affected by the vapor of dry carbon tetrachloride. Copper became coated with a very thin black film but remained otherwise unattacked. An irregular white film was formed on the surface of the tin, and on the monel test piece there appeared an irregular greenish film, but in neither case was there marked corrosion or pitting of the metal. Steel was more or less uniformly attacked, with the formation of an adherent brown deposit. Aluminium reacted so vigorously with the vapor of carbon tetrachloride that in some cases the test piece was completely dissolved.

Table III—Corrosion by Carbon Tetrachloride Vapor and Water Vapor at the Mutual Boiling Point

METAL	Loss in weight Mg./sq. dm./24 hours	REMARKS
Aluminium	307.0	Test piece etched irregularly and covered with gelatinous masses of hydrated Al_2O_3
Tin	5.62	Slight yellow film
Lead	15.08	Black film, slight pitting
Monel	94.20	Slight irregular etching
Steel	298.5	Marked corrosion, test piece covered with layer of Fe_2O_3 and Fe_3O_4, some pitting
Nickel	127.0	Slight black deposit, some pitting
Copper	17.6	Brown film, slight blue deposit
Phosphor bronze	161.0	Irregular green crust
Manganese bronze	78.7	Irregular black film
Tobin bronze	70.4	Slight brown film, faint white deposit
Brass, 60–40	4230.0	Red film (see below)
Brass, 70–30	1957.0	Red film, slight green deposit
Brass, 80–20	682.0	Purple film, irregular green deposit
Brass, 90–10	33.3	Green deposit
"Ambrac"	174.0	Heavy green scale

Table III shows the results obtained when the mixed vapors of carbon tetrachloride and water were allowed to act on the metals. The appearance of the test pieces exposed to the wet and dry vapors is shown in Figures 2 and 3. The reaction of aluminium with the vapor of carbon tetrachloride is very interesting. When exposed to the dry vapor metallic

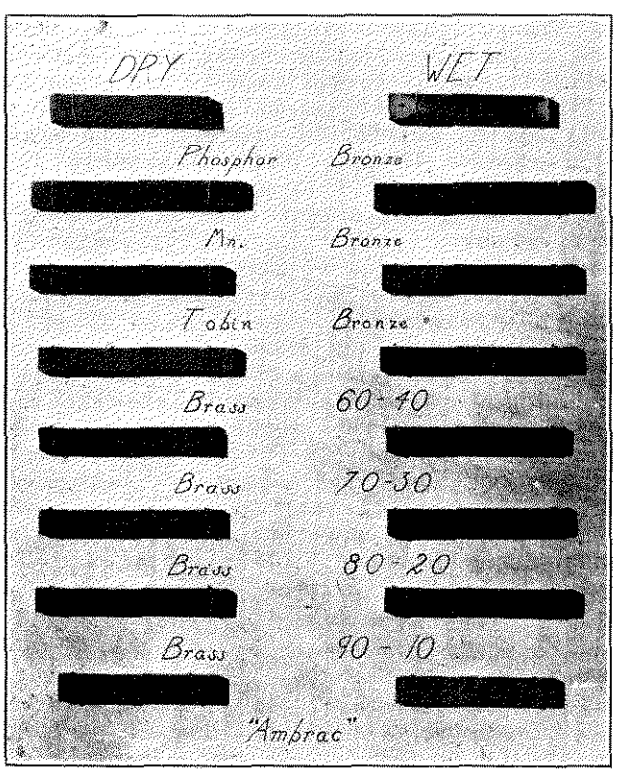

Figure 3—Appearance of Test Pieces after Exposure to Wet and Dry Vapors

aluminium is rapidly attacked and disintegrated with the formation of a dark gray powder. This powder has a very penetrating, resinous odor and "hisses" when thrown into water. Upon examination it was found to consist of a mixture of aluminium chloride and hexachloroethane, together with small amounts of some black substance and some resinous compound. Additional quantities of hexachloroethane were recovered from the refluxed liquid in the distillation flask in which the carbon tetrachloride vapor was generated. The principal reaction between aluminium and carbon tetrachloride may therefore be represented by the equation

$$2Al + 6CCl_4 = 2AlCl_3 + 3C_2Cl_6$$

None of the other metals that were tested appear to react directly with the carbon tetrachloride to form hexachloroethane.

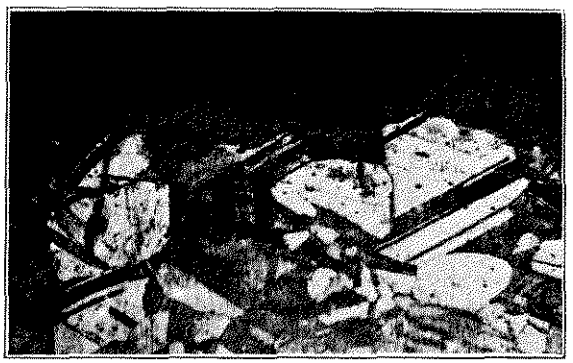

Figure 4—Photomicrograph across Interface between Attacked and Unattacked Portions of 60–40 Brass

In the presence of water vapor aluminium is much less readily attacked by the carbon tetrachloride. The water appears to react with the metallic aluminium or with the aluminium chloride to give aluminium oxide, which forms a protective coating on the surface of the metal and prevents the rapid action of the tetrachloride.

Some interesting phenomena were observed in connection with the corrosion of brasses by the wet vapor of carbon tetrachloride. In all the brasses the zinc was attacked more rapidly than the copper, so that the test pieces soon became covered with a red layer of copper-rich alloy. In brasses rich in copper the action was confined to a thin film at the surface of the metal, but with the 60–40 brass a layer of relatively pure copper about 1.6 mm. ($^1/_{16}$ inch) thick was formed during the 100 hours' exposure. This outer layer was of almost uniform thickness and adhered firmly to the inner core of unattacked brass. Upon analysis it was found to contain 92 per cent of copper, although the brass from which it was derived contained but 60 per cent. Metallographic examination showed that it was not simply a spongy mass of copper left after dissolving the zinc out of the original crystals of the brass, but that it consisted of a dense mass of fine columnar crystals of copper with their axes normal to the original surface of the test piece. The line of demarcation between the brass and the copper did not follow the boundaries of the original crystals of the brass but cut sharply through these crystals. It appears that in the formation of this outer layer the copper was actually dissolved and redeposited. Figure 4 is a photomicrograph taken across the boundary face between brass and copper.

Benzol Poisoning

Progress reports on this subject issued by the Sub-committee on Benzol of the Committee on Industrial Poisons, National Safety Council, Chemical Section, emphasize the importance of this work. Investigations disclosed the fact that fifteen deaths and eighty-three more or less serious illnesses have occurred as a result of industrial benzol poisoning during the last few years. It was reported that out of a group of eighty-four workers exposed more or less continuously to benzol fumes in varying concentration, thirteen of these, or 15 per cent, showed a white blood cell count so low as to be strikingly suggestive of chronic benzol poisoning.