

**Physics.** — *Research on thin layers of tin and other metals. II. The corrosion of metals by technical insulating oils.* By P. J. HARINGHUIZEN and D. A. WAS. (Communicated by Prof. L. S. ORNSTEIN).

(Communicated at the meeting of December 21, 1935).

*Summary.*

The corrosion of tin, copper and lead has been investigated by an optical method, based on the increase of light transmission of thin metal layers due to the corrosion. The relation between the light transmission and the thickness of the layer has been determined for the three metals.

From the experiments it is concluded that the metals build up a protecting film of reaction products on their surfaces. In the case of copper this film is continuously destroyed. Tin and lead have a durate resistant film. Here the corrosion is controlled by the diffusion through that film.

Experiments with different oils showed that the velocity of corrosion is not related to the concentration of the acids formed by the deterioration of the oils.

The results have been expressed by an experimental formula for which an attempt is made to provide a theoretical basis.

*Introduction.*

The corrosion by oils being a problem of technical importance, it seemed interesting to us to investigate the process of corrosion. We have followed the corrosion as a function of time by an optical method. The principle of the method is due to Dr. W. R. VAN WIJK <sup>1)</sup>, who used it for the qualitative testing of different gas oils as regards their corroding action on a given metal. Metal layers, obtained by high vacuum evaporation of a thickness so that they show a measurable transmission for light, were corroded; the increase of the transmission with the time makes it possible to draw conclusions about the process.

In order to obtain quantitative results, knowledge of the relation between the transmission and the thickness of the layers is necessary. For that reason, we have measured this relation in the case of tin, copper and lead, the metals for which we have investigated the corrosion by technical insulating oils at several temperatures.

From *X*-ray diagrams of the thin layers used it appeared that the metal layers have the same crystalline structure as the normal metal. The aggregated crystals however, are very small, what is due to the way in which the layers have been prepared. The fact that the *X*-ray

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<sup>1)</sup> W. R. VAN WIJK, Journ. of Industrial and Engineering Chemistry, 7, 48 (1935).

diagrams consist of rings instead of points, indicates that the crystals have extremely small dimensions.

For tin the dimensions of the microcrystals are so small that a sufficient intensity of rings can only be obtained on very thick tin layers which do not possess any light transmission. An analogous result has been found by PRINS <sup>1)</sup>, who studied the structure of evaporated metal layers by the electron diffraction method. He interpreted this fact by supposing that the white (tetragonal) tin crystals are formed from the gray (cubic) crystals, which are very small. In accordance with OSTWALD'S principle, this metastable modification will be precipitated from the vapour.

The homogeneity and the smoothness of the surfaces are great advantages of these evaporated layers for the study of heterogeneous reactions.

### § 1. Description of the method.

The metal layers were evaporated in high vacuum ( $< 10^{-6}$  mm) on plates of mirror glass, by heating a tungsten spiral, which contained the metal, with an electric current. The dimensions of the glass plates were  $2.5 \times 3.6$  cm; only one half of the area was covered with metal (see fig. 1). The cleanness of the glass was found to be very

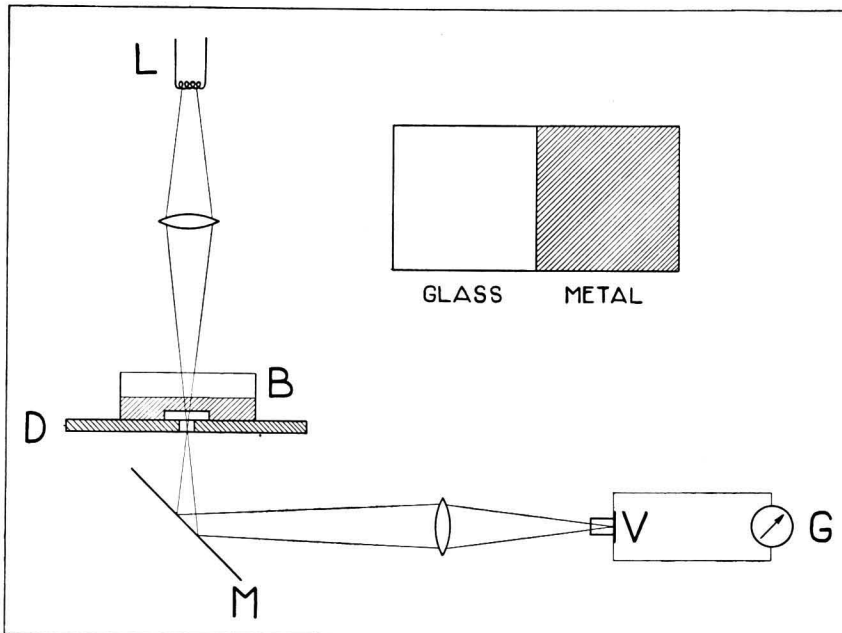


Fig. 1.

important. The following method of cleaning proved to be the best: The glass was first treated with hot chromic acid, and then with nitric acid for several days; before being used the plate was rinsed with water, then with alcohol and finally rubbed very carefully with fine

<sup>1)</sup> J. A. PRINS, Zeitschr. f. Krist., 86, 301, (1933).

blotting paper to remove the last traces of grease, which otherwise would have caused great inhomogeneity in the layer.

The arrangement employed for measuring the transmission is given in fig. 1. The light from the filament  $L$  is focussed somewhere below the glass plate lying in the glass basin  $B$ , which is filled with oil and is put upon the holder  $D$ , which acts as a diaphragm. The transmitted light is reflected by the mirror  $M$  and focussed upon the vacuum thermopile  $V$ . The deflection of the galvanometer  $G$  is proportional to the intensity of the incident light. First the intensity  $I_M$  is measured through the metal layer, then the glass plate is moved so that the light falls through the uncovered part of the glass plate. This intensity is called  $I_G$ . Since the lamp is used on constant current (1 0/00), the transmission of the metal layer is given in percents by the rate  $\frac{I_M}{I_G} \cdot 100$ . This method has the great advantage of eliminating all influences of transmission or reflection of the oil.

The relation between thickness and transmission of the layers has been determined in the following way: Circular object glasses (thickness 0.75 mm, area 4.9 cm<sup>2</sup>) of mirror glass, were weighed on a microbalance with an accuracy of 1  $\gamma$  ( $= 10^{-6}$  grms)<sup>1</sup>). The glasses were cleaned before in the way mentioned above. After evaporating the metal on it, a second weighing gives the quantity of metal per cm<sup>2</sup>. The transmission is measured (in comparison with an equal bare object glass) in air, in oil and in water. The results for tin, copper and lead in oil are given in the figures 2, 3 and 4.

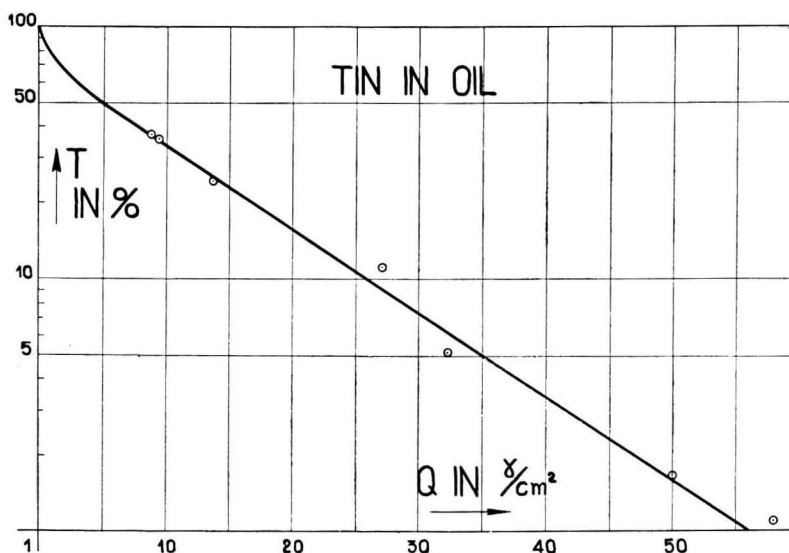


Fig. 2.

<sup>1</sup>) The authors wish to thank Prof. Dr. F. KÖGL, who had the kindness of setting at our disposal the microbalance of the Org. Chem. Lab.

It may be pointed out that except for very thin layers the logarithm of the transmission is a linear function of the quantity of metal. In this range of thickness the metal exists as a continuous layer. The exception for

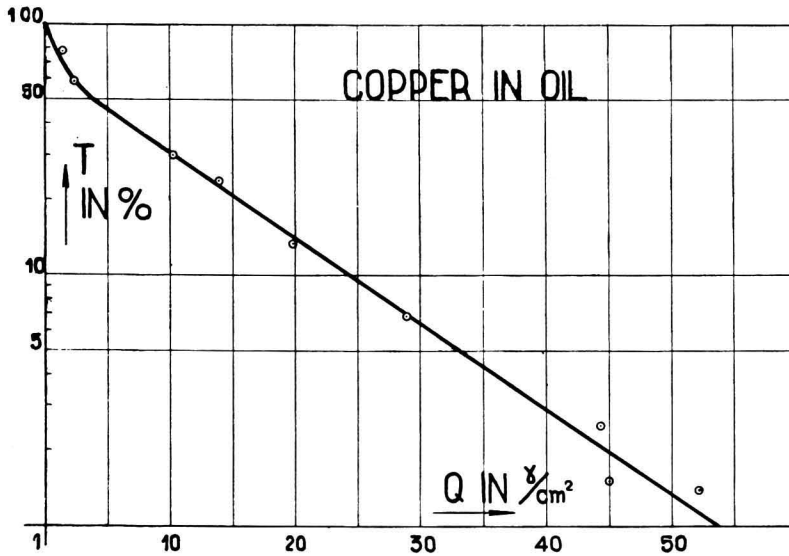


Fig. 3.

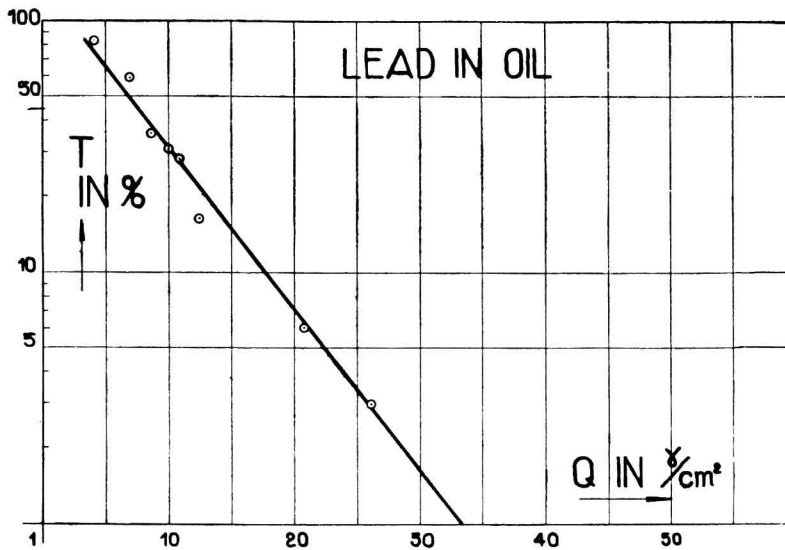


Fig. 4.

very thin layers is due to the ultramicroscopic granularity of these layers as a result of which a certain amount of light is scattered<sup>1)</sup>.

We must lay stress upon the fact that our measurements are not

<sup>1)</sup> See L. S. ORNSTEIN, General discussions of the Faraday Society. Sept. 1935.

made with monochromatic light, but that the thermopile integrates over a range of wavelengths. This method however has the advantage of great accuracy (due to the great intensity of the used light); moreover the simplicity and rapidity of measuring makes it preferable for technical purposes.

In the case of tin we met a complication; for it appeared that the points did not lay on one, but were distributed on two curves. The results are given in fig. 5, in which the normal curve (of fig. 2) is

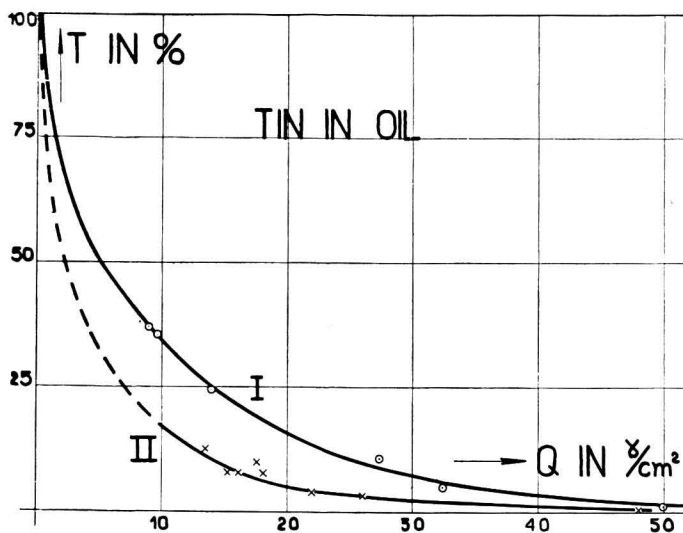


Fig. 5.

called I; the points of curve II show a smaller transmission at the same quantity of metal. Here the transmission is plotted not in a logarithmic, but in an ordinary scale, in order to demonstrate clearly the fact that layers of the "second kind" can only be obtained above a certain quantity of metal. It is certain that the manner of evaporation for the different kinds of layers has no influence, as it was carried out in identical circumstances. The effect appeared at random.

It is possible that the phenomenon is due to the dimorphous character of tin, moreover VEENEMANS<sup>1)</sup> found the same result in the case of antimony, which is also a metal with different modifications.

## § 2. Experimental results.

The metal layers were corroded with an oil in a glass basin, heated in an electrical furnace. We used three oils of different nature, A, B and C (see publ. I of this series<sup>2)</sup>).

<sup>1)</sup> C. F. VEENEMANS, thesis Utrecht 1932.

<sup>2)</sup> P. J. HARINGHUIZEN and D. A. WAS, Proc. Royal Acad. Amsterdam, 38, 1002 (1935).

In fig. 6 is plotted the quantity of copper dissolved at the temperatures  $60^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ , as a function of the time. The graph shows in the first place that the corrosion increases strongly with the temperature;

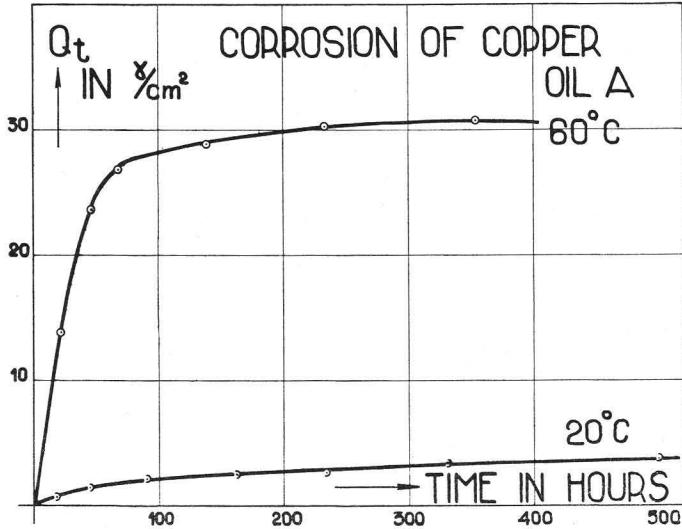


Fig. 6.

in the second place it demonstrates what was found to be a general phenomenon, that, for some reason, the violent attack of the beginning is stopped afterwards. This suggests the idea that a protective film of reaction products is formed upon the surface.

A strong argument for this supposition is given in the fact that after some time a sudden acceleration of the attack reappears. Fig. 7 shows

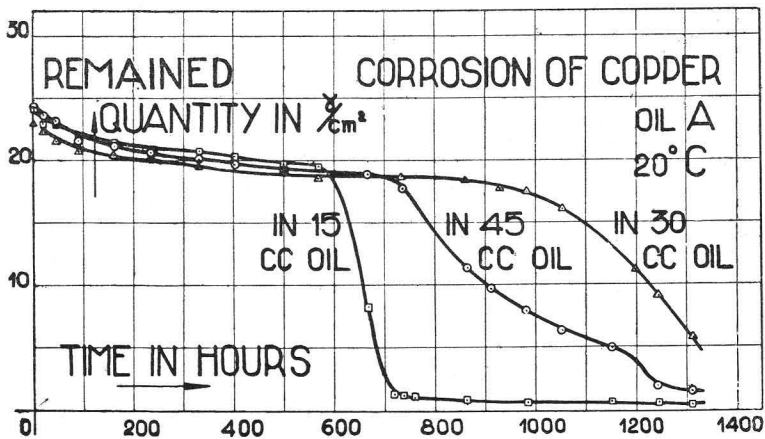


Fig. 7.

this acceleration in the case of copper at room temperature; the three plotted curves represent measurements with different quantities of oil.

It appears that there is not any connection between the quantity of oil and the general feature of the corrosion.

In fig. 8 the corrosion by the three types of oil is plotted. The

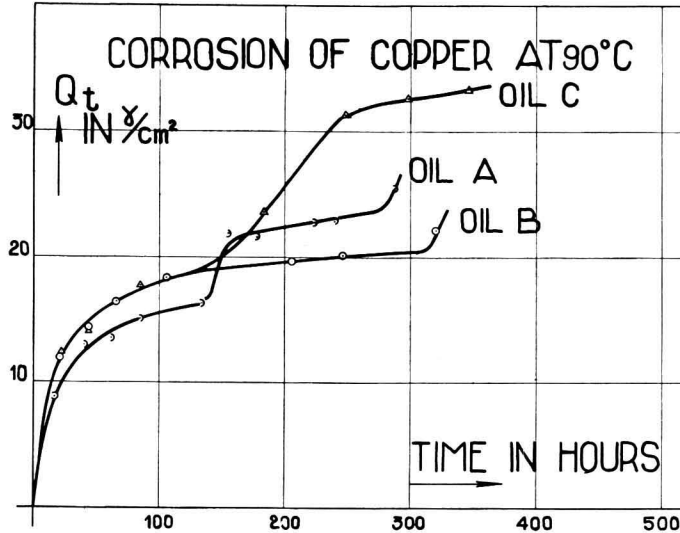


Fig. 8.

mentioned phenomenon of its sudden increase occurred in all cases.

This points to a destruction of the protecting film after any time; the time at which this increase occurs which we have found in all experiments with copper, is not reproducible. It can be concluded, therefore that in practice it is necessary to protect copper against the corroding action of oils by means of a layer of a metal on which a more resistant film is formed.

In this connection we will now discuss some results obtained on tin and lead, which metals come into consideration for protecting the copper. In the case of tin and lead we have never met a destruction of the protecting film; the general curve is given in fig. 9 in which the quantity of dissolved metal is plotted against the time. Except in the beginning of the process, when the protecting film is built up, this function is a linear one. In this range the diffusion of the corroding agent through the protecting film is the controlling factor of the process, while only in the beginning the reaction velocity between agent and metal surface will also be of influence.

With regard to the behaviour of the two metals in practice the beginning of the process is not important, but we have to compare the final process, the slopes of the straight lines in the later part of the curves are important. As far as the work has proceeded viz. 1200 hours the values of these slopes ( $\eta$ ), as determined from fig. 9 are as follows:

tin	0.0021	$\frac{g}{cm^2}$ per hour
lead	0.0044	" " "

It is obvious that while in the initial stage tin is corroded more rapidly than lead the fact that the slope of the curve for lead is more steep than that for tin indicates the probability that under the longer times of contact

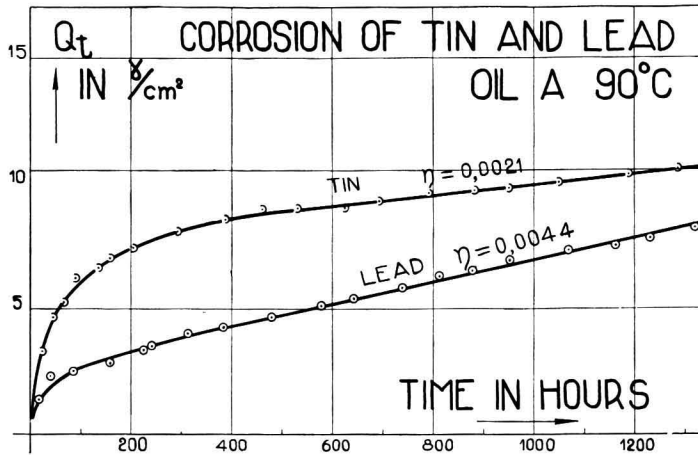


Fig. 9.

usual in industry the corrosion of tin will be less than that for lead.

We have also measured the corrosion of tin by the oils *B* and *C*. Fig. 10 gives the comparison of the behaviour in the three oils. The values of  $\eta$  are:

oil A	0.0021	$\gamma/\text{cm}^2$ per hour.
" B	0.0017	" " "
" C	0.0029	" " "

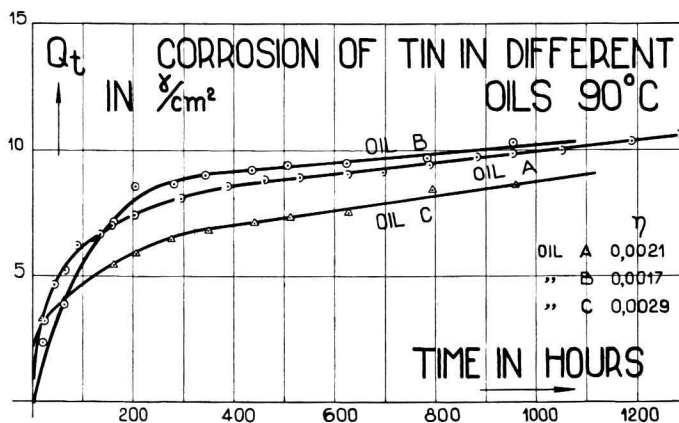


Fig. 10.

As the authors have communicated in these Proceedings<sup>1)</sup>, oil *B* forms

<sup>1)</sup> P. J. HARINGHUIZEN and D. A. WAS. Proc. Royal Acad. Amsterdam, 38, 1002 (1935).



a great deal of acid, due to its deterioration when catalysed by metal; the other oils on the contrary keep a very low acid value.

In the case of contact with tin table I gives the acid values initially and after 1000 hours:

TABLE I.

$t$	oil A	oil B	oil C
0	0.02	0.01	0.01
1000	0.05	5.0	0.02

Comparing these values with those of  $\eta$ , it is clear that the acidity of the oils is not related to the velocity of corrosion. Two causes for the effect come into consideration:

1<sup>o</sup>. Due to the different nature of the oils the respective films may have very different permeabilities, so that this can compensate the divergent acid values. This supposition is not probable, the ratio of paraffines to naphthenes in the oils, which may affect the nature of the film, is not directly related to the values of  $\eta$ .

2<sup>o</sup>. The increase in acidity would be compensated by an increase in the thickness of the protecting film, with the result that the rate of diffusion remains the same, as is required by the linear dependence of the time. However this is impossible, as is shown in the case of oil B. Thus we have plotted in fig. 11 the dissolved quantity of tin as well as the increase of the acid value of the oil. From this graph it can be seen

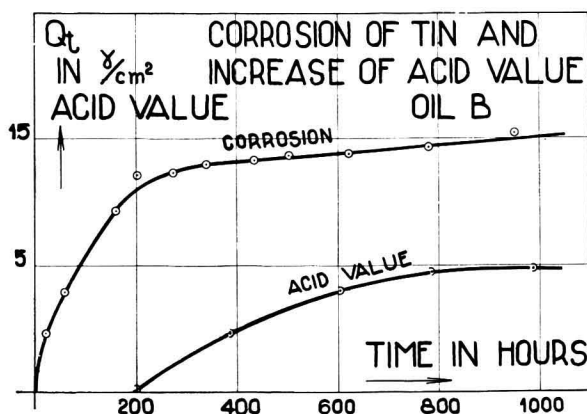


Fig. 11.

that the film has been built up before measurable acid formation occurs; and that afterwards in the same time as that in which the acidity increases 500 times, only 2% of metal are dissolved, which (corresponding to a thickness of about 10 atoms) will not be sufficient to increase

the thickness of the film 500 times. *It would appear justifiable to conclude that the concentration of the agent that produces the actual corrosion is small in comparison with that of the available acid.*

§ 3. *Theory of the corrosion process.*

The curves obtained can be described by the following experimental formula:

$$Q_t = \frac{\alpha t}{1 + \beta t} + \eta t,$$

in which:

$t$  represents the time.

$Q_t$  the dissolved quantity at the time  $t$

$\alpha$ ,  $\beta$  and  $\eta$  are constant.

As mentioned before,  $\eta$  is given by the slope of the straight line.

Putting  $Q_t - \eta t = Q'_t$ , we obtain:

$$\frac{1}{\alpha} (1 + \beta t) = \frac{t}{Q'_t},$$

and this formula is tested by plotting  $t/Q'_t$  against  $t$ , which gives a straight line.

Fig. 12 and 13 show this in the case of tin in the three different oils

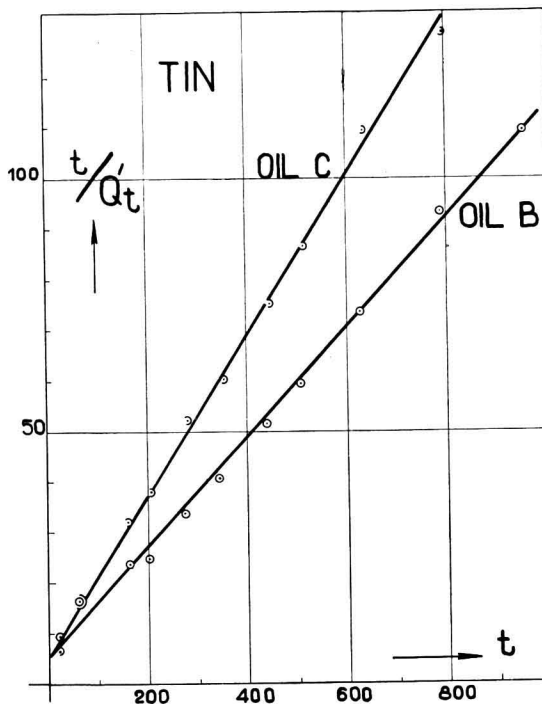


Fig. 12.

and also for lead in oil A. From these figures the values of  $\alpha$  and  $\beta$  can be determined graphically; they are given in table II.

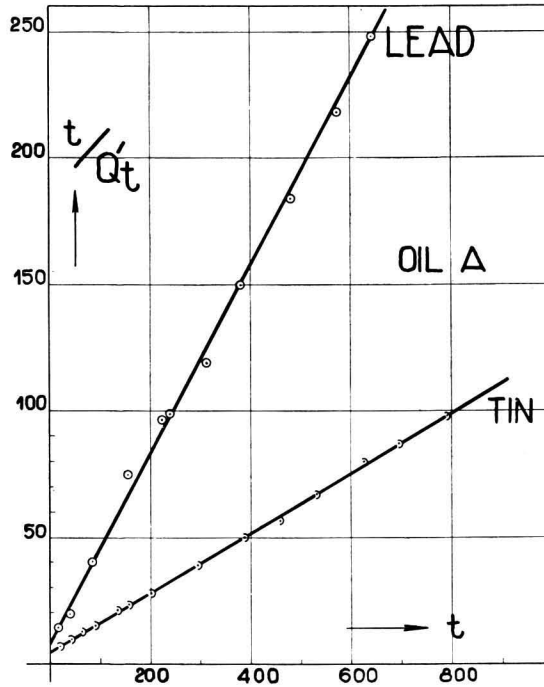


Fig. 13.

TABLE II.

Metal	Oil	$\eta$ in $\gamma/\text{cm}^2$ per hour	$\alpha$ in $\gamma/\text{cm}^2$ per hour	$\beta$
$S_n$	A	0.0021	0.22	0.027
$S_n$	B	0.0017	0.20	0.022
$S_n$	C	0.0029	0.20	0.032
$P_b$	A	0.0044	0.13	0.050

In order to obtain a mathematical representation of the process we will proceed from the ideas suggested by the experimental results.

We suppose a heterogeneous reaction between a metal surface and an acid of the constant concentration  $c_0$ . In consequence of the reaction there will be formed on the surface a film of reaction products, through which the acid must diffuse in order to reach the surface. The velocity of diffusion being very small compared with the reaction velocity, after some time the concentration of the acid at the surface  $c_s$  will decrease

and at last reach a constant value. Then the whole process is only ruled by the diffusion.

If  $Q_t$  is the dissolved quantity of the metal at the time  $t$ , the relation is given by the equation :

$$+ \frac{dQ_t}{dt} = + A c_s - B c_r \dots \dots \dots (1)$$

in which  $c_r$  means the concentration of the reaction product.  $A$  and  $B$  are constants.

The inverse formation of the metal out of its reaction product being very small we can neglect the term  $B c_r$ , which simplifies the equation (1) to :

$$\frac{dQ_t}{dt} = A c_s \dots \dots \dots (2)$$

The decrease of the concentration at the surface  $c_s$  due to the reaction will be proportional to this concentration itself. It will be supplied by the quantity of acid, which diffuses through the film. In order to compute this diffusion current, we will suppose — with some simplification — that the film has a constant thickness  $\delta$ . This approximation is necessary in order to obtain a soluble differential equation.

We assume that the current is proportional to  $c_0 - c_s$ ; this assumption will be correct if  $\delta$  is very small.

From these assumptions follows:

$$- \frac{dc_s}{dt} = + A c_s - \frac{D}{\delta} (c_0 - c_s), \dots \dots \dots (3)$$

(in which  $D$  means the diffusion coefficient of the film), or:

$$- \frac{dc_s}{dt} = \left( A + \frac{D}{\delta} \right) c_s - \frac{D}{\delta} c_0 \dots \dots \dots (4)$$

Integrating this equation we obtain:

$$\left( A + \frac{D}{\delta} \right) c_s - \frac{D}{\delta} c_0 = A c_0 e^{-\left( A + \frac{D}{\delta} \right) t} \dots \dots \dots (5)$$

or:

$$c_s = \frac{A}{A + \frac{D}{\delta}} c_0 e^{-\left( A + \frac{D}{\delta} \right) t} + \frac{\frac{D}{\delta}}{A + \frac{D}{\delta}} c_0 \dots \dots \dots (6)$$

Substituting this value in equation (2) we get:

$$\frac{dQ_t}{dt} = \frac{A^2}{A + \frac{D}{\delta}} c_0 e^{-(A + \frac{D}{\delta})t} + \frac{A \frac{D}{\delta}}{A + \frac{D}{\delta}} c_0 \dots \dots (7)$$

Integration gives:

$$Q_t = \frac{A^2}{\left(A + \frac{D}{\delta}\right)^2} c_0 \left(1 - e^{-(A + \frac{D}{\delta})t}\right) + \frac{A \frac{D}{\delta}}{A + \frac{D}{\delta}} c_0 t \dots (8)$$

Developing in series, one proves that this formula is equivalent to:

$$Q_t = \frac{A^2}{A + \frac{D}{\delta}} c_0 \frac{t}{1 + \frac{D}{2A} t} + \frac{A \frac{D}{\delta}}{A + \frac{D}{\delta}} c_0 t \dots \dots (9)$$

which has the same shape as our experimental formula:

$$Q_t = a \frac{t}{1 + \beta t} + \eta t \dots \dots \dots (10)$$

Comparison of (9) and (10) gives:

$$a = \frac{A^2}{A + \frac{D}{\delta}} c_0$$

$$\beta = \frac{A + \frac{D}{\delta}}{2}$$

$$\eta = \frac{A \frac{D}{\delta}}{A + \frac{D}{\delta}}$$

From this we can compute the values of  $A$ ,  $c_0$  and  $\frac{D}{\delta}$ . We must keep in mind that  $a$  and  $\eta$  must be expressed in  $\gamma$  mols/cm<sup>2</sup> per hour.

Table III gives the results.

TABLE III.

Metal	Oil	$\alpha \cdot 10^4$	$\beta$	$\eta \cdot 10^5$	$A$	$\frac{D}{\delta} \cdot 10^4$	$C_0$ in $\gamma$ mol/cc	Acid conc in $\gamma$ mol/cc	Acid Value
$S_n$	A	18.5	0.027	1.8	0.054	4.9	0.035	1.8	0.02
								-4.5	-0.05
$S_n$	B	16.8	0.022	1.4	0.044	3.7	0.038	0.9	0.01
								-450	-5
$S_n$	C	16.8	0.032	2.4	0.064	9.2	0.026	0.9	0.01
								-1.8	-0.02
$P_b$	A	6.3	0.050	2.1	0.10	34	0.006	1.8	0.02

For comparison the two last columns contain the acid values of the oils and the corresponding value of the concentration of acid in  $\gamma$  mols per cc.

The fact that the computed concentration of the agent that produces the corrosion is many times smaller than the concentration of the acid is in agreement with our experimental conclusion on page 210.

In connection with this fact we can point out that our supposition of taking a constant value for the concentration of the corroding agent, is not contradictory to the facts.

The values of  $c_0$  in oil A in the case of tin and lead (see table III) differ more than we expected. This will be caused by the inaccuracy of the determination of  $a$ . Therefore these experiments will be repeated and also extended to several other metals in different oils.

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