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Data about the role of coating films produced in a chemical manner by corrosion of iron and aluminium.

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(Received 26. November 1948.)

Introduction.

Corrosion of metals has been greatly influenced by the oxydfilm produced on its surfaces. Its development can occur in a natural way, influenced by the oxygen of the air or of other chemical oxidationmaterials.

Previously this progresses had been classified according to oxidation carried out in a dry way and in a moist one. Evans (1) does not consider this manner of classification sufficent. In his opinion processes can be criticised whether they are producing oxidfilm or not. (filmsgiving processes and filmnon — giving processes).

Oxydation of metals, which are exposed to the air, is a phenomenon what has often been examined. This oxydfilms and by the artificially way evolved chemical coating films are of very great importance from point of view of metalprotection.

Oxydation of light and heavy metals.

Pilling and Bewort (2) calculated from specific weight, that by oxydation of ultra- light metals, the products of oxydation would occupy smaller volume than the original metal. Examining this oxydfilm we will find them to be porous and not suitable for protection.

In case of oxidation of heavy metals, unless no force has effected it, the oxyds occupy a greater volume than original metal. Film developed in such a manner is suitable for protection.

Procedure of oxydation of iron can be written with a logarithmical equation: (3)

$$y = k_1 . \log./k_2\ t + k_3$$

where „y“ is the average thickness of oxydfilm in the „t“ time. On higher temperature we have equation (4):

$$y^2 = k_4\, t + k_5$$

„k“ values signify in both of the equations constant values, which are independet of time but are dependet on the temperature.

There has been formed on the surface of aluminium a nearly coherent protective film by effect of air- oxygen. The normal potencial of aluminium is -1. 3 V. Potential values messured in oxidised salt-solutions are more noble and this nobling is due to apperance of oxydfilm.

Development of oxydfilm will be dependent on temperature, on the metal and on its dirtinesses. For e. g. iron in Al_3Fe form is a very common dirtiness of aluminium and its presence is disturbing the evolution of oxydfilm. Not only iron but also dirtinesses of Cu, Si, Zn can occur, whose role becomes clearer and clearer.

On a single, with oxydfilm not coherent covered surface, a more intensitive activity of localements can be observed, according to the positions of different potencials.

When the surface of undirty fim is examined, it is a question, how can be explained the appearance of localelements respectively their activity. The opinions referring to this are very different. In any case it can be estabilished that on surface of such metal appearance of localcurrent is to be observed and this is strictly connected with evolution of oxydfilm, respectively with its presence.

Oxydfilm produced by air shows only a little influence of coating against corroding solutions. This can be explained above all with insignificant thickness of oxydfilm. When the plate is heated and its corrosion determined, we have experienced that coating influence will increase and the lamina will be more resistent against corrosion. Similar phenomenon can be observed on plate pretreated by chemical oxidation and in presence of inhibitors of the solutions. In the first mentioned case metal underwent passivity. According to Faraday (5) under passivating of metals there is to be understood the development of un oxydfilm or of a similar coating film. Müller (6) distinguishes two fasis by evolution of oxydfilm: 1. The coatingsheet covers the metalsurface (surface coating law). 2. The film reaches in depth (depth coating law).

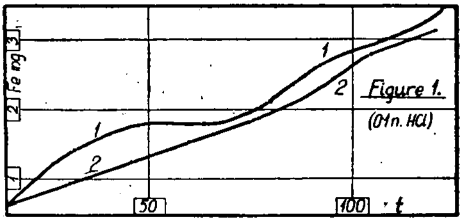


Figure 1.

(01n. HCl)

When in a solution of an electrolyte, platina for catode and the metal to be examined for anode are immersed, and they are conducted into the current, then currentforce will decrease (notwithstanding the fact, that straining between the pair of electrodes is constant) when on the surface of the anode coatingsheet is evolving, metal undergoes passivity and after it the currentdensity will be constant.

$$t_p = B\,[i_0/(F_0 - F)]^{-n}$$

where t_p is temperature of passivity, i_0 density of current, B and n are constant dependet on the electrolyte. F_0- F are uncovered surfaces. In base of this connection we succeded in to determining the surface left uncovered from the coatingsheet, namely the „free surface". Machu (7) employed this evaluating method with very good results by the organic coating-sheets.

It was an important event for oxydfilmexamination when Evans (8) seperated the oxydpellicle by means of Electron microscope (9). These investigations have justified the purposes of Müller. The fact has been proved that after evolution of an initial coatingfilm comes, in case of futher oxidation, an increase of coatingfilm. Further investigations will give an account of structure and position of this films.

Experimental method.

Subject of our examinations was the role of oxydfilms produced in chemical ways, by corrosion of iron and aluminium. These films have been developed by pretreating on the surface of the plate, then it came expositure of the plates to saltsolutions of different concentration and the value of corrosión was determined from the quantity of evolved gas. The apparatus used by our experiments was that used and described by Palmaer (10) where we made a slight change by means of insertion of a manometer next to the büretta for reading in order to be able to control the identity of inside and outside tensions in the moment of reading. (Design of the apparatus is not given for lack of place. I refer to Palmacrs book (10)).

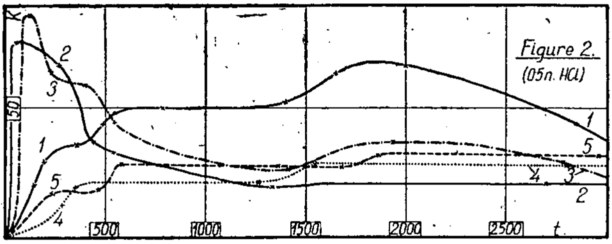


Figure 2.
(05n. HCl)

The aluminium mg—gr got into the solution was evaluated and this value was divisioned with temperature.

$$\text{Al mg./min} = K = F\,(b' - E - e)\,\frac{dv}{dt} \text{ and from this equation}$$

$$F = \frac{T_0}{b_0\,T} \cdot \frac{\text{mol. grav of Al}}{\text{mol. grav. of } H_2 \,.\, 22\,.\,42}$$

where b' is the reading state of barometer, E is the correction of the barometer, e is the steamtension, dv volumechanging of the solution, dt is the difference of temperature.

On the ordinate axe of a coordinate system were showed the K values, and on the abscissa the „t".

Pretreating of iron plates.

The suitable polished and greasless iron plates were pretreated in the following manners:

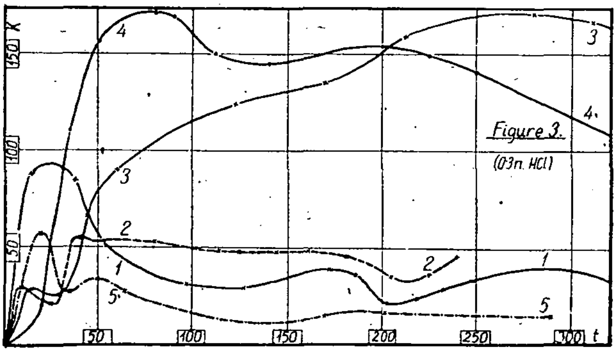
1. Plate without pretreating.
2. 4 hours bathing in a solution containing 5 gr of $KMnO_4$ pro litre. Temperature of the bath is 50 C°. then washed and dried.
3. A similar procedure, but temperature of bath is 100 C°.
4. Plates were kept cool in nitric acid of 1·4 sp. gr. 3 hours long, after they were washed and dried.
5. Plates were 6 hours boiled in such a solution containing 20 gr of $K_2Cr_2O_7$ pro 1. The solution was made acidulous with 20 ccm of nitric acid of 1·4 sp. gr. Having taken it from the solution it was washed with destilled water and dried.

Dirtinesses of used iron plate are given as follows:

C = 0.12%, Si = 0.21%, Mn = 0.40%, P = 0.014%, S = 0.028%

Corrosion of iron plates.

Fig. 1. shows corrosion of plates taken previously in hydrogen (curve 1.) respectively for 48 hours in oxygenathmosphere (curve 2.) Corrosion was determined in a different manner as before. Plates were immersed in 500 ccm 0.1 N hydloclorid acid and stirred with 120 turning pro minute. In every 15 minutes they were taken out 10 ccm of the solution and iron was determined by means of KSCN, after oxidation with $KClO_3$ by colorimetric way. The two curves show clearly the difference between corrosion of the two plates. The frist curve (iron kept in oxygen atmosphere) shows uniform rise, but the second curve shows higher values than the frist one and is waving. It is interesting, that after a certain time meeting of the two curvers may be expected and then no differences can be observed between the corrosion of the two plates. Consequently oxydfilm has an initial coating influence which continues only to a certain limit and after it corrodes similarly to the plate non coated with oxydfilm. So in this case the coatinginfluence of a very thin oxydfilm can be observed.



Curv 1. of figure 2. shows corrosion of iron plate without pretreating. After initial rise the curve goes horizontal and after a little increase decreases gradually.

Curve 2. and 3. give corrosion of plates treated with $KMnO_4$. They are remarkably different from the other curves. The reaction-velocity increases continuously in the initial minute, after a maximum shows a considerable decreasing value. Between the in two manners treated plates was not found an important difference. Microscopic examinaton of the lamella shows a very interesting picture. Very deep holes, relatively dense side by side, were observable on its surface after the corrosion. Explanation of this phnomenon is given as follows: by boiling with $KMnO_4$ a coatingfilm will be evolved of relatively great porosity and little crystals of $KMnO_4$ will retrench in the pors. By influence of the corroding acid this little crystals will get loosen from the pors and will let free-surface for attack. Between the free surface and coatingfilm a difference of potentials will be formed. Attack will start on these points and iron will go in solution. This undergoing in solution is catalized by $KMnO_4$ as long as it is not perfectly transformed, then it decreases the velocity, of reaction.

Curve 4. shows corrosion of plate treated with nitric acid. After a respectively short initial increase the velocity of reaction will be constant and will go nearly horizontal, showing an insignificant decrease. The microscopic picture of the iron surface shows a uniform corrosion after having corroded. Greater holes, different from the others will not be found, this picture is striking to the previously mentioned.

Curve 5. is the plate treated with $K_2Cr_2O_7$ with similar but relatively greater value than the preliminary are. This gives also uniforme corrosion but the surface is deeper especially on the edges.

Pretreating of aluminium plates.

Aluminium plates were pretreated in the following manners:

1. Plate without pretreating.

2. Z. H. Rikagau Kenlyusho S. Miyata method. Its assence is, that by using sodium it forms on the surface a layer of $Al(OH)_3$, and it is changing into Al_2O_3 by sudden heating. It is washed with destilled water then dried.

3. Jirotka's method. The plate is to be put in thin HNO_3 for 30 minutes (which is 24%, differing from the description) in the presence of 0.5% $Cr(SO_4)_3$.

4. The plate is treated with MBV method. It was kept 15 minutes in a bath containing 50 gr. sodium free from water and 15 gr. of K_2CrO_4. Temperature of the solution is 90 C^0 and time of immersion is 15 minutes. After having it washed and dried the plate was bathed in such a solution, which contains 4 gr $KMnO_4$ pro litre. Washing with destilled water then drying.

5. Plate is treated in the same manner as before, but after the first drying the bathing in $KMnO_4$ solution was left out.

Corrosion of aluminium has been examined on following combined plates $Al = 99.5\%$, $Si, Zn, Cu = 0.5\%$, $Zn, Cu = 0.05\%$.

Corrosion of aluminium plates.

Fig. 3. shows the corrosion of plates prepared in different ways. Curve 1. is an aluminium plate without coating, after a relatively quick rise the value of the corrosion decreases. The microscopical picture of the plate shows more or less an uniform corrosion. The corners were more strongly damaged than the middle parts. In the curve No 2. after the initial rise (which ensues through two maximum) the reaction speed is even. The microscopical picture of the plate shows an even corrosion. Plates treated in this manner (Miyata) are well protected against diluted acids. Curve No 3. shows a plate treated with Jirotka' s method. Here causes HNO_3 at the preparation an initial corrosion, on the surface there could be observed a primitive formation of Cr_2O_3. The layer thus formed is very thin and it is not even. For a short while it resists the effect of the corroding acid, then the reactionspeed shows a strongly rising value. The plate shows rather a strong, but relatively an even corrosion. The difference between the curves 4. and 5. is considerable. The miscriscopical examination of the curve 5. before the corrosion showed the formation of an even layer. This layer consists of a mixture of Al_2O_3 and Cr_2O_3. Cr_2O_3 fills the gaps which are not covered by Al_2O_3. It

showed the minimum rate of corrosion,, protects very well and shows an even corrosion. While curve No 4. shows the maximum rate. The reaction speed is rapidly increasing and only a slight decrease is to be observed, then slower but gradual increase is noticeable. Surprising, if we take in consideration that the treatment of the plates are alike, they differ only when treated with $KMn0_4$. The early microscopical examination showed an even layer, where gaps were filled with. MnO_2. Here too is observable the embedding of $KMnO_4$ crystalls. The plate has a shade of brownish-yellow colour. Owing to the effect of the acid the protective layer is decomposed after a slight resistance and starts a very strong corrosion. It seems probable that the MnO_2 layer, formed through the early treatment, functions anodically and there starts a very strong local current. Not only it does not offer protection, on the contrary, it speeds up the corrosion of the metal.

Summary.

We examined the effect of chemical protective fims on iron and aluminium. We compared films with different structure and coating power. We saw that anodically acting protective materials have a demolishing influence, respectively after initial protection of films with uniportant coating-influence comes increased corrosion., It was obvious that by developing of protective film it must be taken in consideration uniform and thickness of the protective-film and the previous corrosion.

Described experiments are the beginning of a series of investigations started for protection of iron and aluminium against corrosion. I am indebtted to Professor dr. Árpád Kiss, who supported my work with his assistence and to Klára Kovács, Ervin Jungreis and István Kerekes students of the university who helped me by the experiments.

Szeged (Hungary) November 1948.

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