

tion is purified with charcoal it has a red colour, then it is hydrogenated in the usual manner with 0.1 g Pd-charcoal. It absorbed 65 ml hydrogen. The catalyst is filtered off and the colourless solution is freed from the solvent at 30°, a graish-drab solid foam is obtained, which is dried over phosphorus-pentoxide and solid sodium hydroxide in a vacuum desiccator.

Analysis. Calculated for $C_9H_{11}O_5N.HCl$: N, 5.6%. Found: N, 5.00%.

For the investigation relating to the blood pressure enhancing effect a 1/1000 solution was used. The decarboxylation experiments were accomplished in a 1/100 molar solution under the conditions laid down by Blaschko and co-workers. The aqueous nor-adrenaline-carboxylic-acid solution was fixed with a phosphate buffer at pH 7.5. The decarboxylase ferment was extracted with water from the kidney of a guinea-pig. In the case of the threo-derivatives obtained by saponification we did not experience CO_2 formation, whereas the substance obtained by saponification of acidified erythro series evolved on the average (0.4 m) 12.5 min CO_2 .

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Examination of layer inhibiting the corrosion of Aluminium on the base of the differential-effect

Preliminary Report

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The interpretation of the protecting power of natural and artificial coating layers covering the metal surface may be attempted on the base of the general theory of corrosion.

On corrosion of metal anode places are formed, which are in conducting correlation on the surface, on the action of the local current inducted by the polyelektrode-systeme evolved in this manner, the ground metal goes into solution. The local current is determined by the general equation of the polyelektrode-corrosion theory:

$$i_L = \sum i_1 \frac{E - E_p}{\sum f(w_1 + w_2 + \dots + w_n)} \quad (1)$$

where E is the calculated EMF of the procedure running down, E_p the polarisation brought about by the irreversible anodic and cathodic processes which depends upon the current density, thus upon the intensity of the current passing through the other local-elements, w the resistance of the single local elements, $f/w_1 + w_2 + \dots + w_n$) not only the function of the conducting power of the electrolyte and of the geometrical measures of the element, but also the complex function of the current passing through the other elements of the circuit. In the sense of the equation mentioned above the polarisation and the resistance of the local element exert a decreasing effect on the corrosion. Both depend upon the properties of the coating layer. Every coating film is porous and thus the resistance of the local element consists of the resistances of the pores (w_p) and of the material of the layer. (w_s). $w_1 = w_p + w_s$. The differential-effect found by Thiel and Eckell enables their determination (1).

The connection of the dissolving metal with platinum increases to a great extent the evolution of hydrogen and consequently the velocity of the dissolution. The total current potential is not equivalent with the total sum of the original local current and the additional external current. i_L is the pure local current in Am. (calculated from the amount of evolved H_2) i_g is the total current on external charging (calculated from the amount of evolved H_2) i_e the external current on charging (recorded by ampéremeter).

$$i_L + i_e - i_g = \Delta \quad (3)$$

Δ is the differential-effect.

Determining simultaneously the potential too:

e' is the measured metal-potential using i_L local-current

e'' the measured metal-potential using i_g total current.

The coating layer polarisation is according to Müller (2), taking into consideration the local anodepotential ϵ_{me}

$$e' = \epsilon_{me} + i_L \cdot w_p \quad (4)$$

$$e'' = \epsilon_{me} + i_g \cdot w_p \text{ thus} \quad (5)$$

$$w_p = \frac{e'' - e'}{i_g - i_L} \quad (6)$$

Thiel and Eckell found that the differential-effect is the linear function of the external current potential.

$$\Delta = K \cdot i_e \quad (7)$$

Applying the law of Kirchoff:

$$K = \frac{w_p}{w_p + w_s} \quad (8)$$

From which the resistance of the layer can be expressed:

$$w_s = w_p \frac{1 - K}{K} \quad (9)$$

The pure anode and cathode potentials can be calculated too:

$$\varepsilon_{me} = e' + i_L \cdot w_p \quad (10)$$

$$\varepsilon_s = \varepsilon_{me} = i_L \cdot (w_s + w_p) \quad (11)$$

On the base of the theory mentioned above it can be expected that the increasing of the anodic current-density has an analog effect to the rising of the natural corrosion currents and thus the mechanism of dissolution can be deduced.

Our apparatus will be suitable for the measuring of the dissolution-potential, of the current-potential passing through, and of the volume of the evolving hydrogen. Reported in detail (3). In the periods i_L only the local-current is operating, in the periods i_g the additive external current-potential too.

On comparing natural oxid-films and chemically reinforced ones the following corrosion mechanism seems probable in the case of aluminium.

a) Within the incubation periods where there is no dissolution the attacking electrolyte diffuses through the pores towards the ground-metal. Dissolution commences if the EMF of the developing local elements is sufficient to overcome the layer- and pore-resistance.

b) The layer-resistance decreases within the incubation period and the coatinglayer partly peels off. This may be considered to occur, because the measured mixture-potential will become more negative, consequently the potential of the ground-metal prevails more and more. On having an active surface the current-potential and the dissolution-velocity increase.

c) The induction of the local current causes the peeling off of the coatinglayer which till then adhered steadily, and on the other hand, through the corrosion products, the evolution of a secondary loose coatingfilm.

I. Table.

The effect of the connection of an external current of 20 mA.

t	I. 0.5 n HCl		II. 0.5 n CH ₃ COOH		III. 0.5 n CH ₃ COOH MBV		IV. as in III. after 1200 min.	
	mV	mA	mV	mA	mV	mA	mV	mA
0	717	20	324	20	144	20	270	20
3	818	16			157	21	292	19.8
4	818	14				22		
5		13	368	19.8	191	22.5	288	19.7
10		11	392	19.5	233	22.8	308	19.5
15		11	408	19.2	262	23.2	320	19.3
20			414	19.2	171	23.3	233	19.2
25			416	19.1	297	23.3	340	19.0
30	819	9	423	14.1	300	23.2	340	19.0
	$\Delta = -0.0003$		$\Delta = +0.9210$		$\Delta = +0.0245$		$\Delta = +0.0240$	
	$w_p = 7.2273$		$w_p = 89.4$				$w_p = 162.2$	
	$w_s = 1.0353$		$w_s = 10.4$				$w_s = 17.4$	

I. Here the natural oxidfilm already peels off and the increase of the current-density causes the increase of the polarisation. The differential effect is negative, indicating the increase of the local hydrogen evolution effected by the current. $w_p > w_s$ from which can be concluded that the coatingfilm includes conducting parts.

II. Table.

The examination of the MBV film. (on base of the average results).

Min.	e', e'' Volt	i_B /Amper	H_2/cm^3	i_B /Amper	i_g /Amper	Δ	K	w^D	w_s	E_{me}	E_s
30	-0.5952		0.125	0.00060		+0.0175	0.8750	113.46	16.209	-0.5320	-0.45420
60	-0.3291	0.02000	0.642		0.0031	+0.0206	1.030				
90	-0.6032		0.961	0.00370		+0.0236	1.0412				
120	-0.2305	0.02260	0.567		0.0027	+0.0245	1.0480				
150	-0.6002		0.967	0.00460		+0.0123	0.0200	117.11	25.450	-1.14016	-0.47013
180	-0.2840	0.15000	1.531		0.0073	+0.0106	0.7067	71.14	11.405	-0.80330	-0.51931
210	-0.5970		0.622	0.00230		+0.0185	0.9068	153.60	15.785	-1.04220	-0.55100
740	-0.3183	0.02040	0.719		0.0048	+0.0171	0.8896	107.20	13.291	-0.83290	-0.55580
770	-0.5863		0.480	0.00230		+0.0135	0.8503	117.87	19.940	-0.85740	-0.54050
800	-0.3034	0.01587	0.990		0.0047	+0.0123	0.7750	79.19	22.986	-0.67560	-0.56320
830	-0.5883		0.235	0.00110		+0.0245	0.9629	331.50	12.755	-0.95290	-0.57420
860	-0.2570	0.02550	0.484		0.0021	+0.0235	0.9216	169.15	14.395	-0.65220	-0.50210
890	-0.6021		0.012	0.00006							
1280	-0.5515		0.080		0.0004	+0.0300	1.5309				
1310	-0.3126	0.01940	2.311	0.01100		+0.0240	1.2071				
1340	-0.5482		1.337		0.0064						

II. In acetic acid the increase of the current-density promotes too peeling off of the film, but the differential-effect is positive, consequently the evolution of the local hydrogen is diminished. Thus the deposition of a voluminous precipitate of the corrosion products is possible in the pores, which is proved by the greatly increased pore-resistance. Bringing in this manner the local-current in association with the polarisation, to below their original value. After switching off of i_e , the local-current recovers its original value and can even increase, as through the progress of the peeling off of the oxidfilm the active surface increases too.

III. In the case of a chemically reinforced oxidefilm, on connection of the external circuit, the peeling off of this layer sets in to such an extent, that in contrast to the two preceding cases, the intensity of the current passing through increases. The mixture-potential becomes far more negative, also evidencing the liberation of the ground-metal. Simultaneously the evolution of the local hydrogen decreases, which is explained by the greatly increased resistance in the small pores of the MBV layer. Namely the H^+ ions abandon the pores rapidly, owing to their great migration-velocity, effected by the local current, whereas the diffusion-velocity of the acid does not differ essentially from that of the salt, thus an H^+ ion impoverishment develops in the pores. Above 4.1 pH the aluminium-acetate hydrolyses considerably, hydroxyde and basic-compounds separate out, enhancing to a great extent the resistance of the pores.

IV. After the elapse of 1200 minutes the complete peeling off of the MBV film can be assumed and the conditions resemble those of the unprotected aluminium.

The differential-effect is throughout positive, signifying practically circumstances favourable to the coating layer producing processes. „K“ the value of the correction coefficient may range between 0—1. (4). If it is „0“ the potential of the ground-metal can be measured, if it is „1“ than that of the coating layer and in intermediary cases a mixture potential. In our experiments it approaches „1“, also proving a coherent coating film. Its value shows in general a decreasing tendency during the corrosion. The fluctuations of the calculated resistance and of the local electrode potentials are due to the difficulties of measuring of the H_2 volume.

The detailed solution of the corrosion mechanism and protecting power will enable the examination of coating layers possessing different character under divergent circumstances.

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