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VERTICAL DISTRIBUTION OF PHOTOGRAPHICALLY ACTIVE PARTICLES EMITTED BY METALS IN ATMOSPHERIC CORROSION

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(Presented by A.N.Terenin, Member of the Academy, Nov. 19, 1949.)

The phenomena connected with the emission of photographically active particles in the atmospheric corrosion of metals are so little understood that so far it has been impossible to establish, not only the mechanism of the phenomenon, but even the composition of the particles. Of course the essential obstacle is the fact that the quantity of emitted particles is extremely small, and study of this phenomenon has been possible only by the photographic method. The need is to accumulate experimental data of sufficient reliability to provide a well-rounded account of the phenomenon.

In a previous paper [1] we studied the kinetics of the particle emission. In the present work, the author has undertaken to find out how the photographically active particles are vertically distributed with distance from the surface of the metal. The research method was the use of an "air wedge". A strip of metal was placed in a horizontal plane; then a photographic plate was set at a certain angle, with its emulsion side turned toward the active surface of the metal. The angle between the metal and the plate was varied between 16° and 90° in different experiments. Before the exposure, the metal sheet was cleaned with emery cloth to free the surface of its oxide layer; to keep it sufficiently even, the emery cloth in this operation was fixed to the surface of a mirror-glass.

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1) Effect of surface treatment. The first problem dealt with was the part played by surface treatment. For this purpose, four strips of zinc were surfaced as follows: 1) with a file, 2) with fine-grained emery cloth, 3) with coarse-grained emery cloth and (4) with a 10% solution of sulfuric acid. Photographic images of all four strips were, of course, made on a single plate, thus keeping the exposure, temperature and developing conditions completely identical.

The exposure-time was two hours, temperature during exposure 80°C, angle of the photographic plate to the metal 25°.

The image obtained on the photographic plate was subjected to photometric analysis, the results of which are shown in Fig.1. The distances between the metal and the photographic plate, in mm, are plotted as abscissae, and the corresponding values of the optical density as ordinates.

From Fig.1 it will be seen that the optical density is linearly dependent on the distance between the metal and the photographic plate. This relationship was exhibited in over a hundred graphs.

The graphs in Fig.1 show that the slope of the straight lines does not depend on the nature of the treatment given the zinc strips. The different distances of the straight lines from the coordinate origin are explained by the surface treatment's affecting the amount of active surface, which in turn affects the number of active particles liberated in unit time.

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2) Activity of different metals. After making it clear that the method of cleaning the metal does not affect the slope of the straight lines, we proceeded to study how the blackening of the photographic plate depended on the distance, for different metals. The metals investigated were zinc, aluminum and magnesium. They were placed on a glass plate in a horizontal position, and the photographic plate, in this case, was placed at a slope of 19°30' to the plane of the metal. Exposure time two hours, temperature during exposure 65°C. The temperature is of considerable importance in our experiments; carrying out the experiments at temperatures higher than room temperature is a necessity dictated by the level of sensitivity of the plates to the influence emanating from the metal; increasing the temperature increases the sensitivity. On the other hand, the quantity of active particles emitted from the metal is dependent on the temperature, being, as we found, exponentially related thereto. The experiments were made in a thermostat, the temperature of which was kept constant to a precision of the order of 1-2°C. We employed "iso-ortho" photographic plates, of Hunter and Driffield sensitivity 250.

The photometric results are shown in Fig.2, on the same system of coordinates.

As will be seen from Fig.2, we get quite the same angle of slope in each of the straight lines, a fact which may

be explained by supposing that identical particles are emitted from the different metals, while on the other hand the different positions of the curves for the several metals may be explained by supposing that different numbers of particles are emitted by each metal during the time of the experiment. Zinc emits the greatest quantity of particles, then comes aluminum, and the smallest quantity is emitted by magnesium. Thus the effect does not follow the series of electric potentials (magnesium, aluminum, zinc).

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3) Vertical distribution of the photographically active particles. Let us write the equation of the straight line representing the density-distance relation, thus:

$$\frac{h}{h_o} + \frac{D}{D_o} = 1,$$

or

$$D = D_o - \frac{D_o}{h_o} h, \qquad (1)$$

where h is the farthest reach of the effect of the photoactive particles (optical density for this distance being zero); D_o is the maximum value of the optical density (corresponding to zero distance between the metal and the photographic plate).

The equation for the straight-line part of the characteristic curve of the photographic emulsion-layer is written as

$$D = \gamma \ln Et^p, \qquad (2)$$

where γ is the contrast factor, E is the intensity of the incident light, t is the exposure time, and p is Schwarzschild's constant.

Now let light of some mean frequency ν fall on the photographic plate; then $E = n h\nu$, where ν is the number of photons falling on the plate in unit time, and $h\nu$ is the mean photon energy. Equation (2) may now be rewritten as:

$$D = \gamma \ln nh\nu t^p \qquad (2a)$$

In the phenomena under consideration, the photographic plate is being struck, not by photons, but by photoactive particles. Assuming each particle to have a certain mean energy, let us replace the photon energy $h\nu$ in equation (2a) by a mean particle energy a, where a is equal to the amount of energy required to bring about the elementary or unit photochemical change.

As to whether the characteristic curve of the photoemulsion, as found for the action of light, may validly be applied to our case, we point out that we are not here making use of the very probable analogy. We are taking our departure from the great amount of emperimental data which we have produced; data which convincingly demonstrate that the emulsion indeed has a definite characteristic curve for the metal effect; moreover, that this characteristic curve is similar to the light-curve and includes a straight-line portion which serves as our photometric range of frequencies.

On this basis, we may write the equation of the straight-line part of the characteristic curve for the metal effect as follows:

$$D = \gamma \ln nat^p, \qquad (3)$$

(where n is the number of photoactive particles falling on an emulsion layer placed at a distance h from the surface of the metal), or:

$$\exp(D/\gamma) = nat^p, \qquad (3a)$$

whence

$$n = \frac{1}{at^p} \exp(D/\gamma) \qquad (3b)$$

Substituting in (3b) the equivalent of D from equation (1), we obtain

$$n = \frac{1}{at^p} \exp\left(\frac{D_o}{\gamma} - \frac{D_o}{\gamma h_o} h\right),$$

or

$$n = n_o^{-\frac{D_o}{\gamma h_o} h}, \qquad (4)$$

where $\frac{\exp(D_o/\gamma)}{at^p} = n_o$ is the number of particles falling on the photographic plate when $h = 0$, that is, when it is in direct contact with the surfaces of the metal. n should not depend on the contrast factor, and indeed does not depend on it, for with an increase in γ there is also a proportional increase in the maximum value D_o of the optical density.

Thus if we start from the assumption that the number of particles falling on the photographic plate is always a definite fraction of the number of particles to be found at any given height, then we conclude that the particle count varies exponentially with distance from the metal.

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REFERENCE

[1] I.L.ROIKH, Dok. Akad. Nauk, 63, No.2 (1948).

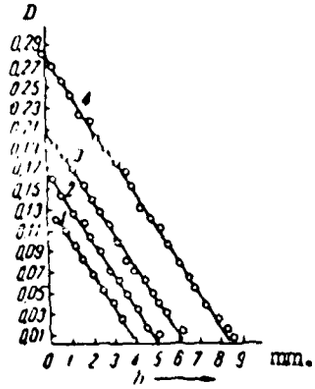

Fig.1. Zinc plate, exposure 2 hours, t = 80°C, α = 25. Surface prepared:
1) with a file
2) with fine-grained emery cloth
3) with coarse-grained emery cloth
4) with 10% H_2SO_4.

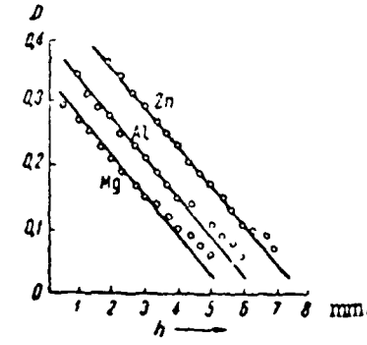

Fig.2.