EMISSION OF PHOTOGRAPHICALLY ACTIVE PARTICLES
IN THE ATMOSPHERIC CORROSION OF METALS

by

I. L. Roikh

TEMPERATURE DEPENDENCE OF THE EMISSION OF PHOTOGRAPHICALLY
ACTIVE PARTICLES IN THE ATMOSPHERIC CORROSION
OF MAGNESIUM AND ZINC

by

I. L. Roikh and F. Ye. Mazayev
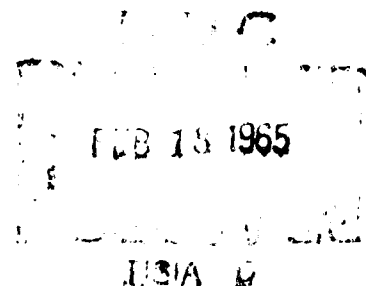
Translated from
Dok. Akad. Nauk, 63 (1948), 2, 119-122,

and

Dok. Akad. Nauk, 72 (1950), 2, 335-338.

by

E. R. Hope

EMISSION OF PHOTOGRAPHICALLY ACTIVE PARTICLES
IN THE ATMOSPHERIC CORROSION OF METALS

by

I. L. ROIKH

(Presented by A.N.TERENIN, Member of the Academy,
September 9, 1948)

1) As early as 1896, Colson {1} stated that the freshly cleaned surfaces of the metals zinc, magnesium and cadmium would produce a latent photographic image. Colson ascribed this effect to metallic vapors. Then a paper by Russel appeared {2}, in which he concluded that the blackening of the photographic plate was due to hydrogen peroxide liberated, as he thought, from the metals. Russel was unable to produce any direct experimental evidence in support of this hypothesis, and for this reason he took his departure from indirect theorizings, based on the fact that a number of photographically active organic substances related to the terpenes, when oxidized, liberated hydrogen peroxide capable of causing the blackening of photographic plates.

Further researches cast no light on this question, and to this day there are no data on which to judge the make-up of the photographically active particles given off by the metals. We think it relevant to remark that the observed effect is due to particles, and not to light. This fact was plain even from the older researches, and from a whole series of experiments which we carried out before we heard of the previous work. Conclusions of a different nature, at which A.A.Ul'yanov has arrived {3}, are not based on reliable experimental evidence.

Charged particles of positive sign do also make their appearance over the metallic surfaces. Our experiments did not show any photographic activity in these particles.

Besides the emission of photographically active particles of unknown constitution, and of the said charged particles, the metals emit ultra-violet rays of extremely low intensity, so weak that one can not record them photographically through a quartz filter 0.2 mm in thickness, even with exposures of several weeks' duration. So far, the only method which has permitted us to establish the existence of this radiation and to study it is mitogenesis. We were able

to show, on the basis of extensive experimental data, that the metals emit ultra-violet rays. By the same mitogenetic method we obtained the emission spectrum of this radiation.

Our theory is that all three phenomena, (1) the emission of photographically active particles, (2) the formation of charged particles, (3) the emission of ultra-violet rays, must be viewed in mutual relationship. There is reason to believe that the said three phenomena are an accompaniment of the process of atmospheric corrosion.

---

2) In the present paper, we are setting forth the results of an experimental research on the kinetics of the emission of photographically active particles in the corrosion of magnesium, aluminum and zinc. First we should mention that these particles are emitted only after the removal of the protective film of oxide. If this film is present, it is impossible to obtain any photographic effect with the metals. This fact in itself indicates that the particle emission is connected with the process of atmospheric corrosion. The kinetics of the emission testify to the same thing.

In making photographic tests with the metals, one encounters a real difficulty, namely that by no means every photographic material is usable for the purpose. Moreover, we found that a preliminary heating would considerably sensitize the photographic plate to this effect. The process, however, turned out to be reversible; after some time, the sensitivity disappeared. A similar effect is brought about by heating the plate after the exposure, but in this case the sensitizing action is weaker. The experiments described below were performed with plates which did not require sensitization.

---

3) Our kinetic experiments consisted in moving the metal samples to successive positions underneath the photographic plate, to make a series of exposures across the plate. Exposure times were 2, 4 and 24 hours. Here we are giving only the curves for the 24-hour exposures; the curves for the other exposure-times are similar. The time-rate of oxidation of the surface varies; thus as the metal is moved across the plate, images of different optical density are formed. In moving the samples, the distance between the plate and the metal was kept unchanged.

- 2 -

The experiments were carried out with fresh metal filings , which because of the larger active surface give a strong photographic effect. The distance between the metal filings and the plate was 1 mm. The sensitivity of the plates was 70 according to the Hunter and Driffield method. The number of images which could be obtained on one plate was limited by the size of the latter (length 40 cm). The temperature in the laboratory was 25°C, humidity 65%.

The optical density of the images was determined by means of a photometer (set up in the laboratory) with a selenium photo-element. From comparison of the optical densities produced on the negative by the same metal sample in its successive exposures, we may derive a curve for the variation of the blackening effect with time, and this variation, in our opinion, is connected with the process of oxidation and formation of the protective film.

If we know the optical densities, it is possible to calculate figures representing more closely the number of particles falling upon the photographing plate. Obviously the number of particles will have a most direct relationship to the accretion of the oxide film, and graphs constructed so as to take this factor into account would be a closer representation of the processes under consideration. However, because of the small values of the optical density, the course of the curves shows only insignificant variations, and therefore we may, without prejudicing the result, take it that the figures plotted as abscissae correspond to numbers of particles falling upon the photographic plate.

---

4) Fig.1 shows the curve for aluminum, as obtained from the successive shifts of the aluminum filings at 24-hour intervals. Time in hours is plotted as the abscissa, optical density as the ordinate. Each circlet shows the density which builds up in the corresponding period.

Fig.2 is the kinetic curve for magnesium, showing the variation in the amount of blackening for each 24 hours.

For zinc, this curve turns out to be of quite a different character. Fig.3 is the kinetic curve for this metal, as obtained under identical conditions. We see from the graph that here there is no monotonic decline. The process has a pulsating decrement.

Here we cannot suppose that a straight line could be drawn through the experimental points and the scatter

ascribed to the error of measurement; this would be incorrect, because (1) the kinetics of aluminum and magnesium were investigated under precisely the same conditions (tests with different metals were made on a single photographic plate) and showed no scatter; thus there is no basis for ascribing the scatter to measurement-error with zinc alone; (2) the curves for zinc, made with different exposure times, are of exactly the same character.

Our curves of the emission kinetics of the photographically active particles might very properly be compared with curves obtained by weighing the metallic samples at corresponding intervals of time. Agreement between these curves would provide direct confirmation of an immediate relationship between the kinetics of particle emission and the corrosion process. However, because of circumstances over which we have no control, we were unable to carry out measurements of this kind, and therefore have had recourse to data available in the literature.

---

5) Vernon [4] studied the kinetics of the atmospheric corrosion of aluminum by weighing sheets of the metal at fixed time-intervals. The results obtained were graphed with time as abscissa and increase of weight at ordinate. The curve which he obtained shows how the weight increases with time, and thus gives us information on the speed of accretion of the oxide film.

Let our point of departure be that the change in film thickness, dL, in time dt, conforms to the following equation:

$$\frac{dL}{dt} = k\,\frac{1}{L}$$

where k is some constant.

Since the increase in thickness of the film must be proportional to its weight, the above equation may be expressed in the following form:

$$\frac{dL}{dt} \sim \frac{1}{W}$$

where W is the weight of oxide.

If in adopting Vernon's curve we introduce, not the weight-increase W but its reciprocal, we shall obtain a curve

- 4 -

showing how the thickness of the film increases with time. Fig.4 is such a curve as obtained by us: 1/W is plotted as ordinate, and time in hours as abscissa. The same scale is chosen for the abscissae as that which we used for the kinetic curves of the photographically active particle emission.

Let us now compare the graphs of Figs. 4 and 1. We cannot expect complete agreement here, since (1) our measurements and Vernon's measurements were carried out under different conditions; (2) the measurements were made for different factors, namely weight of oxide and blackening of the photographic plate; (3) we very likely used aluminum of different qualities. Nevertheless the variations of Vernon's curve for aluminum sheets and of our curve for aluminum filings resemble each other quite closely.

From the above comparison, we may draw the conclusion that between the optical density due to any given quantity of photographically active particles emitted by a metal, and on the other hand the thickness of the oxide film, there is a definite relationship. With the passage of time, there is a decrease both in the rate of blackening and in the rate of thickening of the oxide film. Thus the kinetic curve of emission of the photographically active particles will also serve to characterize the progress of atmospheric corrosion.

REFERENCES

{1} C.Colson, C.R., 123, 49 (1896).

{2} W.Russell, Proc. Roy. Soc., 61, 424 (1897); 62, 102 (1898); 64, 409 (1898).

{3} A.A.UL'YANOV, Dok. Akad. Nauk, 16, No.4 (1937).
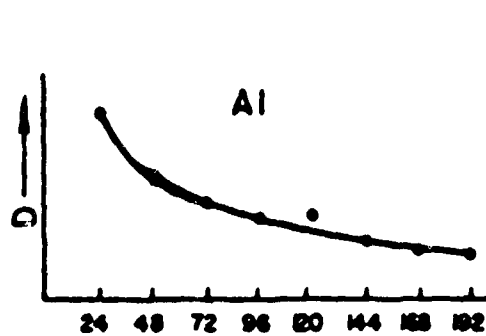
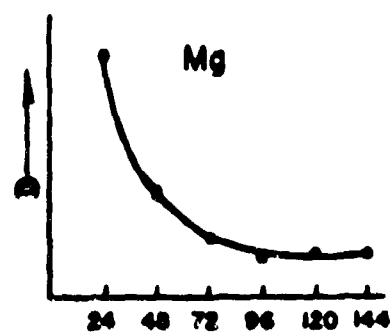{4} Quoted from N.Mott, Nature 145, 792 (1940).

Fig 1.

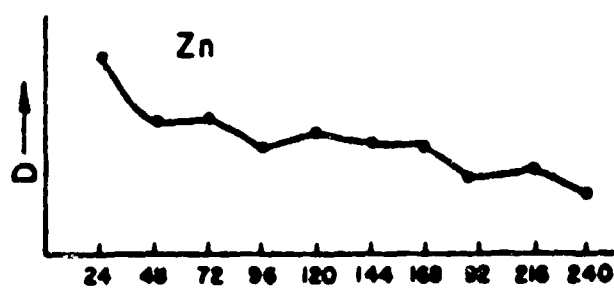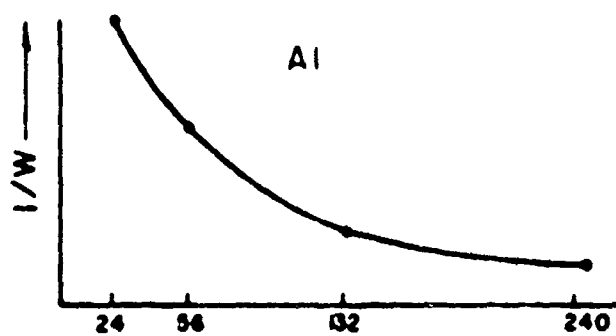Fig 2

Fig 3

Fig 4

EMISSION OF PHOTOGRAPHICALLY ACTIVE PARTICLES
IN THE ATMOSPHERIC CORROSION OF METALS

by

I. L. ROIKH

(Presented by A.N.TERENIN, Member of the Academy,
September 9, 1948)

1) As early as 1896, Colson [1] stated that the freshly cleaned surfaces of the metals zinc, magnesium and cadmium would produce a latent photographic image. Colson ascribed this effect to metallic vapors. Then a paper by Russel appeared [2], in which he concluded that the blackening of the photographic plate was due to hydrogen peroxide liberated, as he thought, from the metals. Russel was unable to produce any direct experimental evidence in support of this hypothesis, and for this reason he took his departure from indirect theorizings, based on the fact that a number of photographically active organic substances related to the terpenes, when oxidized, liberated hydrogen peroxide capable of causing the blackening of photographic plates.

Further researches cast no light on this question, and to this day there are no data on which to judge the make-up of the photograpnically active particles given off by the metals. We think it relevant to remark that the observed effect is due to particles, and not to light. This fact was plain even from the older researches, and from a whole series of experiments which we carried out before we heard of the previous work. Conclusions of a different nature, at which A.A.Ul'yanov has arrived [3], are not based on reliable experimental evidence.

Charged particles of positive sign do also make their appearance over the metallic surfaces. Our experiments did not show any photographic activity in these particles.

Besides the emission of photographically active particles of unknown constitution, and of the said charged particles, the metals emit ultra-violet rays of extremely low intensity, so weak that one can not record them photographically through a quartz filter 0.2 mm in thickness, even with exposures of several weeks' duration. So far, the only method which has permitted us to establish the existence of this radiation and to study it is mitogenesis. We were able

TEMPERATURE DEPENDENCE OF THE EMISSION OF PHOTOGRAPHICALLY ACTIVE PARTICLES IN THE ATMOSPHERIC CORROSION OF MAGNESIUM AND ZINC

I.L. ROIKH and F.Ye. MAZAYEV

(Presented by A.N. TERENIN, Member of the Academy,
February 21, 1950.)

A number of metals, when their surfaces have been freshly cleaned, possess the ability to act on a photographic plate in the same way as light [1]. This effect may be ascribed to active particles of unknown composition, which are emitted from the metals in the process of atmospheric oxidation. On this question the opinions of different writers are highly contradictory. Some ascribe the action to the vapors of the metals [1], others to hydrogen peroxide [2]; still others, to light [3]. The available experimental data force us to the conclusion that the effect is due to the emission of particles, but we do not have sufficient basis for believing them to be hydrogen peroxide.

Although the problem is fifty years old, the number of papers dealing with it is insignificant, and moreover the treatment is only of a qualitative nature. One of the authors of the present paper has studied the kinetics of the emission of the photographically active particles by metals, and has come to the conclusion that it is similar to the kinetics of atmospheric corrosion, of which measurements were made by gravimetric means. From this we draw the conclusion that the emission-kinetics of these photographically active particles can serve as a characteristic descriptive of the corrosion process.

The present work is devoted to the question of the effect of temperature on the emission of photographically active particles by magnesium and zinc in atmospheric corrosion. The authors have undertaken to establish the mechanism and relationships involved.

Experimental Procedure.

The experiments were made on plates of magnesium and zinc. The zinc plates were cut out of a single sheet, produced from a melt of the commercially available chemically pure granulated metal. The magnesium samples had the following composition: Mg 99.825%, Si 0.014%, Fe 0.040%, Al 0.013%.

The metal plate of 4 × 2 × 0.5 cm³ size was processed to give it a flat surface, in order to ensure the best possible contact with the surface of the photographic plate. For purposes of bringing the metal and photographic plate to the particular temperature required for the experiment, they were placed in a thermostat for five minutes. Before this was done, the surface was polished with emery cloth to remove the oxide layer, so that the final cleaning, immediately before the exposure, would take the least time and not permit any perceptible corrosion of the metal. After the preliminary heating to the required temperature, the surface of the sample was again cleaned for 30 seconds to get rid of the oxide layer which can form even during a 5-minute heating, and then the metal was immediately placed on a mica diaphragm, with a 1 × 1.5 cm² window, laid directly on the photographic emulsion. The thickness of the diaphragm, and therefore the distance between the metal and the photographic plate, was 0.06 mm. Mica was chosen as the material for the diaphragm, because it does not let the photographically active particles through. The exposure time was 10 minutes for each of the temperatures used. The specified conditions were strictly maintained in all the tests carried out.

The results of our measurements are influenced by two processes, between which a clear distinction should be made: 1) the effect of temperature on the particle emission from the metal: 2) the effect of temperature on the sensitivity of the photographic emulsion. It is the first process with which the present paper is concerned. As for the second process, it occurs because the photographic plate is placed in the thermostat along with the metal.

We shall start from the assumption that the temperature-dependence of the emulsion sensitivity is the same for any of our sources. This assumption is our reason for using light /for purposes of standardization/; in contrast to the metal effect, light intensity does not depend on the temperature of the thermostat. The luminous intensity of the incandescent lamps (fed by an accumulator) was determined by exposing a photographic plate for 1/25 second at the same temperatures and under the same conditions as with the metal.

Each series of tests was made on different areas of a single photographic plate. All the plates obtained in the series were developed and otherwise processed simultaneously. The duration of the development was 8 minutes at 18°C. The negatives obtained were photometrically measured with a photometer using a silver sulfide valve photo-element (produced by the Institute of Physics, Academy of Sciences of the USSR). The measured area was 2 × 2 mm².

Results of measurements.

The measurements were made in the temperature interval -13° to +100°C. The temperature-variation in any exposure did not exceed ±2°C. To start with, a few series were run for purposes of establishing the optimum conditions, and then two series of tests were run for the effects of light and of the metal respectively. Each point of the curves was taken as the mean of the measurements for three areas of the blackened surface and of the fogging. Fig.1 shows the results of the measurements for magnesium. Here D is the optical density of blackening. The upper curve represents the integrated effect (i) of the particles emitted from the metal surface, and (ii) of the temperature effect on the plate. The lower curve shows the temperature-variation in the sensitivity to light of the photographic plates employed.

Similar data for zinc were obtained by the same method. They are shown in Fig.2.

It is curious that the effect is present at minus 13°C. By no means every photographic plate will show the effect at such a temperature. In the interval from -13° to + 17°C, the effect of temperature on the light-sensitivity of the photographic emulsion is barely perceptible.

To obtain a more graphic presentation of the temperature-dependence of the metal photographic effect, the data for the metals and for light were processed as follows. From the ordinates of the magnesium and zinc curves, we calculated the corresponding values of the curve for light. The differences obtained were then plotted as ordinates, against the reciprocals of the corresponding absolute temperatures as abscissae. Thus the curves of Fig.3 were obtained, showing the relation between the blackening of the photographic plate and the reciprocal of the absolute temperature of the magnesium and zinc, with due allowance for the effect of temperature on the sensitivity of the emulsion layer.

We also carried out measurements by another method, which showed directly the relationship between the metal photographic effect and temperature.

To accomplish this, the photographic plate, placed underneath the sample (with the emulsion side up, toward the metal), was maintained at a constant temperature by means of a stream of water continuously bathing the glass of the plate during the whole time of exposure (about 10 minutes). The temperature of the stream was 18°C. The steadiness of the temperature in the emulsion layer was checked by means of a thermocouple connected to a mirror galvanometer. The zinc, held at a distance of 1.2 mm above the photographic plate, was fixed to the bottom of a special bath, which was maintained at
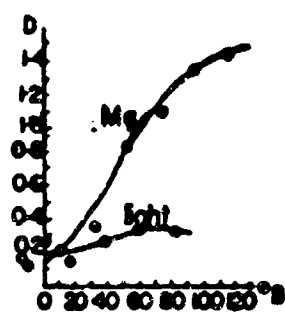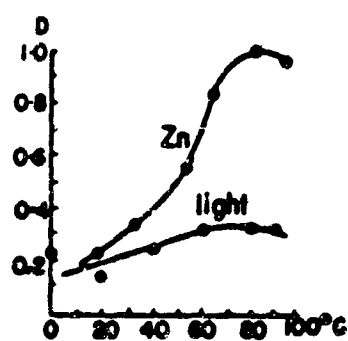
FIG. I

FIG. 2

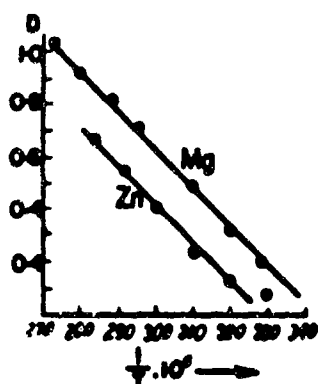

FIG.3

the desired temperature by means of an electric heating coil.
Before each exposure at each successive temperature, the zinc
plate was cleaned with emery cloth to remove the oxide film.

For each different temperature, different areas of
the photographic plate were moved under the test metal. The
blackening thus produced was then measured photometrically.
This direct method gave us the same relationship between
blackening of the plate and temperature of the active zinc
surface as that given by the method described above, but the
scatter of the plotted points was a little greater.

Consideration of the Results.

The straight lines in Fig.3 do not directly represent
the number of active particles emitted from the metals; what
is shown here is only the variation of the optical density.

The relationship between the photographically active
particles emitted by the metal and the temperature may be
obtained in quantitative form by the same means as employed in
a paper by one of the authors {5}, in investigating the vertical
distribution of the photographically active particles.

The experimental curves of Fig.3 correspond to the
equation:

$$\frac{D}{D_o} + \frac{1/T}{1/T_o} = 1 \tag{1}$$

where D_o is the maximum value of the optical density; $1/T_o$ is
the maximum value of the reciprocal absolute temperature of
the metal, the value at which the optical density becomes zero;
D is the optical density corresponding to reciprocal tempera-
ture $1/T$.

The equation of the linear portion of the charac-
teristic curve of the emulsion layer for the metal effect may
be written as follows:

$$D = \gamma (\ln nt - \ln n_1 t_1) \tag{2}$$

where n is the number of particles falling upon unit area of
the photographic plate in unit time; n_1 is the corresponding

number of particles for the point of intersection of the linear part of the emulsion curve with the axis of the abscissae (in paper {5} the term $\ln n_1 t_1$ was not taken into account); t and t_1 are the corresponding exposure times. Schwarzschild's constant p is taken as equal to unity.

From equation (2) we obtain:

$$n = n_1 t_1 \cdot \exp\left[D/\gamma\right] \qquad (3)$$

Substituting in equation (3) the value of D from equation (1) we find:

$$\frac{n_1 t_1 \cdot \exp[D_0/\gamma]}{t} \exp\left[-\frac{D_0}{\gamma}\frac{T_0}{T}\right] \qquad (4)$$

Let A stand for the coefficient $\dfrac{n_1 t_1 \cdot \exp[D_0/\gamma]}{t}$; then equation (4) takes the form:

$$n = A \cdot \exp\left[-\frac{D_0}{\gamma}\frac{T_0}{T}\right] \qquad (5)$$

From the fact that the optical density is directly proportional to the contrast coefficient γ it follows that the ratio D_0/γ is a constant and does not depend on the photographic material. Hence if we take as our point of departure that the number of particles falling upon the photographic plate is always a certain definite fraction of the particles emitted by the metal, we arrive at the conclusion that the number of particles issuing from the metal in the process of atmospheric corrosion is an exponential function of the temperature. This relationship brings to mind the well-known formula:

$$N = N_0 e^{-Q/RT} \qquad (6)$$

where N_0 represents total number of collisions, N the number of effective collisions, and q the energy of activation per gram-molecule. Comparison of equations (5) and (6) indicates the possibility of determining the activation energy of the photographically active particles.

We should mention that T.N. Krylova {6} of the Laboratory of the State Optical Institute has studied the relationship between oxide film thickness and temperature in aluminum, chrome, nickel, iron and copper, using a polarimetric method. Our investigations were made in the interval from

- 10 -

some tens of degrees to 500 degrees Centigrade; mainly in the hundreds range. Comparison of our findings with Krylova's results confirms that the emission of the photographically active particles is due to the corrosion of the metals, and indicates the simplicity and relatively high sensitivity of the photographic method of studying this corrosion.

Received January 21, 1950.

REFERENCES

{1} C. Colson, C. R., 123, 49 (1896).

{2} W. Russel, Proc. Roy. Soc., 64, 403 (1899).

{3} A. A. UL'YANOV, Transactions of Conference on Corrosion Problems, May 7th to 10th, 1938.

{4} I. L. ROIKH, Dok. Akad. Nauk., 63, No.2 (1948).

{5} I. L. ROIKH, Dok. Akad. Nauk., 70, No.2 (1950).

{6} T. N. KRYLOVA, Izv. Akad. Nauk, SSSR, Division of Engineering Sciences, No. 10, 89 (1938).