



LX. The photoelectric fatigue of metals

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LX. *The Photoelectric Fatigue of Metals.* By H. STANLEY ALLEN, M.A., D.Sc., Senior Lecturer in Physics at University of London, King's College*.

THE recorded facts relating to the diminution of the photoelectric activity of metal surfaces with time are somewhat confusing and contradictory. The difficulties have been in part removed by the researches of Hallwachs and his fellow workers †. Hallwachs maintains that the photoelectric "fatigue" is not primarily due to illumination, and that the size of the vessel in which the plate is kept affects to a marked degree the rate at which the fatigue takes place. Ignorance of the latter result goes far to explain the contradictions amongst the earlier experiments.

My investigations, which have been in progress for some years past, have led me to the same conclusions; and in view of the importance of these conclusions in explaining the changes involved in fatigue, it seems desirable to put on record a short account of my results.

In the following paragraphs it is shown that in the case of zinc, (1) light is not the primary cause of fatigue, (2) the fatigue is practically independent of the electric field, (3) the fatigue takes place in an atmosphere of hydrogen as in ordinary air, (4) the fatigue proceeds more slowly when the plate is kept in a small vessel.

To explain the last result we are forced to the conclusion that the fatigue must be due to some substance (ozone, Hallwachs; in the case of zinc, ozone, water vapour, Ullman) present in small quantity in the atmosphere surrounding the plate. The fatigue must be associated with the condition of the gaseous films on the surface of the plate or with the gas occluded in the metal.

The foregoing remarks apply to fatigue in gases at ordinary pressures; in a vacuum other sources of fatigue may possibly be present ‡, though recent results tend to show that with a perfectly clean metal surface in a very high vacuum there would be no fatigue §.

* Communicated by the Author.

† W. Hallwachs, *Phys. Zeit.* v. p. 489 (1904); *Ber. d. math.-phys. Klasse d. Kgl. Sächs. Gesellsch. d. Wissensch. zu Leipzig*, lviii. p. 341 (1906); *Ann. d. Phys.* xxiii. p. 459 (1907); *Abh. d. naturwissensch. Gesellsch. Isis in Dresden*, i. p. 65 (1909). H. Beil, *Ann. d. Phys.* xxxi. p. 849 (1910). E. Ullmann, *Ann. d. Phys.* xxxii. p. 1 (1910).

‡ As, for example, changes in pressure due to absorption of gas by the metal (Dember, *Phys. Zeit.* ix. p. 188, 1908). A change in pressure due to gradual absorption of gas by charcoal at the temperature of liquid air may have been the cause of the apparent fatigue of zinc in a vacuum recorded in my first paper (§ 12).

§ Millikan and Winchester, *Phys. Rev.* xxix. p. 85 (1909).

Method of experimenting.—The apparatus used in the present research was identical with that described in my earlier papers referred to below. I desire again to express my thanks to the Government Grant Committee of the Royal Society and to the Council of King's College for defraying the cost of the greater part of this apparatus. The mercury-vapour lamp of fused quartz supplied with current from a special set of accumulators was used as a source of ultra-violet light throughout this investigation. Provided sufficient time (from 20 to 30 minutes) is allowed for it to assume a steady state, this gives a sufficiently constant stream of radiation.

The photoelectric current between the positively charged wire gauze and the metal plate was measured by means of a Dolezalek electrometer in connexion with a suitable condenser. Readings of the rate of leak were usually taken at intervals of two minutes. Most of the results recorded were obtained with a zinc plate polished with fine emery-paper; both the initial activity and the rate of fatigue showed considerable variations from day to day, probably in consequence of the atmospheric conditions, but the results obtained on any particular day were usually concordant. In most cases the figures given represent the mean of two or three concordant determinations.

(1) *Light is not the primary cause of fatigue.*

In my earlier investigations I found that the rate at which fatigue takes place is not much affected by the intensity of the illumination* or by the character of the source of light (mercury-vapour lamp or Nernst lamp †). Later experiments carried out to determine the influence of light on fatigue confirm the conclusions of Hallwachs. The photoelectric fatigue of zinc proceeds in darkness almost at the same rate as when the metal is continuously exposed to light.

The results of these experiments are embodied in the following tables (I., II., and III.). The tests in Table I. were made with a zinc plate polished with fine emery and rouge, tested in the air of the room, readings of the activity being taken at intervals of two minutes. The plate was exposed continuously to the mercury-vapour lamp except where an asterisk appears in the table. In the latter case the plate was shielded from ultra-violet light but not from the dim light of the room. The activity is expressed as a

* H. S. Allen, Proc. Roy. Soc. (A) lxxviii. § 7, p. 489 (1907).

† H. S. Allen, Proc. Roy. Soc. (A) lxxxii. § 5, p. 164 (1909).

percentage of the initial activity, measured immediately after polishing.

TABLE I.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100	100	100	100
II.	75	*	77	76	77
III.	66	*	*	67	64
IV.	57	58	*	*	58
V.	54	55	55	*	*
VI.	49	51	51	48	*
VII.	47	49	47	44	48
VIII.	46	46	45	43	44
IX.	43	45	42	42	43

The fatigue is not affected by shielding the zinc from ultra-violet light for a period of about five minutes, no matter at what stage in the process the shielding takes place.

In the tests recorded in Table II. the zinc plate was polished with fine emery-paper only. The initial activity is given in arbitrary units in the first row of the table, and below is given the activity at the end of a fatigue period of 16 minutes, expressed as a percentage of the initial activity.

TABLE II.

Zinc plate in air of room. Fatigue period, 16 minutes.

		<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
Initial activity	{ Arbitrary units ...	318	290	288	237	211
	{ Percentage	100	100	100	100	100
Final activity.	Percentage	47	44	43	44	46

In test *a* the plate was exposed to ultra-violet light continuously. In test *b* it was shielded from ultra-violet light for 5 minutes, while in tests *c*, *d*, and *e* it was shielded from ultra-violet light for 15 minutes.

Experiments were also carried out in a closed testing-vessel of brass fitted with a quartz window. The zinc plate was polished with fine emery, placed in position as quickly as possible, and the first reading was taken two minutes after polishing. The initial activity was found by extrapolation,

and in the table has been taken as 100. In experiments *a*, *d*, and *e* the plate was illuminated continuously by the mercury-vapour lamp. In *b* and *c* it was in complete darkness for 9 minutes, as indicated by the asterisks in the table. During this period the testing vessel was closed with a light-tight wooden cover.

TABLE III.

Zinc plate in testing vessel. Fatigue period, 16 minutes.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
I.	100	100	100	100	100
II.	91	93	92	92	89
III.	85	88	87	83	80
IV.	79	*	*	79	78
V.	78	*	*	78	75
VI.	75	*	*	77	71
VII.	73	*	*	72	70
VIII.	71	73	75	71	69
IX.	67	73	74	71	68

It appears from the results in the table that the fatigue takes place in complete darkness, though there is evidence of a small increase in the rate of fatigue under the influence of the ultra-violet light.

We conclude that light cannot be the primary cause of fatigue, though it may play a secondary part in accelerating or retarding fatigue. These secondary actions are illustrated in my earlier experiments on amalgamated zinc*, or on polished zinc at different distances from the mercury-vapour lamp †.

Ullmann ‡ arrives at similar conclusions, attributing the secondary actions of light to the formation of ozone and to the heating of the plate.

I have also examined the action of Röntgen rays on the plate and could detect no decisive change in the rate of fatigue, at any rate for an exposure of one or two minutes to the rays from a focus-tube at a distance of about 50 cms. Hallwachs § records a similar result.

* H. S. Allen, Proc. Roy. Soc. (A) lxxviii. § 11, p. 492 (1907).

† H. S. Allen, Proc. Roy. Soc. (A) lxxxii. § 2, p. 163 (1909).

‡ Ullmann, *Ann. d. Phys.* (4) xxxii. § 5, pp. 15-20 (1910).

§ Hallwachs, *Ann. d. Phys.* (4) xxiii. p. 467 (1907).

2. *Fatigue independent of the Electric Field.*

The rate at which fatigue takes place does not depend on the strength of the electric field applied. This is illustrated in Table IV., which contains results of experiments made in the air of the room and of others made in the brass testing vessel. The zinc plate used was polished with fine emery-paper.

TABLE IV.

Zinc plate. Fatigue period, 16 minutes.

	In air of room.		In testing vessel.	
	110 volts.	480 volts.	110 volts.	480 volts.
I.	100	100	100	100
II.	85	89	95	93
III.	80	83	91	88
IV.	75	79	88	85
V.	71	75	83	83
VI.	68	70	81	80
VII.	65	66	79	78
VIII.	62	60	77	77
IX.	59	58	76	76

Again the percentage fatigue was the same whether the gauze was charged (to 100 volts) positively (as of course it must be when a measurement of the photoelectric current is being made) or negatively. This is shown in Table V.

TABLE V.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100
II. to VII....	Gauze positive	Gauze negative.
VIII.	63	62
IX.	60	60

It was thought that possibly more effect would be produced by keeping the zinc plate at a high (positive or negative) potential with the rest of the apparatus earthed. The results in Table VI. show no effect of this kind when the potential of the zinc plate is ± 100 volts.

TABLE VI.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100	100	100
II. to VII....	Gauze +ve	Zinc +ve	Gauze +ve	Zinc -ve
VIII.	50	49	51	51
IX.	45	46	47	47

When the zinc plate was under examination in the brass testing vessel and was charged positively, a small effect was sometimes observed on reversing the direction of the field for the purpose of taking a reading of the photoelectric current. The effect in question corresponded to a small increase in the observed current, the increase amounting to about ten per cent. of the anticipated value of the current. The increase only persisted for a few minutes after the direction of the field was reversed. This effect is comparable with that observed by Campbell * in the case of the leak from hot bodies, the reading taken immediately after reversal being greater than the normal.

3. Fatigue of various Metals in Air and in Hydrogen.

Zinc.—In my earlier papers (*loc. cit.*) I have shown that the fatigue of zinc proceeds in such a way that the activity for some hours after polishing can be represented as the sum of two exponential terms. This would indicate that after a prolonged period the activity would approach asymptotically a zero value. It has been found, however, that the zinc plate retains a small sensibility after several days (in one case after 26 days); a result which points to the existence of a state in which the zinc plate would show a small residual activity. This would mean, provided the atmospheric conditions remained invariable, the addition of a small constant term to the two exponential terms.

Experiments were made with the zinc plate when the testing vessel was filled with hydrogen, prepared by the action of pure hydrochloric acid on pure zinc and dried by

* N. R. Campbell, *Phil. Mag.* ix. p. 549 (1905).

passing over solid caustic potash*. The fatigue in hydrogen was found to be very similar to that in air.

Some results as to the fatigue of other metals are here briefly summarized.

Silver.—One of the most interesting cases examined was a plate of pure silver supplied by Messrs. Johnson, Matthey & Co. The plate was polished with rouge paper and put in position in the brass testing vessel. After two hours' continuous exposure to the light of the mercury-vapour lamp the activity remained unaltered.

It is remarkable that Ladenburg †, who carried out fatigue experiments in a vacuum, mentions silver as one of the metals showing marked fatigue, but it must be remembered that his surfaces were "polished once with emery and oil."

When the air in the testing vessel was replaced by hydrogen, the same result was obtained as in air; that is, no fatigue could be detected after two hours' exposure to the source of light.

The same plate tested later in the air of the room showed fatigue effects, the activity falling to half its initial value in two hours. We have here an example of the influence of the size of the vessel to be discussed later.

Aluminium.—This metal was found to behave in much the same way as zinc. Its activity can be represented by the sum of two exponential terms. When examined in air in the closed testing vessel, using the mercury-vapour lamp as the source of light, the first term fell to half value in 6 minutes, the second in 190 minutes. In hydrogen the values were not very different, being 7 minutes and 165 minutes, respectively.

Copper.—When a copper plate was examined in the testing vessel, the fatigue proceeded slowly from the outset; about 3 hours would be required for the activity to fall to one-half of the initial value. In hydrogen the fatigue took place at about the same rate as in air. In the air of the room more rapid fatigue was observed.

* It should be noted that the metal plate was polished and put in position in the testing vessel, the air was displaced by a current of hydrogen, and readings of the activity were commenced a few minutes after polishing. It is not probable that the gas was entirely free from water-vapour, nor is it likely that the air-film on the surface of the plate was immediately changed. It is to be wished that experiments could be carried out in which the plate should be polished *after* being placed in a good vacuum or in an atmosphere of the gas to be employed in the investigation.

† E. Ladenburg, *Ann. d. Physik*, xii, p. 558 (1903).

4. *Fatigue depends on the size of the containing vessel.*

The influence of the size of the containing vessel on the rate at which fatigue takes place was verified during the present investigation. Examples of this influence have already been recorded in the earlier parts of the paper. If we compare the results of Tables I. and II. with those of Table III., we find that the fatigue is more rapid in the air of the room than in the testing vessel. The same difference is also shown in Table IV. Similar effects are mentioned in § 3 with regard to silver and copper.

Inasmuch as the rate of fatigue varied somewhat from day to day, probably being dependent on the state of the atmosphere at the time, it seemed desirable to have a direct comparison between the fatigue in the room and that in the testing vessel when the air was in the same condition. The results of experiments made on the same day are recorded in Table VII.

TABLE VII.

Zinc plate. Fatigue period, 16 minutes.

In air of room.		In testing vessel.
EMERY.	ROUGE.	EMERY.
100	100	100
86	89	90
79	79	82
72	73	79
67	67	77
64	64	75
59	58	72
57	55	71
53	52	69

The fatigue is diminished by putting the plate in the smaller receptacle. Incidentally we notice that the fatigue proceeds at the same rate when the plate is rubbed with emery-paper only as when this is followed by the application of rouge paper.

Conclusion.

There has been much discussion as to the nature of the change associated with photoelectric fatigue. The principal

views of the character of the change may be summarized as follows:—

1. A chemical change such as oxidation of the surface.
2. A physical change of the metal itself, as for example a roughening of the surface.
3. An electrical change in the formation of an electrical double layer (Lenard *).
4. A disintegration of the metal due to the expulsion of electrons by light (Ramsay and Spencer †).
5. A change in the surface film of gas or in the gas occluded in the metal (Hallwachs).

Hallwachs has shown from the behaviour of copper and its oxides that oxidation cannot be the cause of fatigue, and the results of the present paper confirming those of other observers are inconsistent with the second, third, and fourth views. We must therefore conclude with Hallwachs that the main cause of photoelectric fatigue is to be found in the condition of the gaseous layer at the surface of the plate. This does not exclude the existence of secondary causes of fatigue in particular cases.

The fact that the activity at any instant can be expressed by means of exponential terms is not inconsistent with the theory put forward. It is sometimes assumed that equations of the type here indicated necessarily refer to unimolecular changes. But in certain cases reactions are met with which, though really polymolecular, behave like unimolecular reactions ‡. Thus certain gaseous reactions take place on the surface of the walls of the containing vessel, and the velocity of the reaction is proportional to the pressure of the gas. The chemical change then appears as a reaction of the first order. Thus a purely surface action may simulate the character of a unimolecular reaction.

In conclusion I may be allowed a few words of personal explanation. I have been represented as a supporter of the theory that photoelectric fatigue is due to a kind of radioactive change induced by light. Although when my first paper was written I was prepared to recognise the *possibility* of this explanation, I was careful to state that the nature of the modifications § of the surface suggested was left an open question. The view which I favoured for a long time was that these modifications of the surface corresponded with the

* P. Lenard, *Ann. d. Phys.* viii. p. 196 (1902).

† Sir W. Ramsay and J. F. Spencer, *Phil. Mag.* [6] xii. p. 397 (1906).

‡ H. M. Dawson, *Nature*, lxxi. p. 532 (1905).

§ "Whether physical or chemical modifications of zinc."

amorphous and crystalline phases described by Beilby*, photoelectric fatigue being a gradual change from the amorphous to the crystalline form through an intermediate (labile) phase.

The experiments described in this paper show that such a view is untenable, at least in this simple form, and that we must look to the gaseous films on the surface of the metal for the explanation of the chief effects of photoelectric fatigue.

Wheatstone Laboratory,
University of London, King's College.
June, 1910.

LXI. *Positive Electrification due to Heating Aluminium Phosphate.* By A. E. GARRETT, B.Sc.†

[Plate XI.]

I. *Introduction and Experimental Arrangements.*

IN a paper published in the 'Philosophical Magazine' for October, 1904, by Dr. R. S. Willows and myself, it was found that the halogen compounds of zinc when heated are able to discharge both positively and negatively electrified bodies. A more detailed examination of this phenomenon was subsequently carried out by one of us ‡.

In those experiments the temperature to which the salts were raised was in no case higher than 360° C., and no series of observations at pressures lower than a few mm. were undertaken.

Sir J. J. Thomson § made some experiments to determine whether the base or the acid is instrumental in producing the ionization, and came to the conclusion that the nature of the ionic charge is determined by the acid. Thus he found that phosphates when heated produce a very large excess of positive ions, halogen compounds produce an excess of positive ions, and nitrates an excess of positive at first, but when heated sufficiently to be converted into oxides they produce an excess of negative. Incidentally he found that aluminium phosphate gives off a very large excess of positive ions.

Now the halogen and other compounds used in the previous

* G. T. Beilby, *Phil. Mag.* viii. p. 258 (1904); *Proc. Roy. Soc. (A)* lxxii. p. 227 (1905); lxxix. p. 463 (1907).

† Communicated by the Physical Society: read June 10, 1910.

‡ *Garrett, Phil. Mag.*, June 1907.

§ *Cambridge Phil. Soc. Proc.*, p. 105, 1907.