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PHOTO-ELECTRIC THRESHOLDS AND FATIGUE

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Abstract

Photo-electric fatigue.—Using elements of the highest purity, clean surfaces were prepared, in a vacuum of the order of 10^{-6} mm of Hg, by means of an electromagnetic filing device. A linear relation was found between the logarithm of the photo-electric current and the logarithm of the time elapsed since polishing the specimen. The rate of fatigue depends upon the element used and the factors which produce fatigue and, for a given substance, increases numerically as the threshold is approached. Increasing the pressure increases the rate of fatigue. The action of light has a negligible effect.

Photo-electric thresholds.—The values for Ca, Fe, Co, Ni, Cu, Zn, and Ge are, respectively, 4475, 3155, 3165, 3040, 2955, 3180, and 2880A. Within a period of several hours at least photo-electric fatigue causes no change in these values when a high vacuum is used. Evidence for a shift towards shorter wave-lengths is obtained for lower vacua.

The "patch" theory.—A theory in which contamination takes place at discrete areas of the surface of the element is proposed to account for the experimental facts obtained.

IF RADIATION of certain frequencies is allowed to fall upon material substances, electrons are emitted from the latter, a phenomenon known as the photo-electric effect. If, however, the radiation frequency falls below a minimum value, depending upon the substance used, the effect ceases. The wave-length corresponding to this minimum frequency is called the photo-electric threshold. Much conflicting evidence has been offered on the question as to whether this threshold is an intrinsic property of the element under consideration or depends upon the condition of the surface upon which the radiation falls. If our present ideas regarding the structure of matter have any claim of representing even approximately its actual state, the probablity of obtaining a surface which is *absolutely* homogeneous seems very small. If we can produce conditions by which a fresh surface is prepared in a high—but not necessarily the highest—vacuum, any contamination which may take place, from any probable cause whatever, will probably take place slowly enough and at discrete areas of the surface so that, for a considerable time, certain portions of the original surface will continue to exist and to eject electrons corresponding to an incident radiation frequency which need not increase so long as any portion of the original surface continues to exist. A theory of this sort, along the lines of which Woodruff,[1] and Richardson and Young[2] have made suggestions, will be considered more in detail in connection with the data of this investigation. Before presenting the evidence the statement is made that, so far as these

* The writer wishes to express his thanks to Professor Ernest Merritt, Professor J. R. Collins, and Mr. H. W. Banta for their helpful suggestions during the progress of the work.

[1] Woodruff, Phys. Rev. **26**, 655 (1925).

[2] Richardson and Young, Proc. Roy. Soc. **A107**, 377 (1925).

experiments are concerned, a "patch" theory seems adequate for an explanation of the facts.

In this paper a report of photo-electric measurements, involving threshold determinations and fatigue effects, for a series of elements of the highest purity is made. The results are then discussed in connection with the patch theory. To determine the thresholds the photo-electric currents per unit intensity were plotted against the wave-lengths used and the curves extended until they intercepted the latter axis. This method involves the measurements of the intensity distribution of the incident radiation and the saturation currents corresponding to given monochromatic illuminations.

Measurement of the Intensity Distribution of the Incident Radiation

A Gallois quartz mercury-arc lamp[3] was used as a source of illumination, and monochromatic radiation was secured by passing the light through a Bausch and Lomb monochromator fitted with a constant deviation quartz prism. This monochromatic radiation was directed upon a sensitive linear thermopile connected to a Coblentz galvanometer.[4] The monochromator slit width used in the intensity measurements, as well as throughout the entire work, was 0.10 mm, a value which, in the spectral region used, was found to be effective in preventing overlapping of the lines. With a 120-volt storage battery as source, the lamp was operated with a potential difference of 84 volts across its terminals and a current of 2.60 amperes. With the aid of an inductance in series with the lamp, constant operating conditions could be maintained. In order to eliminate the disturbing effects from electromagnetic machinery in and around the laboratory upon the galvanometer all readings were taken very late at night or early in the morning.

The following table gives the average relative intensities of the lines measured, that of 2537A being taken arbitrarily as 100.

Table I. *Relative intensities of incident radiation.*

Wave-length	Intensity	Wave-length	Intensity
4259A	418.	2967A	70.0
4050	352.	2894	21.4
3650	479.	2804	34.8
3330	38.9	2650	76.3
3130	300.	2537	100.
3022	130.	2400	15.5

Measurement of Photo-electric Currents

The principle involved in measuring the photo-electric currents consists of placing the specimen at the axis of an evacuated cell which contains a metal cylinder, and charging this cylinder to a sufficiently high potential so that the electrons emitted from the specimen under the influence of the

[3] George, Rev. d'Optique **4,** 88 (1925).
[4] Coblentz, Bull. Bur. Stand. **9,** 56 (1913).

incident radiation will be drawn to the walls of the tube. The rate at which the specimen becomes positively charged, which can be determined by means of an electrometer, will be a measure of the current. As fresh surfaces of the element must be prepared in vacuum, the cell must also contain a device for the performance of this task.

The plan of the photo-electric cell is shown in Fig. 1. The specimen S is attached to a brass rod and insulated from the soft iron cylinder A by means of a fused quartz tube Q. The collar C contains a small hole and set screw for the purpose of connecting a wire, leading from the electrometer, to the specimen. B is another soft iron cylinder to which is attached a brass rod R and a file F. By means of electromagnets which may be slipped over the glass tubing the iron cylinders with their attachments may easily be moved back and forth. In order to prepare a fresh surface of the specimen A was moved backward and B forward until the file was in contact with the specimen and the rod R was in the guide tube R'. The electromagnet coaxial with A was then moved forward so that the specimen pressed firmly against the file. The latter could then be moved to and fro, and the filing easily accomplished When this was done the file could be moved out of the way into the position shown in the diagram. The specimen was then moved forward until it was within the cylinder of oxidized copper, O. This was connected by means of the wire L to the positive terminal of a 45-volt battery, the negative terminal being grounded. Monochromatic radiation passed through the quartz window W and impinged upon the specimen.

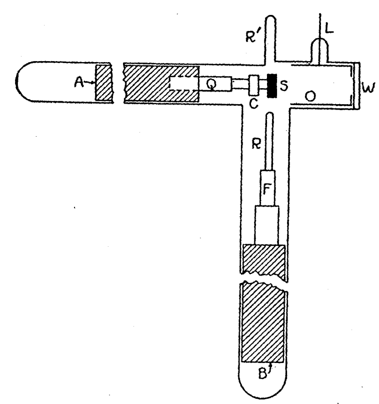


Fig. 1. Diagram of photo-electric cell.

When it was necessary to put a new specimen into the apparatus, the file was carefully cleaned and washed with alcohol. Great care was taken to see that no particles from the specimen previously used remained on this part of the apparatus.

The vacuum was produced by means of a two-stage, water cooled, mercury diffusion pump, backed by a Cenco Hyvac oil pump. There were also inserted in the system between the diffusion pump and the cell the customary liquid-air trap and a trap containing cocoanut charcoal. The latter could be heated and then cooled in order to adsorb residual gases in the system. A MacLeod gauge was used to measure pressures. On this instrument it was possible to estimate pressures of the order of 10^{-6} mm of mercury, and in the investigations here reported the minimum reading was obtained in every case.[5]

[5] Some investigators have reported the measurement of pressures of the order of 10^{-7} mm of mercury with a MacLeod gauge. The use of this instrument depends upon the applicability of Boyle's law at low pressures, which throws some doubt upon the validity of these measurements.

All the glass used was of Pyrex and on the high vacuum side of the apparatus there were no stopcocks or wax joints, with the following exceptions. The quartz plate (*W* in Fig. 1) was sealed to the cell with deKhotinsky cement. The wires, which were sealed into the glass, from the specimen and the oxidized copper cylinder, were of platinum. This metal does not make an absolutely tight seal into Pyrex, and a drop of deKhotinsky cement was used on the outside of the tubing at the two places where the wires were sealed into the glass.

The photo-electric currents were measured by the rate of drift method, using a Compton electrometer with a sensitivity of about 2000 mm per volt.

A special effort was made to secure elements of the highest purity for this work. The calcium and cobalt were obtained from Kahlbaum; the zinc was furnished by the New Jersey Zinc Company; the Bureau of Standards supplied samples of copper, iron, and nickel; and the Cornell University Department of Chemistry purified the germanium.

Variation of Current with Time: Photo-electric Fatigue

Although the photo-electric current was steady during the time required to take a set of readings for a given spectral line, all the elements showed fatigue during the course of the observational period. In order to make use of the readings in threshold determinations it was necessary that some method be devised to reduce the photo-electric current corresponding to each spectral line to a common time basis. This can be done conveniently and accurately, since the results of this investigation show that a linear relation exists between the logarithm of the photo-electric current and the

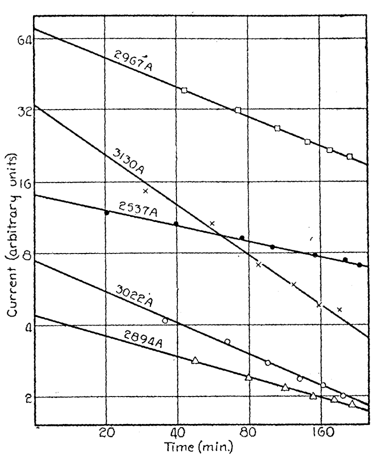


Fig. 2. Photo-electric fatigue in cobalt.

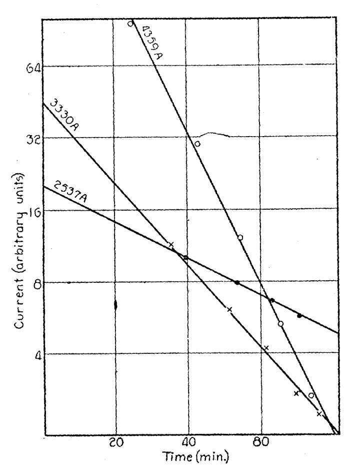


Fig. 3. Photo-electric fatigue in calcium.

logarithm of the time elapsed since polishing the specimen. Because of the static charges developed during the course of the polishing it was rarely possible to take accurate readings until at least ten minutes after the process was completed; but from this time until, in some cases, up to seven hours after polishing, this linear relation was found to hold consistently.

A number of typical curves showing the above relation will be found in Figs. 2 to 4. The ordinates are the reciprocal times for the spot of light on the electrometer scale to drift 10 cm, which are, of course, proportional to the currents; the abscissas represent the time after polishing, in minutes. Logarithmic paper has been used for the plotting of the curves. The order of magnitude of the ordinate scale is not necessarily the same throughout a single diagram; it was desired merely to exhibit conveniently the results corresponding to a number of monochromatic radiations for a given element.

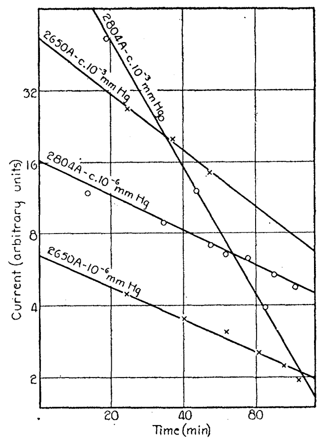


Fig. 4. Photo-electric fatigue in copper, showing effects of high and low vacua.

It will be noticed in the case of each element that the slope of the curve is greatest for the radiation from the spectral line of the longest wave-length from which it was possible to obtain an effect. It will also be noticed that the slopes of the curves become progressively less as radiation of shorter wave-lengths is used. This fact is perhaps most strikingly shown in the case of calcium. (See Fig. 3.) The range of wave-lengths covered is more than 1800A. The slope of the curve corresponding to 4259A, which is near the threshold, is -2.08; for 3330A, it is -1.15; and for 2537A, -0.51. The occurrence of this type of phenomenon is characteristic of all the elements investigated and indicates that the rate of fatigue increases as the threshold is approached. So far as these results show a greater decrease in the photo-electric activity in the regions of longer wave-lengths they are in agreement with those of Suhrmann,[6] although he makes no mention of having found a systematic relation between current and time.

It should be mentioned that, in the case of zinc, some observations were obtained in which the photo-electric current remained practically constant, or showed a slight increase, for about half an hour after the surface was scraped. Then fatigue set in, following the relation found in the cases of the other elements. There were observations, however, in which the zinc showed what may be called the "normal" behavior, and in view of the general consistency of this behavior in the cases of the other metals it has seemed reasonable for the present to attribute the above mentioned results to spurious effects, which have not yet been located.

It is interesting to notice that the rate of fatigue seems to be the greatest for calcium, an element upon which the gases in the atmosphere rapidly produce surface changes. For elements upon which the air seems to have less effect the decrease in photo-electric activity was much smaller, e.g. germanium showed the smallest fatigue effects of all the substances. In connection with this point, experiments made with copper in high and low

[6] Suhrmann, Ann. d. Physik **67,** 43 (1922).

vacua contribute some interesting information. Typical results are shown in Fig. 4. There it is easily seen that the rate of fatigue increases greatly with increase of pressure. In the case of the 2804 line the slope of the curve, under the best possible vacuum conditions, is -0.49; when the pressure is increased to the order of 10^{-3} mm of mercury, the value of the slope increases numerically to -1.76. In the case of the 2650 line the difference is not so great, although the effect is perfectly definite. These results indicate that the interaction between the residual gases in the apparatus and the surface of the element is a factor in producing fatigue. It must be stated, however, that these observations are not extensive enough to warrant the statement that gaseous contamination is the sole cause, or even the primary factor, in producing fatigue. This statement is offered as a precautionary one, although it should at the same time be borne in mind that much of the evidence obtained in this series of experiments may be offered in support of a gaseous contamination theory of fatigue.

Later in this paper a theory will be proposed which will account for the above facts, as well as those to be mentioned below. These experiments, however, show fairly definitely that the variation of photo-electric sensibility is not caused primarily by the action of light. This is in keeping with the findings of Hallwachs[7] and Allen.[8] The principal experiment on this point consisted of two series of observations on nickel, each lasting over a period of seven hours. In one case the specimen was illuminated continuously by light from the quartz mercury-arc lamp; in the second case, it was carefully shielded from the light except during the brief periods required for readings. The current-time linear relation was found in both cases and the slopes of the curves were identical within the limits of experimental error. These results indicate that the effect of light in producing fatigue is negligible. Other less extensive experiments conducted throughout this investigation are entirely confirmatory.

Photo-electric Thresholds

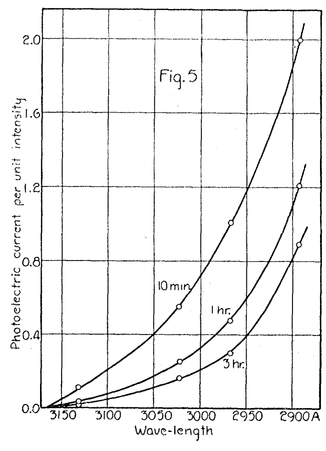
The general method for determining the photo-electric thresholds was as follows: The values for the currents corresponding to a given time after polishing were found from the fatigue curves already mentioned. From these values and the energy distribution of the incident radiation the currents per unit intensity were computed and plotted against the respective wave-lengths. The point where the curve cuts the latter axis will be the threshold.

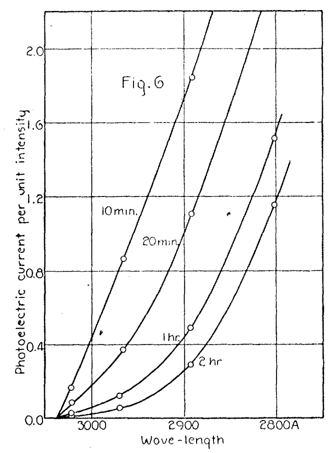
In Figs. 5 to 8 characteristic curves are shown. In Figs. 5 and 6 are plotted a series of curves showing the currents per unit intensity for different times after polishing the specimen. One very important characteristic may be pointed out at once: Although there is a large variation in the currents per unit intensity with time, the curves for a given element inter-

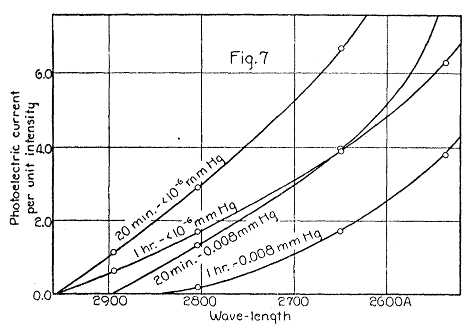
[7] Hallwachs, Phys. Zeits. **5**, 489 (1904).
[8] Allen, Ann. d. Physik **32**, 1111 (1910); Phil. Mag. **20**, 565 (1910).

sect at a common point on the wave-length axis, which indicates that, within the limits of experimental error, *there is no change in the threshold value.*

It is realized that in extrapolating a curve which is not linear, objections may be offered to the accuracy of the results. Every effort, however, has been made to draw each curve independently of the others. Check observations taken with an intervening period of from two to six months







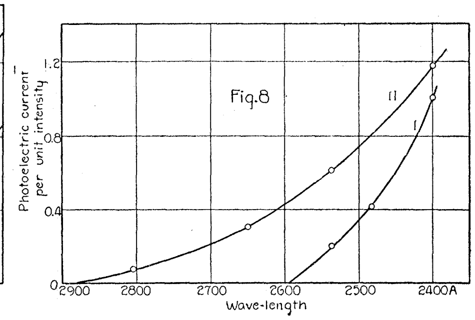


Fig. 5. Photo-electric threshold for cobalt.
Fig. 6. Photo-electric threshold for nickel.
Fig. 7. Photo-electric thresholds for copper with high and low vacua.
Fig. 8. Photo-electric thresholds for germanium: (I) prepared in air (II) prepared in high vacuum.

give values, the extremes of which do not differ (except in the case of calcium) by more than 20A. In the necessary cases filters were used to cut out any possible stray radiation from shorter wave-lengths. An analysis of the results indicates that the maximum error in determining the threshold probably does not exceed 10A. (In the case of calcium this value may be 20 or 25A.)

In Table II is given a list of the photo-electric thresholds determined in this investigation.[9] These photo-electric thresholds have also been con-

[9] The values for iron, cobalt, and nickel differ only slightly from those given in a preliminary report at the New York meeting of the American Physical Society, February, 1928. See Phys. Rev. **31,** 709 (1928).

verted into the equivalent values in volts of the energy required to release the photo-electrons from the element under the specified conditions.

TABLE II. *Results of threshold measurements.*

Element	Threshold	Work Function	Element	Threshold	Work Function
Calcium	4475A	2.76volts	Copper	2955A	4.18 volts
Iron	3155	3.91	Zinc	3180	3.89
Cobalt	3165	3.90	Germanium	2880	4.29
Nickel	3040	4.06			

For the purpose of comparison there are also given in Table III some of the threshold values obtained by other workers. It can easily be seen that there is considerable variation in the results taken as a whole. In making a general comparison of the results of this investigation with those of other workers, there seems to be no definite relation between the threshold values and the vacuum conditions of the experiments.

TABLE III. *Threshold values of other workers.*

Element	Hamer[10]	Hughes[11]	Richardson and Compton[12]	Werner[13]
Calcium	4000A	3700A		
Iron	2870			
Nickel	3050			2850A
Copper	2665		3090A	2750
Zinc	3425	3016	3570	

In the case of germanium it is interesting to compare the value given here with that found by the writer in a previous investigation using much poorer vacuum conditions.[14] (See Fig. 8.) The latter result was 2590A compared with 2880A in the former. The lower value indicates a shift which may, perhaps, be attributed to contamination by the atmosphere of the specimen before it was placed in a vacuum of the order of 10^{-3} mm of mercury.

That a shift in the threshold towards the shorter wave-lengths may take place in a moderate vacuum is shown in Fig. 7. The curves here show clearly that when a high order of vacuum is maintained there is no observable change in the threshold, but that there is a displacement towards the shorter wave-lengths coincident with an increase in pressure.

THE "PATCH" THEORY

In order to explain the fatigue phenomena and the constancy of the photo-electric thresholds, reference is made to the "patch" theory suggested

[10] Hamer, Jour. Opt. Soc. Amer. **9**, 251 (1924).
[11] Hughes, Phil. Trans. Roy. Soc. London, **A212**, 205 (1912).
[12] Richardson and Compton, Phil. Mag. **24**, 575 (1912).
[13] Werner, Upsala Universitets Årsskrift (1914).
[14] Welch, Jour. Opt. Soc. Amer. **14**, 233 (1927).

by Richardson and Young. The theory proposed here was suggested by that of Richardson and Young, but it has been developed along lines which will account for the results obtained in this investigation.

Let us suppose that the filing process produces a surface which is nearly, but not absolutely homogeneous. Or, if we assume a perfectly homogeneous surface, it is reasonable to suppose that within a short time it may become contaminated in spots. At present there is insufficient evidence for making any statement regarding the precise nature of this contamination or of the non-homogeneity of the surface. This, however, is unnecessary for the development of the theory up to its present state. Now, it may further be assumed that these patches increase in area and in "thickness." The term "increase in thickness" is used advisedly: it means nothing more than an increased retarding effect on the escape of electrons from the element.

Let us postulate a light quantum with energy $h\nu_0$. If the interaction between radiation and matter takes place in the region of the uncontaminated surface, an electron will be ejected. But if the interaction takes place at one of the patches, the retarding effect of this patch will not permit the ejection of the electron. If the light quantum has energy somewhat greater than $h\nu_0$ it will be effective not only in the uncontaminated areas, but also in the places where the patches are the thinnest. As the frequency of the incident radiation increases the area from which the electron emission can take place becomes greater.

If there is an increase in the size of the patches the area over which the light quantum $h\nu_0$ is effective is diminished. Radiation of frequency ν_0 will still be able to cause the ejection of electrons, but there will be fewer of them, and the current will be correspondingly diminished. If the thickness of the patches is also increasing there will be diminutions in the number of emitted electrons corresponding to higher frequencies. It by no means follows, however, that the thickness of the patches will increase at the same rate as their area.

Since the experimental results show a linear relation between the logarithm of the photo-electric current and the logarithm of the time, this relation may be expressed by the equation

$$i = Ct^{-\alpha}$$

where i is the photo-electric current, C is a constant depending upon the units, t is the time, and α is a quantity which is a function of the element used and the factors which produce fatigue and, for a given substance, increases numerically as the threshold is approached. Probably this relation is not strictly true, especially during the first few minutes after filing. When, under favorable circumstances, it was possible to obtain readings very soon after preparing the surfaces, the values were smaller than are required by the equation, which demands that the current be very large immediately after polishing.

It seems that a theory of patches, such as that outlined here, is adequate for the explanation of the results of this investigation. The increase in area and in thickness of the patches will account for fatigue and also for the differences in the rate of fatigue when the frequency of the incident radiation is varied. If the contamination of the surface takes place slowly there will occur for a long time the emission of the electrons with radiation of the "true" threshold frequency. This is verified by the fact that the threshold values do not change, within the limits of experimental error, for a period of several hours, at least. If the experiments were carried on over a period of several days, the threshold would perhaps be shifted towards the shorter wave-lengths. At any rate, the electron emission from the specimen would, for radiation near the threshold frequency, probably be so small that it could be detected only with an electrometer of very high sensitivity, if at all.

If the patches are produced, wholly or partly, by gaseous contamination, as the experiments on copper and germanium suggest, it should be possible to obtain further information by introducing known gases at different pressures into the photo-electric cell. An investigation of this type, however, would necessitate an extensive study of the surface chemistry involved.

There is, of course, the possiblity that contamination at the surface of a metal may produce an increase in its photo-electric activity. These experiments have given no definite evidence for the existence of such a phenomenon, although at present there seems to be no reason for its being inconsistent with the "patch" theory.

The details of the theory and their experimental verification have not been carried to the point where, in the mind of the writer, their application to existing data may satisfactorily be made. In particular, one possible cause of contamination remains be to investigated: the effect of vapors from the deKhotinsky cement where the quartz window was sealed to the apparatus. Up to the time of this paper it was not possible to secure a satisfactory quartz to Pyrex seal in order to eliminate these possible vapors. Plans for the carrying out of a series of experiments with this type of apparatus are under way and it is hoped that it will soon be possible to publish the results.

CORNELL UNIVERSITY,
June, 1928.