CERTAIN CHARACTERISTICS OF LIGHT-NEGATIVE
SELENIUM.

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THE change of resistance in light-positive selenium under the action of light occurs in one of two distinct types. Which is followed seems to depend in some manner upon the magnitude of the change, or, in other words, upon the sensitiveness of the unit.¹ When units of low sensitiveness, which are also of low resistance, are exposed to light, their conductivity increases rapidly at first, and then more and more slowly, while the conductivity of the high sensibility, or high resistance units rises quickly to a maximum value, and then falls off more and more slowly. But whichever type of action is followed, the selenium always shows an increase of conductivity immediately after exposure to light.

Ries² records the action of a selenium unit, where the fifth day after its manufacture the falling off in conductivity after the maximum had been reached was great enough to bring the conductivity in the light to a value below that which it had shown in the dark. But he concluded that this strange effect was due to the presence of moisture.

The first selenium units which decreased their conductivity immediately upon exposure to light were reported in 1910 by F. C. Brown,³ and termed *light-negative*. Six of these units were made, all of which showed a very low resistance, five hundred to ten ohms, and one had even a less resistance. The sensibility of these units was never above fifteen or twenty per cent.

The discovery of light-negative selenium opened up two new fields of investigation: first, the problem of ascertaining the conditions necessary for the reproduction of such units at will, and second, the determination of the characteristics of those units which were already made.

The method used by Dr. Brown in the production of his light-negative selenium was somewhat as follows: He powdered the black, glassy selenium and placed it upon an ordinary porcelain insulating cleat which had been wound with a double spiral of German silver wire. Enough selenium was placed upon this cleat to give a surface of about two square

¹ "Unit" is used in this paper in preference to "cell."

² Phys.-Zeitschr., Vol. 9, 1908, p. 569.

³ Phys.-Zeitschr., II. (1910), 481, also PHYS. REV., XXXIII, p. 1, 1911.

centimeters. The porcelain was heated in air for perhaps half an hour and then allowed to cool to approximately 100° . It was reheated in a sand bath or oven slowly to about 210° and very slowly cooled. In each case it was taken from the oven when the temperature was not lower than 100° . These units were made by Dr. Brown in the winter and early spring of 1910. My attempt at their reproduction was not begun until the fall of 1910. After three months' work, with the opportunity of counsel with Dr. Brown, and under similar conditions, I was still unable to reproduce light-negative units. I did make one that for a time had an extremely low negative sensibility. Its resistance was about 25,000 ohms. All other units that were crystallized by this method were of very low sensibility. The possible variations in conditions and the length of time required to make one unit conspired to make the search for the proper conditions a tedious one. The conditions essential to the successful manufacture of the light-negative units are yet unknown.

PROBLEM AND METHOD.

In an attempt to get at the real nature of these cells their characteristics were investigated along the following main lines:

1. Variation of conductivity with intensity of incident light.
2. Variation of conductivity with time of exposure.
3. Variation in form of recovery curve with intensity of incident light.
4. Variation in form of recovery curve with time of exposure.

But one of the units at hand (made by Dr. Brown) could be used satisfactorily. Its resistance lay between 280 and 309 ohms. The best readings were all taken when this resistance was from 290 to 295 ohms.

The selenium unit was made one arm of a Wheatstone bridge. The resistances of the arms were approximately equal. The voltage across the selenium was always less than one volt. A sensitive galvanometer with a period of 2.6 seconds was used. It gave a deflection of 2.9 centimeters for each .1 ohm change of resistance in the selenium arm. The source of light was a forty-watt tungsten lamp, mounted upon a photometer bar. This sort of lamp was superior to a carbon lamp because it gave less radiant heat per candle power and showed less fluctuation of candle power with voltage. The constancy of candle power was obtained by constancy of voltage, an approximation sufficiently accurate.

To guard against outside disturbances several precautions were taken. To avoid moisture and sudden changes in temperature, the unit had been placed in a bath of paraffin oil upon manufacture, and was left there. The vessel containing the unit was placed inside a larger vessel, which was all blackened except a space directly in front of the sensitive surface

of the selenium. The two vessels were placed inside a blackened paste-board box. This box was suspended by a cord to cut off the effect of shocks or jars. To eliminate electrostatic induction, the outside of the box was covered with tin foil. The room was only partially darkened, but the selenium was properly shielded by screens of black paper placed on the photometer bar. Temperature readings were made by a thermometer placed in the oil just above and to the front of the sensitive surface of the selenium. The precautions stated above did not eliminate unsteadiness; in fact, whether or not they were of definite assistance was not ascertained.

With the selenium in the dark, the bridge was balanced as closely as convenient. The deflection was read, and then the light from the lamp, which was at a given distance, was suddenly thrown upon it, and the deflection of the galvanometer read every few seconds during the period of exposure. Periods of exposure lasting one, two, and three minutes were taken, after which the light was suddenly cut off, and in each case the galvanometer deflections were read every few seconds during the first one or two minutes of recovery. Two or three complete sets of readings were taken for each time of exposure at the given distance, and then the lamp was moved out to such a position that the intensity would be one half its first value, and the same operation repeated. The law of inverse squares could be applied without serious error due to area of source. Four such positions of the lamp were used and much time spent in trying to get readings at a fifth position, but the cell had become so unsteady that this could not be conveniently done. The temperatures and initial resistances were recorded for each exposure.

EXPERIMENTAL WORK.

Unsteadiness.—At the outset difficulty was encountered, for the selenium under observation had no definite steady resistance even in the dark. At times there were small rapid variations in resistance, amounting to something like one or two tenths of an ohm in either direction. At other times the unsteadiness of the selenium manifested itself in long gradual shifts of resistance, which might take place in either direction with apparently equal ease. These long steady sweeps might amount to as much as one, two, or even three ohms. If one considers that the largest effect produced by the influence of light was a change of only five tenths of an ohm, the impossibility of taking readings when the cell is in an unsteady state will be apparent.

When work was first begun upon the cell, its periods of instability were not very frequent, and consequently not very annoying, for it was

noted that when the cell remained steady before the light was thrown upon it, it seldom became more unsteady upon exposure. After the selenium had been used for two or three weeks the time between steady periods became longer and longer.

In general, a jar caused an increase in resistance, although it hastened the recovery to dark conductivity after an exposure was made. A sudden change in temperature made the unit extremely unstable, causing the conductivity to change back and forth in a most irregular manner. The temperature changes undergone during the night time may have accounted for the fact that the selenium was found to be more stable in the afternoon. The unsteadiness could scarcely have been due to loose contacts external to the unit.

When all disturbances were guarded against as thoroughly as possible there still remained an instability which must be due to something in the selenium structure itself.

RESULTS.

Light-Negative Action.—In Fig. 1 a portion of the data is plotted. The heavy vertical line indicates the time at which the light was cut off. This figure shows the three-minute exposure curves with the four different intensities of light used. It will be seen that in only a few cases do the curves exactly agree with one another during the exposure, while during the recovery even a wider disagreement is shown. Therefore, before any generalizations could be drawn the mean curve had to be determined.

Fig. 1.

Through the points in the curves so drawn, the best smooth curve possible was drawn for each single exposure and recovery, and from these curves the centimeter deflections were read for the times 10, 20, 40, 60, etc., seconds after exposure, and for the same times after the light had been cut off. From these values of the deflection, and from the initial value of the conductivity in the dark, the percentage change of conductivity was computed for each deflection so read. The mean percentage change of conductivity for the given times, at the given intensities, were determined and plotted as the ordinates in the curves of Fig. 2. It is

evident that the deflection after an exposure of one minute should be the same, whether the light were thrown off at the end of that minute or left on for a longer time, and hence for the one-minute curves of Fig. 2 an

Fig. 2.

average has been taken of the percentage change observed during the one-minute exposure, together with the same observed during the first one minute of the two- and three-minute exposures. Likewise, for the two-minute curves an average was taken of the values obtained during the two-minute exposure with those obtained during the first two minutes of the three-minute exposure. Of course this was not possible in case of the recovery curves, so the recovery curves are each simply the average of two or three sets of observations, while, for instance, the one-minute exposure curves are each the average of as many as eight sets of observations.

The curves given in Fig. 2 show several points. The more intense the incident light (the intensities are shown by indicated points in Fig. 3),

Fig. 3.

the greater is the total change in conductivity for a given period of exposure. With an intensity one half as great the change in conductivity

observed is more than one half as great. The curves of Fig. 3 show the relation between the percentage change of conductivity and the intensity of the incident light, for periods of exposure of one, two, and three minutes respectively.

As to what relations we should have expected from consideration of the light-positive cells it would be hard to say, considering the various formulæ that have been established by different investigations.¹

However, I have replotted my curve between change of conductivity at the end of three-minute exposure and intensity, using the distances from the source as abscissæ, so this curve might be compared with a similar one of Carpini reproduced by Ries. Curve I., Fig. 4, is the partial curve on an enlarged scale for the light-positive unit of Carpini, while Curve II. shows the light-negative one used in this investigation.

Fig. 4.

Fig. 5.

The two curves are in general the same shape, in fact, the agreement between the action of the light-negative and that of the light-positive units, under exposure to light of various intensities, is quite as close as that between two samples of light-positive selenium.

We also see that the longer the time of exposure the greater is the total change of conductivity for a given intensity of exposure. The relation between the conductivity change and the time of exposure for the four different intensities investigated are given in the curves of Fig. 5.

Another thing which seems apparent from the shape of the curves is that the less intense the light, the more quickly does a given per cent. of the total change take place, that is, the more quickly does the conductivity-time curve become parallel to the time axis. To show more plainly that this is true the scale to which each curve is plotted has been changed until, at the end of three minutes exposure the change in conductivity, so plotted, comes to the same point for all four intensities.

¹ See Chap. VIII., Ries, Die Elektrischen Eigenschaften und die Bedeutung des Selen für die Elektrotechnik.

Curve I., Fig. 6, represents the change produced by the action of the faintest light, while Curve IV. represents that produced by the action of the most intense light.

The recovery curves are seen to be, in general, the reverse of the exposure curves, sloping sharply at first, and then more and more slowly approaching the original value of the conductivity in the dark. The greater has been the total change, the less complete is the recovery within a given time after the light has been cut off. Curves in Fig. 7 show that

Fig. 6.

Fig. 7.

when the scales of plotting have been reduced, as in Fig. 6, for the exposure curves, that the same per cent. of the total recovery is reached first where the total change has been least. This is an effect similar to that shown in Fig. 6 for exposure to lights of different intensities.

Curve I., Fig. 8, shows the percentage change in conductivity after

Fig. 8.

the selenium has been allowed to recover for one minute from an exposure of one minute, plotted with the intensity of the light to which it has been exposed. Curves II. and III. show the same for one-minute recoveries from exposures of two and three minutes respectively. These are all long, slightly concave, curves.

The next set of curves shows the percentage change in conductivity after the selenium has been allowed to recover for one minute from an exposure to lights of given intensities, plotted against the time of exposure. Curve IV., Fig. 9, represents the relations for an exposure to the most intense light, while Curve I. represents the same for an exposure to the least intense light. These are also long curves, but are slightly convex.

Fig. 9.

While the curves of Figs. 8 and 9 are not of the same shape, yet the curvature is so slight in each case that, in general, they show an agreement in the light-negative units with the facts found by Miss Louise McDowell in regard to the Bidwell type of light-positive units. She states¹ "the effect of increased duration of excitation upon the form of recovery curve is similar to the effect of increased intensity."

Light-Positive Action.—When the unit was first put in use several weeks elapsed before it was observed to act at any time as a light-positive

Figs. 10-11.

unit.² But as the work progressed this happened an increasing number of times, until, in all, eleven cases of this light-positive action were recorded. Some of these positive deflections were followed closely. Fig.

¹ PHYSICAL REVIEW, XXIX., p. 35, 1909.

² Brown in an article previously cited reports this light-positive action as occasionally observed in some of the other units.

10 shows the form of one type of action, both after the light has been thrown upon the selenium, and after it has been cut off. The exposure curve is of the form of the regular exposure curves observed with a Ruhmer unit, while the conductivity curve after the light is off reminds one of the recovery curve for the light-negative unit. At least three such cases as this occurred.

After plotting this curve, the occurrence of its exact opposite was recalled, and its appearance watched for. It was never caught, however, except in the case of the partial curve plotted in Fig. 11. Here the exposure curve is of the light-negative form, while the recovery curve is similar to that of the light-positive unit.

One surprising thing about this light positiveness in the light-negative unit is the ease and suddenness with which it comes and goes, leaving no trace of itself. The table below will show this point well.

	Time.	Interval.	Resistance in Ohms.
Fig. 4. Curve II. Negative . . .	5:56	6 min.	291.01
Fig. 10. Positive	6:02	11 min.	290.97
Fig. 4. Curve III. Negative . . .	6:13		290.7

It is seen that a perfectly regular light-negative curve was taken, then within a period of six minutes the light-positive curve of Fig. 10, while within another period of eleven minutes it has regained its former character and gave another perfectly regular light-negative curve.

It seems that all this simply shows how nearly this selenium is existing in the two forms at the same time. In the earlier part of this article we noted how the high resistance selenium had a high sensibility, and how the sensibility decreased with resistance through several types. Now if we can think of the resistance becoming so low that the sensitiveness passes through a zero point, and then to a negative value, we can understand how the units whose negative sensitiveness is as low as that of the one we are discussing, would be existing so close to the border line of sensitiveness that the sudden darkening or lighting might be a sufficient stimulus to throw from one form over into another.

A second unit of resistance close to five hundred ohms was set up, but it was found that it was even more unsteady than the unit of three hundred ohms which had been used. Perhaps this might have been expected, for the higher resistance would seem to indicate that this unit was existing still closer to the border line of sensitiveness than the former one.

Impurities.—The question first asked when the light-positive action of selenium was discovered was whether or not the whole effect was not

due to the presence of an impurity such, perhaps, as a selenide formed by the selenium and the metal of the electrode. Pfund¹ answered this question by making sensitive units using carbon, which will not combine with selenium, as his electrodes.

In the manufacture of his units, Dr. Brown used German silver wire which the selenium attacks to some slight extent, but the cells of Ries which approximate those of Brown were made with carbon electrodes. No attempt has yet been made to manufacture the light-negative units using carbon.

The striking similarity which we find between the action of the light-negative and that of the light-positive selenium makes it probable that this negative effect is due to some peculiar structure of the selenium itself, or due to an impurity which will act in a similar manner to the selenium. It may be that if impurities affect the manufacture of these units they act simply to aid in the formation of the crystals or an arrangement of them such as may be necessary to cause light-negative action. Indeed, this seems the more reasonable, for selenium is unique in its sensibility to light.

Temperature Effect.—In this limited investigation nothing was attempted to show the effect of differences in temperature upon the dark resistance of the selenium, yet with each observation the temperature and dark resistance were both recorded in hope that some correction for temperature might be applied.

So irregular were the relations found between the two that no statement could be made in regard to the variation one with the other, whether we consider all the readings or only those for a single day. Brown² shows that within certain limits the conductivity is increased by a rise of temperature.

SUMMARY.

It is impossible to make any general statements concerning light-negative selenium, but so far as the selenium unit here investigated is concerned, the following conclusions are in agreement with experiment:

I. The making of light-negative selenium seems to require very particular conditions which were not ascertained after several months of effort.

II. The resistance of the light-negative selenium is very unsteady, both in the light and in the dark.

A sudden jar or a sudden change in temperature adds greatly to this unsteadiness.

¹ Phil. Mag., Vol. 7, p. 26, 1904.

² Phys. Rev. XXXIII, p. 1, 1911.

III. The change in conductivity of the light-negative selenium when exposed to light is very small, being less than one per cent.

IV. Exposure Curves:

1. Change of conductivity increases with increased intensity of light, but not proportionately.
2. Change in conductivity increases with time of exposure, rapidly at first, and then reaches a nearly steady condition.
3. With a faint light the larger per cent. of the total change takes place within the first few seconds of exposure.

V. Recovery Curves:

1. In general, they are the reverse of the exposure curves.
2. The more intense the light to which the selenium has been exposed the less complete is the recovery in a given time after the light has been removed.
3. The longer the selenium has been exposed to the light the less complete is its recovery within a given time.
4. The less has been the total change in conductivity during exposure the greater is the per cent. of recovery taking place in a given time.

VI. Sensibility of the light-negative selenium seems to exist so close to the border line of sensitiveness that a slight stimulus will completely change its sign.

VII. The evidence indicates, but does not prove, that the negative effect is due to the selenium structure itself and not to an impurity present.

I wish to express my thanks to Professor G. W. Stewart, under whose supervision these experiments were conducted, and also to Professor F. C. Brown for his kindly interest in the progress of the experiments.

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