

1912

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Recommended Citation

Brown, F. C. (1912) "The Effect of Rupture by Abrasion on the Electrical Conductivity of Selenium," *Proceedings of the Iowa Academy of Science*, 19(1), 179-184.

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THE EFFECT OF RUPTURE BY ABRASION ON THE ELECTRICAL
CONDUCTIVITY OF SELENIUM.*

BY F. C. BROWN.

Sometime ago while filing away the surface of the selenium in a Giltay cell in order to find out directly certain limits on the depth of penetration of selenium by light**, I discovered a new effect.

This effect of mechanical rupture on light-positive selenium resembles in a general way the many other well known effects in these varieties of selenium. Rupture produces an increase in the conductivity, but this increase is not permanent. The recovery is extremely slow, often requiring more than a month for the selenium to attain the electrical condition existing before rupture. The experiments are especially interesting because of their bearing on the dynamic equilibrium theory of light sensitive selenium.***

The three components of selenium exist in dynamic equilibrium in a sort of solid solution. But the equilibrium is constrained to act in certain regions or configurations. The rupture of the surface of the selenium necessarily destroys this configuration, and consequently the equilibrium condition. The restoration of the equilibrium condition reminds one of the restorative growth of crystals, such as is well known to occur when certain large crystals have been fractured or broken.

The rupture mentioned has been produced by the author by filing and by Giltay by a sand blast. The method of procedure was to file away uniformly the surface of the selenium from between the wires of a Giltay cell. The selenium that was filed away was generally weighed in order to estimate the relation between the conductivity and the amount of selenium and also to ascertain the effect of continued filing.

THE PRODUCTION OF THE RUPTURE.

I shall first describe the method of production of the rupture which Mr. J. W. Giltay had the kindness to describe to me in a letter. His account reached me only a few days after I had completed my preliminary experiments on this subject, and while he does not give the dates of his experiments it is entirely possible that he discovered the phenomenon first.

The rupture was produced by Giltay by a mild sand-blasting. The apparatus used by him is shown in Fig. 1, and is described in his own words as follows: "The sand falling apparatus consists of a square wooden tube, ending at the upper end with a conical piece and at the lower end in a box. In this box is placed a wooden frame in a slanting position as shown. This frame carries a net of wire on which the article to be sand blasted is placed. In the box is also placed a wooden drawer, of which two are required. One of these drawers

*The results published in this paper were also published in the *Physikalische Zeitschrift* under date of Nov. 15, 1912.

**See paper in *Phys. Rev.* 34, p. 201, 1912.

***See *Phys. Rev.* xxxiii p. 403.

is filled with sand and the sand falls into the other one that stands in the box. Then the full drawer is taken out and replaced by the other one, and the same play is repeated as often as required." In Giltay's apparatus the rupture is produced by the sand falling against the surface of the selenium.

My method of producing the rupture was by the use of a fine swiss file, so ground that it would remove the selenium from between the wires but would not act on the wires. It is difficult to say just what would be the difference in the rupture produced by the file from that by a sand-blast. Perhaps the file would be more coarse in its action. However, as far as the facts go there is no indication of any difference in the rupture by whichever method it is produced. If so the filing method has the advantage in that the amount of selenium removed can be determined.

THE RUPTURE EFFECT.

The discovery of this new effect was somewhat accidental. I was using a file to remove the surface layers of the selenium in a Giltay cell, in order to find out if all the selenium on the cell were conducting, and also with the hope of increasing the light sensitiveness, i.e., the ratio of the conductivity in the light to that in the dark. The first test showed the conductivity to increase when the selenium was filed away. In the second test the selenium, about 0.06 gm., between eight parallel wires of the Giltay cell was considered. The conductivity in the dark was 87 scale divisions. After filing away a very small amount of selenium from all over the surface, the conductivity actually increased five fold. More than one-half of the selenium was removed before the conductivity in the dark fell as low as 170 div. By continuing the process until only a thin film of selenium was remaining, the conductivity fell after 24 hours in the dark to 20 div. The light sensibility was then 66 to 1, by a test that gave about 30 to 1 prior to the surface rupturing. The conductivity both in the light and in the dark was at first increased by the filing action. This indicates a change in the properties of the selenium by the action.

Giltay's discovery was also somewhat accidental. He states: "I had two cells, both showing somewhat bluish color as sometimes happens with my cells ———. The dark resistance was

for 31b. $R=190,000$ ohms, and in diffuse light $R/22.5$

for 32b. $R=300,000$ ohms, and in diffuse light $R/25$.

As the cells when blue do not look well, I treated No. 31b with the sand blast so (see Fig. 1) in order to get the usual color of the selenium surface. I expected the resistance and also the sensitiveness to get somewhat larger, owing to the selenium layer getting somewhat thinner. After having been sand-blasted both cells were put into the dark box, and the next day both cells were measured again. This showed:

31b. $R=70,000$ ohms, and in diffuse light $R/8.2$

32b. $R=300,000$ ohms, and in diffuse light $R/25$

After 15 days both cells were again measured. The temperature of the room, ——— was much lower now, ———. The cells now showed:

31b. $R=140,000$, in diffuse light $R25R/25$

32b. $R=430,000$, in diffuse light $R/44$

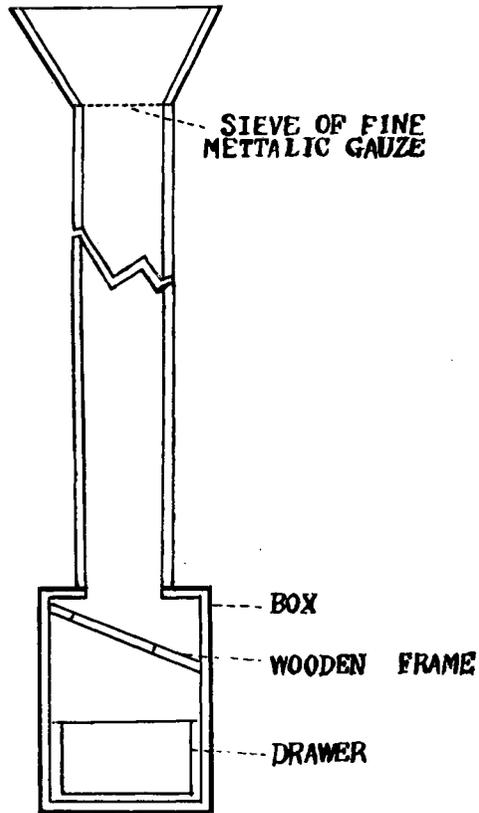


Fig. 1

This seems to prove that the dark resistance was lowered by the sand-blast, and also that the sensitiveness was lowered the same as by heating the cell. ——— I must add however that I have only once made this experiment owing to lack of time." ———

It may be noted here that after the fifteen-day interval, cell 31b increased its resistance by 100 per cent, while in the same time 32b increased by only 43 per cent. It is probable that the amount of the increase by the latter was for both cells due to temperature change, but the additional apparent increase was no doubt merely a recovery from the sand-blasting effect.

THE SLOW CHANGE FOLLOWING RUPTURE.

It was after I noted that in Giltay's experiments the selenium apparently recovered from the sand-blasting effect that I looked for a recovery from the filing action. The conductivity did decrease very slowly in the different tests that were made. The following table gives a sample of one set of observations:

1	.0022 gms.	Jan. 13,	9:25 A. M.	2.5 at 25°C	86	34 /1			
			9:30	18.					
			9:45	15.					
			12:00	14.4					
			3:00 P. M.	13.					
			5:00	12.			215	18 /1	
			Jan. 14,	12:00			8.6 at 23°C		
			Jan. 15,				7.4 at 22°C		
			Jan. 17,				6.5 at 22°C		
			Jan. 18,				6.3 at 22°C		
Jan. 23,		6.0 at 21°C							
2	.0098 gms.	Jan. 24,	10:40		53	21 /1			
			11:00	3.0					
			Jan. 25,				2.5		
			Jan. 26,				1.8 at 20°C		
			Jan. 29,				1.7 at 21°C		
			Jan. 30,				1.4 at 19°C		
3	.011 gms.	Feb. 16,	8:00		49	38 /1			
			8:05	1.4					
			10:30	1.1					
			3:00 P. M.	.75					
			Feb. 17,				.5	12	24 /1
			Feb. 20,				.45		
			Mar. 11,				.2 at 26°C	8.8	44 /1
			Apr. 3,				.16 at 24.5	7.9	48 /1
			Apr. 29,				.14 at 24°C	7.8	56 /1

The foremost fact that is clear from a study of the table is that the filing changed the electrical properties of the selenium. After the first removal of the selenium by the file the conductivity increased as a result from 2.5 to 18.0, and that in the light from 86 to 215. The treatment however was given in the diffuse light of the room and consequently a small part of the increased conductivity in the light must be explained as due to incomplete recovery from the light. But the increased conductivity in the light can not be explained otherwise than on the basis of altered properties of the selenium. The amount of the increase of conductivity seems to diminish after the first filing.

In all instances it is clear that there is a slow decrease in the conductivity after filing, much slower than any change in selenium by any other known

agency. After the third filing on the sample just mentioned, the conductivity of the sample was still changing slowly after a period of more than two months. It is not so clear however whether all the change is of the nature of recovery toward the same condition prevailing before the filing process began. There was probably 0.06 gram of selenium on the sample of the cell. After removing somewhat more than one-third of this amount and waiting for equilibrium the conductivity was 0.14, or only about one-twentieth of what it was before the removal. It would seem from this that a large part of the change was not a recovery. Another set of observations for another sample of selenium is shown by the curves in Fig. 2. By the third filing which took place on the fifth day less than one-half of the selenium was removed and yet the conductivity was reduced from 7 to 1.7 finally. It may be that not only the removed selenium but also that near the surface is rendered incapable of conducting. As is well known* the light-sensitive selenium is reduced by powdering to the non-conducting amorphous form. The surface of the cell does present a black, glaring appearance, like the vitreous selenium, after the filing. However it seemed to me that the surface color changed during the course of a month to the usual gray.

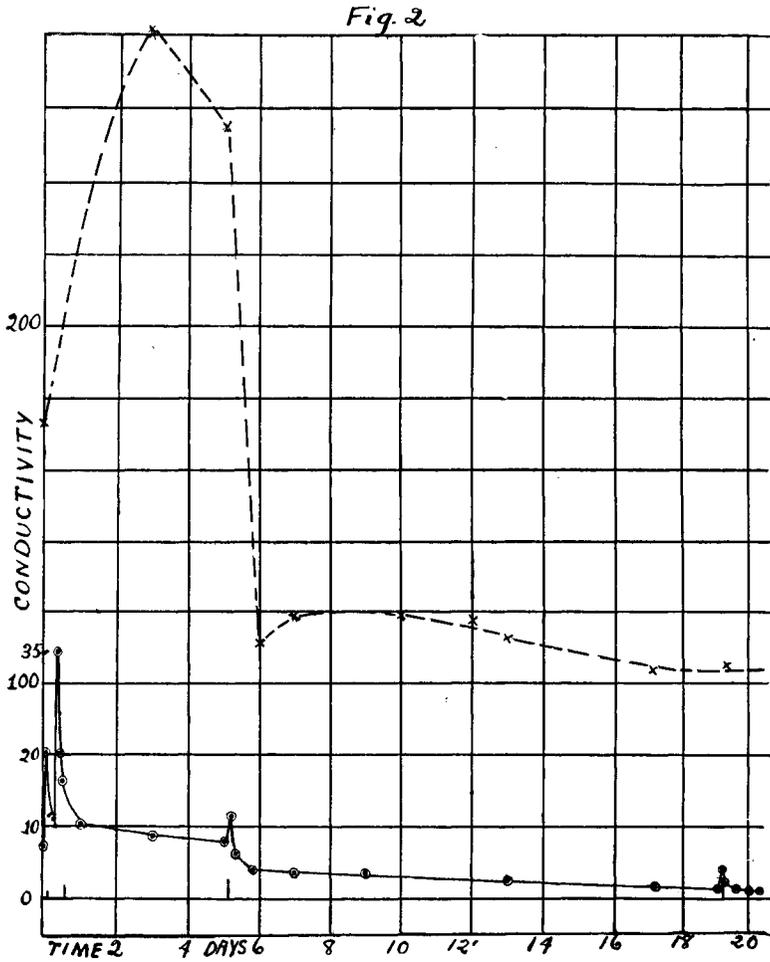
THE NATURE OF THE EFFECT COMPARED TO OTHER EFFECTS.

The only other known mechanical effects that might be related to the one described in this paper, are probably the pressure effect and the radium effect. Pressure does decrease the resistance to a most remarkable extent** but the effect displays little or no hysteresis. The resistance returns to its original value very quickly. In fact I know of no other effect from which the recovery is so rapid. However Montèn later observed that with pressures as large as 30,000 atmospheres there was a slight hysteresis effect. This difference between the pressure effect and the rupture effect is probably what is implied in the names. The hydraulic pressures applied were uniform on the surface and so took no part of the selenium beyond the elastic limit, while by filing or sand-blasting parts of the selenium were actually broken off, and perhaps a large part of the surface crystals were strained beyond the elastic limit.

One might expect that the rays from radium would produce an effect of the nature of rupture by abrasion. In the paper by Brown and Stebbins (loc. cit) the results of short exposures to radium of 2,000,000 activity are described. The decrease of resistance was of the same order of magnitude as that produced by abrasion. Also the recovery is slower than it is from light exposures, but not so slow as the recovery from filing. Therefore it is quite possible that the radium effect is a rupture effect. A study of long exposure of selenium to radium, perhaps many days, would give further evidence on this point. No doubt the resistance would continue to decrease until the radium were removed, instead of reaching an equilibrium condition in a few minutes as happens with light exposures of corresponding intensities.

*See paper by A. P. Saunders, Jour. Phys. Chem. 4, p. 423.

**See paper by Brown and Stebbins, Phys. Rev. 26, p. 273, and also by Montèn, Archiv for Math., Astr., och Fysik, 4, p. 1, 1908.



THE EFFECT OF ABRASION ON LIGHT-NEGATIVE SELENIUM.*

The fact that light-negative selenium is unstable and increases its resistance by merely jarring, would lead one to expect that rupture by abrasion would produce a similar increase, rather than the decrease produced in light positive selenium.

The unit of light-negative selenium which I tested had a resistance of about 19.2 ohms in the dark with .14 volts across its terminals, and 20.7 ohms when exposed to the diffuse light of the room. After rubbing a file across one quarter of the selenium surface, the resistance increased to 26.2 ohms. And after merely drawing the file across the second quarter it further increased to 28 ohms, and again similar treatment to the third quarter caused the resistance to rise to 36.9 ohms. As I did not wish to risk spoiling the sample unnecessarily I did not carry the treatment further. After one week in the dark, the resistance had recovered to only 34 ohms in the dark. When two months had elapsed the conductivity had recovered to 20.7 ohms in the dark and 21.8 ohms in the light of the room. It should be noted that the recovery was almost complete and also that the process was just as slow as was the recovery with the light-positive selenium. It is interesting and important that the abrasion effects are of opposite sign in the light-positive and light-negative selenium, and also that the effects appear otherwise alike.

THE NATURE OF THE EFFECT.

The most elementary explanation of the rupture effect by abrasion may be based on the kinetic theory of matter, in which the essential constituents of the matter are constrained to act within certain configurations. When the light-sensitive selenium is in equilibrium in the dark, the moving parts are constrained within certain configurations, or fixed boundaries, perhaps the boundaries of the crystal surfaces. The same boundaries may prevail more or less when the selenium is exposed to light. The filing for example destroys these boundaries and so the moving parts of the selenium begin readjusting slowly until a new equilibrium is established. The parts of the selenium must be in motion all the time. The abrasion merely puts these motions out of their usual course. The electrical conductivity fortunately in selenium signifies whether or not the equilibrium state is reached with certain parts or how fast it is being approached. Probably all matter of crystalline structure undergoes similar changes as a result of rupture, but unfortunately most forms of matter do not show in a pronounced way this electrical change as a counterpart.

In two previous papers on the nature of light action in selenium,** I showed that the various kinds of behavior of different varieties of selenium, under the action of light, could be explained by assuming three components, which were in equilibrium according to the reaction $A \rightleftharpoons B \rightleftharpoons C$. The rates of change maintained one set of fixed values in the dark and another in the light. It was necessary to assume that the different varieties of selenium had different initial rates of change in the dark, but no explanation was offered as to why this should be true, i. e. why all selenium should not tend toward the same equilibrium value and the same conductivity in the dark. It was suggested however

*See paper by F. C. Brown in Phys. Zeits. 11, p. 482, 1910, and also paper by Lilah E. Crum, on Some Characteristics of Light Negative Selenium, 33, p. 538, 1911.

**Phys. Rev. 33, p. 1 and p. 403, 1911.

that perhaps in the making of any variety of selenium that something in the selenium itself causes it to maintain given rates of change. On this view definite rates of change establish definite configurations, and the one must go with the other in any equilibrium state. If filing destroys a fixed configuration it must also alter the rates of change. The fact that different varieties of selenium can have different rates of change under the same temperature, pressure, humidity and electrical conditions, merely proves that there is another condition which varies in different samples of selenium, and further indicates that that this varying condition may lie in the selenium itself. If so the condition would be a matter of history. It is really not strange that the previous treatment of the selenium should determine its fixed rates of change and properties also. Rupture by abrasion perhaps undoes a certain amount of history, and further perhaps may make possible a growth or change under altered conditions. In any event it is necessary to regard light-sensitive selenium as made up of changing and moving parts, which reach equilibrium but never come to rest.

SUMMARY.

1. The effect of rupture by abrasion has been studied on both light-positive and light-negative selenium.
2. The specified types of rupture produce a temporary increase in the conductivity of the selenium of the Giltay cell.
3. Rupture of the same nature produces a change of conductivity in light-negative selenium of opposite sign to that in light-positive selenium.
4. Both varieties of selenium recover from the effect, but more slowly than they recover from any other known agencies, that alter the conductivity.
5. The changes in conductivity following rupture are favorable to certain views of the kinetic theory of matter.

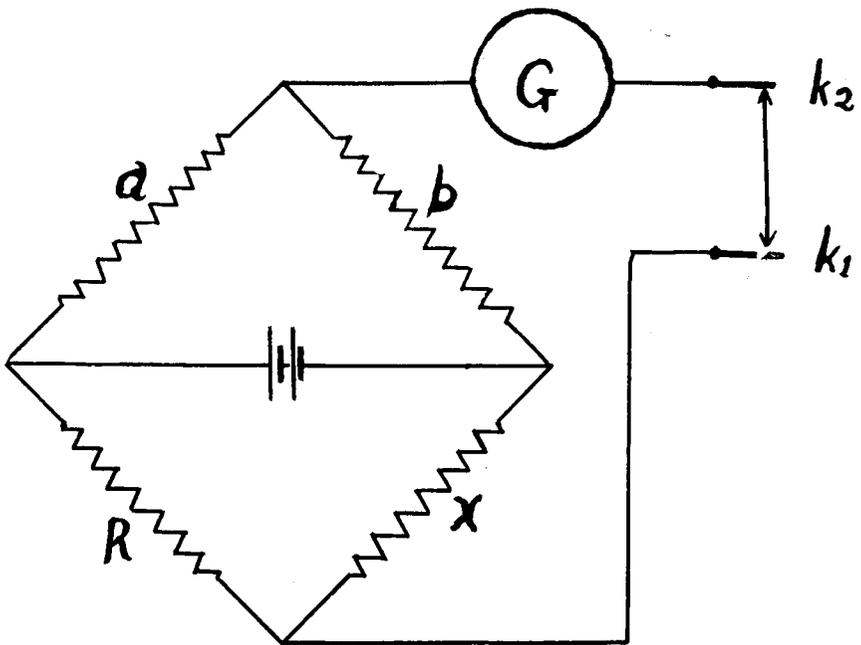
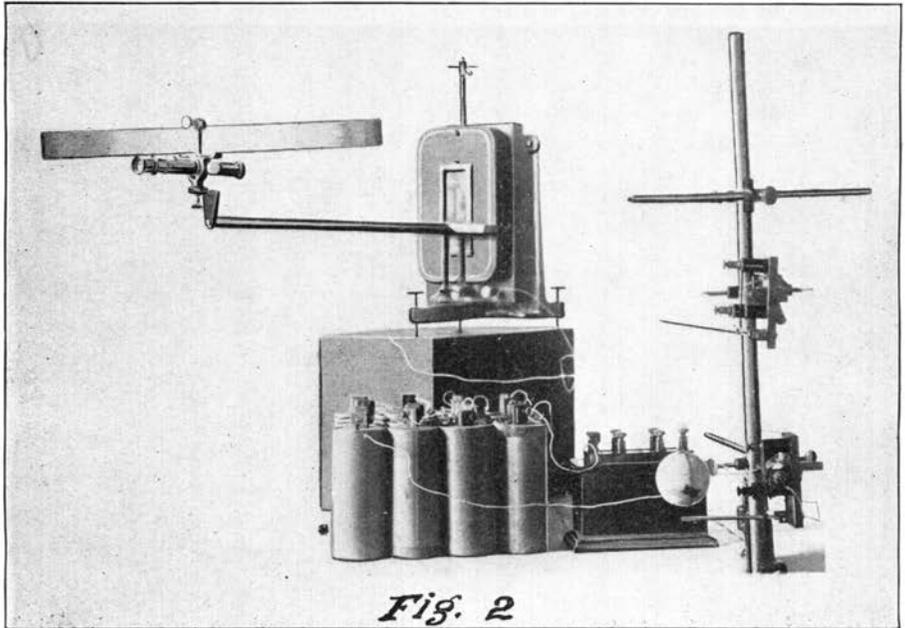


Fig. 1



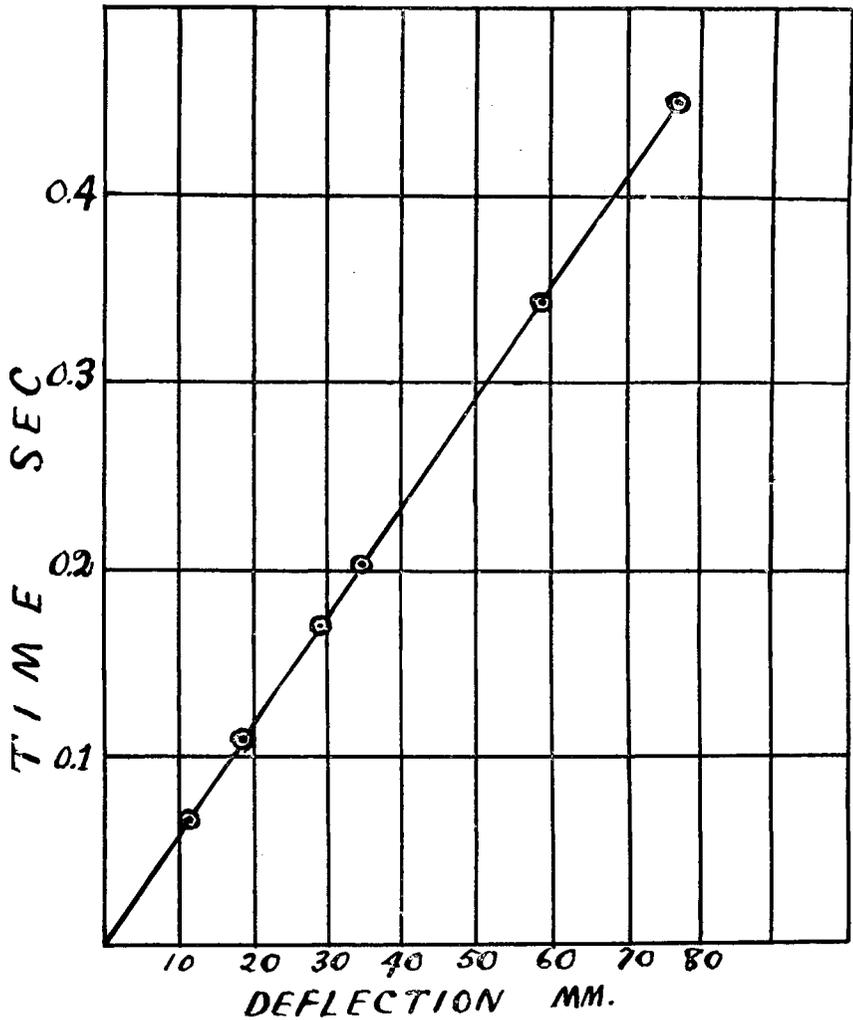


Fig. 3.

