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About the Inner Photoelectric Effect of Gelatineous Dyestuffs.

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Introduction.

According to B. Gudden and R. W. Pohl a splitting of electrons comes into existence in every substance illuminated by a light of suitable wavelength under suitable circumstances (1). If these split electrons are conducted by an outer electric field in the same substance in which they were split from the atom, then we call this phenomenon an inner photoelectric effect. The current caused by the moving of split electrons is called photoelectric negative primary current. On account of the moving of molecules caused by heat, the positive rest of the atom takes over an electron from one of its neighbour situated nearer to the cathode, in consequence of this, the neighbour will be positive. Thus it may well be that the ion itself does not wander, only the position of the negative charge gets nearer to cathode, this causes a current called positive primary current by B. Gudden and R. W. Pohl (2).

In an ideal case when the substitute of split electrons is so fast that the shifting of charge does not cause any permanent change in the substance, the primary current is constant. The primary current is without inertia and proportional to the absorbed energy, and to field strength if the field strength is not high. If the field strength is high the primary current approaches a maximum (3).

In most cases the speed of substitute of electrons — the strength of positive primary current — depends on the quality of material, temperature and illumination. The substitute of electrons goes so slowly, that after the first splitting of electrons the inner photoelectric effect occurs in a new material from the point of view of photoelectric effect. Consequently, the strength of positive primary current is not constant in time. In addition, other phenomena may occur which cause a secundary current (e. g. electrolytic conduction, rise of space charge etc).

In case of semiconductors the circumstances are most complicated. These have a little conductivity also in darkness: the current is called dark current. Here the negative primary, positive primary, secundary and dark currents are flowing simultaneously under illumination. The difference between currents measured in light and in darkness (shortly, photocurrent) cannot be considered as a photoelectric current. Only one thing is sure i. e. that it is of photoelectric origin. The observed change of conductivity may form an important part of koherer effect, which may be concluded from the fact that the change of conductivity depends on its former condition and in some cases (e. g. selenium) on mechanical shuttering. In these cases the secundary current may be a multiple of the original photoelectric current.

If we want to investigate the pure photoelectric primary current we have to quicken the substitute of split electrons as much as possible and we have to hinder the rise of greater secondary currents. This may be attained by using little thickness and by choosing as little intensity as possible and as short a time of illumination as possible. Further we return the substance to its original condition after every measurement (by simple waiting, or heating or by red illumination).

Experimental.

The investigation of outer photoelectric phenomena show that the shorter the wavelength the more intensive is the splitting of electrons. (4). Therefore I used a spark as a source of light, the electrodes of which were aluminium plates. The light of the spark was focussed on the phosphor by means of one lense.

The substance of phosphor was rhodulin orenge N (5). The absorbing area of the plate was 1×3 mms and its thickness was 0,1 mm. The directions of illuminating light and of the electric field during the experiment were perpendicular. The experimental equipment is sketched in Fig. 1.

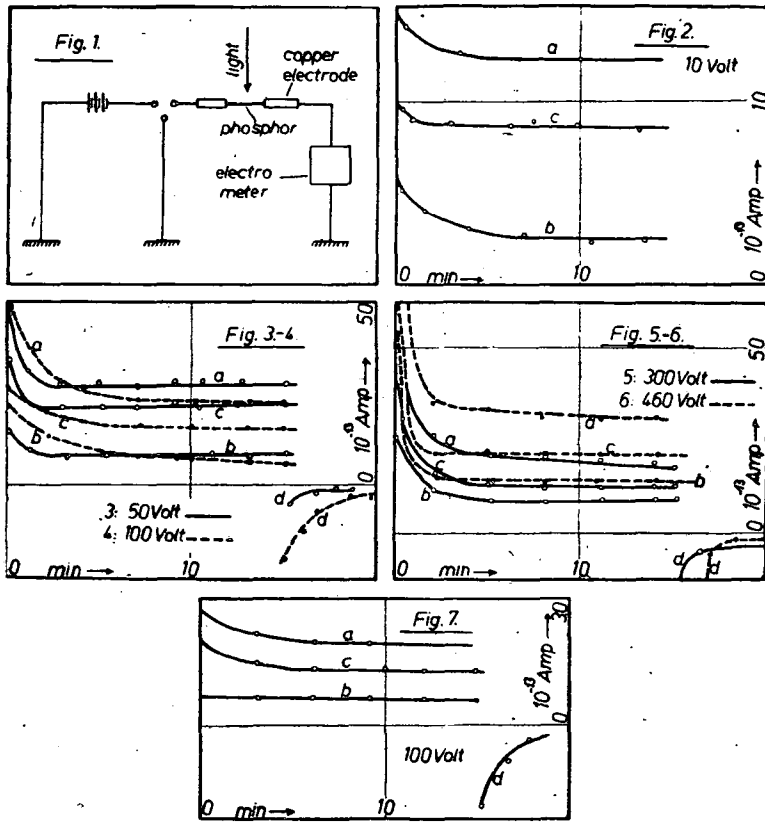
A common dyestuff plate does not show any measurable inner photoelectric effect. If the plate is heated before measuring then a measurable photoelectric current is obtainable. The heating was carried out in an electric furnace. I raised the temperature of the plate to a degree of 150° C at a rate of 3° C/min, and I kept it at this degree for 3 hours. It is not allowed to put the dyestuff plate immediately into a space of a temperature of 150° C on account of the alteration of plate (6).

I used a Lindemann electrometer for measuring the current. I calculated the intensity of current from the capacity and speed

of the charging of electrometer in the usual manner. The little capacity and great sensitiveness of the electrometer made an exact measurement of very small intensities (10^{-14} Amp.) possible

The changing of sensitiveness of electrometer enabled us to have a short measuring time (a few seconds) in every experiment. In this way the results were not influenced by secondary currents. Secondly I have to return the phosphor to its original condition after each measurement. This was carried out simply by resting the phosphor for 5 minutes in darkness without an electric field.

The photocurrent was calculated from the results of two measurements carried out immediately one after the other. I measured



the intensity of current first during irradiation and immediately afterwards in darkness. The difference between the results of these measurements was the photocurrent.

Results.

A) Photocurrent Under Use of a Constant Outer Voltage.

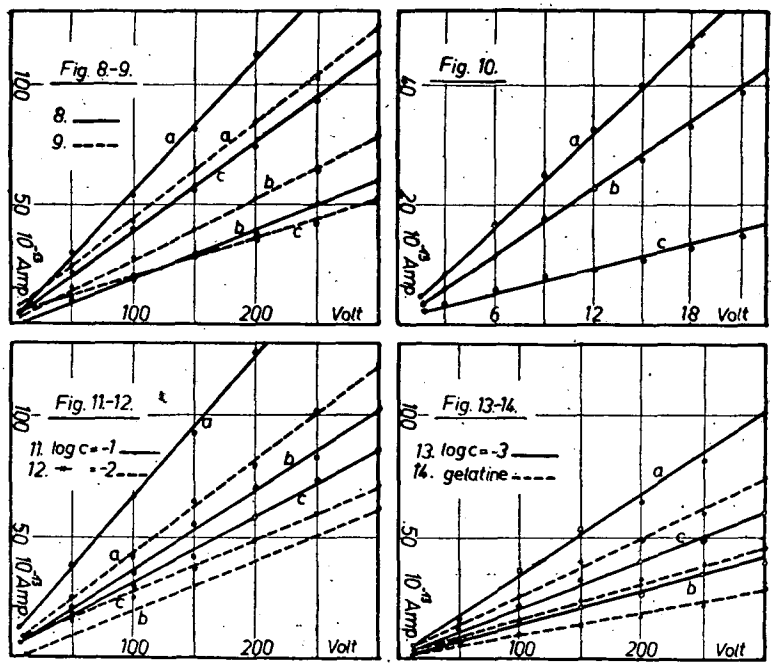
If the phosphor is kept under constant potential and is permanently irradiated by light, then we receive the current curves shown in Fig-s 2, 3, 4, 5, 6. The abscissa represents time, while the ordinate represents intesity of current flowing through the phosphor. Each figure shows current curves belonging to 10, 50, 100, 300

and 460 V-s outer voltages respectively. The curve *(a)* represents the intensity measured under illumination while the curve *(b)* represents that dark current. The third curce *(c)* represents the photocurrent. If the outer voltage is switched off we receive a current flowing in the opposite direction called secondary current. (Curve *d*).

The more important rules drawn from the results are as follows:

1. Each kind of current decreases in time and only after a certain time takes a constant value.

2. In cases of greater voltage the values of photo- and dark currents, at the beginning, not only decreases at a high rate from the absolute value to a constant value, but the decrease is more abrupt. (Table I. 2. and 3. line).



3. The photocurrent is a smaller percentage of dark current, at the beginning value, than under the same outer voltage at the constant value (The last line of Table I).

4. The photocurrent is a greater percentage of dark current when the outer voltage is smaller, although the absolute value of photocurrent is increasing when the outer voltage is increased (The last line of Table I).

5. The value of secondary current, at the beginning, is greater when the outer voltage is greater. Similarly the steepness of curves belonging to secondary current also increases when the outer voltage is increased (*d* curve on Fig-s 2, 3, 4, 5, 6).

It is well known that the intensity of current flowing in gelatineous dyestuffs under outer voltage, is diminishing for a short time, then becomes constant (7).

Table I.

		Beginning value	Constant value	Difference between beginning and const. value	Percentage calculated from beginning and constant value	Beginning value	Constant value	Difference	Percentage	Beginning value	Constant value	Difference	Percentage	Beginning value	Constant value	Difference	Percentage	Beginning value	Constant value	Difference	Percentage
Outer Voltage Volt-s		10				50				100				300				460			
Dark curreut	Unit: 10^{-13} Amp	5,2	3,4	1,8	35	11	5	6	55	20	6	14	70	35	8	27	77	55	14	41	75
Photocurrent		10	9,2	0,8	8	15	13	2	13	27	10	17	63	45	11	34	66	65	17	48	74
Percentage, calculated from dark current and photocurrent		192	270	—	—	136	260	—	—	135	167	—	—	129	137	—	—	118	121	—	—

Fig. 7. shows the inner photoelectric effect of a gelatineous dyestuff plate formerly kept under 100 V outer voltage for 15 min-s, consequently its resistance was constant from the point of view of dark current. Yet it is to be seen that its resistance from the point of view of photoelectric current is not constant in time, although, compared with the correspondent Fig. 4. we see that the difference between beginning and constant value is not so great, further that the constant value is reached sooner. The constant value of photocurrent is the same in both cases.

B) The Photocurrent as the Function of Outer Voltage.

If the value of photocurrent as the function of outer voltage is investigated, we receive the curves shown in Fig-s 8, 9, 10. As is to be seen the intensity of photocurrent increases linearly with the increasing of outer voltage, i. e. Ohm's law is valid not only for dark current but also for photocurrent.

Table II.

Outer voltage		10	50	100	150	200	250	300
Dark current	unit:	not measurable	3	7	11	15	20	24,2
Photocurrent	10^{-13} A	12	8	15,6	22	29,8	37,6	45
Percentage		267	223	200	198	188	186	

Table III.

Outer voltage		10	50	100	150	200	250	300
Dark current	unit:	1,5	13	24	40	53	63	78
Photocurrent	10^{-13} A	4	10	18	29	36	42	51
Percentage		266	77	75	72,5	68	66,5	65,5

Table IV.

Outer voltage		1,5	3	6	9	12	15	18	21
Dark current	unit:	3	6	11	17,4	22,8	26	34	39
Photocurrent	10^{-13} A	1,6	3	5,6	7,8	9,8	11	14	15,6
Percentage		53,5	50	47,2	45	43,5	42,5	41	40

The photoeffect measured immediately after heating is shown in Fig. 8. There is no measurable dark current under small voltage (about 20 V), only the photocurrent is measurable. The value of photocurrent is always greater than that of dark current, but the percentage is decreasing when outer voltage is increased (Table II).

Fig. 9. shows the same current as Fig. 8. excepting that the gelatineous dystuff plate was kept for one day, after heating, in open air until the measurements were carried out. Comparing the results with those received immediately after heating, we see that the percentage is smaller in the case of plates kept for one day in open air (Table III.).

If we keep the plate in open air for two weeks after heating and afterwards measure the photoeffect, we receive the results shown in Fig. 10. On account of the great conductivity we can use only small voltage because the dark current would be too great if we used great voltage. In this case the photocurrent is always smaller than the dark current and the percentage is also smaller than in the two former cases (Table IV.).

C) Photocurrent as the Function of Concentration.

The inner photoelectric effect of gelatineous dyestuff plates having concentrations of —1,0 —2,0, —3,0 and that of pure gelatine plate is shown in Fig-s 11, 12, 13, 14. The greatest photocurrent flows through the plate of greatest concentration under every voltage. The percentage shows that the absolute value of photocurrent, in cases of plates of greater conductivity, is greater, yet, the photocurrent is a smaller percentage of dark current than in cases of smaller conductivity (Table V.).

Conclusions.

The photocurrent cannot be considered as a pure photoelectric primary current. We can only say that it is of photoelectric origin. In this way we can explain the dependence of photocurrent on the former condition of plate (Comparing the 4. and 7. experiments). Many kinds of currents slow simultaneously on account of using a source of light which contains not only the short wavelengths which split off the electrons from the atom, but long waves, too. The photocurrent is not constant in time which shows that a secondary current of considerable greatness is flowing. I have to suppose the rise of a very great space charge in the dyestuff plate which lessens the further photocurrent. The existence of this space charge in the dyestuff plate is proved by switching off light and outer electromotive force. When switching off light and electromotive force I get a very abruptly decreasing current of opposite direction. This current is the ceasing of space charge. The absolute value of space charge is increasing with the increase of outer voltage according to experimental results. The difference of beginning and constant values of photocurrent is proportional to space charge, as primary current is decreased by space charge. The decrease is not constant in time because an equilibrium is developing between the beginning space charge and the intensity of photocurrent. Therefore the photocurrent reaches a constant value in a comparatively short time. We receive a photocurrent of greater percentage in equilibrium under every outer voltage, than before equilibrium. This shows that the equilibrium is more advantageous for the splitting of electrons than the unstable state. The photocurrent and also the dark current are increasing proportionally to the increase of outer voltage, but the percentage decreases. This means that the circumstances are more advantageous for the photocurrent — in connection with dark current — when using of small voltage.

Taking into consideration the results of 8., 9., and 10. experiments we may conclude that the inner photoelectric effect is hindered by colloid water just as it had been found for outer photoelectric effect. On investigation of outer photoelectric effect the loss of colloid and capillary water occurs in vacuum in every case. When measuring the inner photoelectric effect we have to heat the phosphor plate in every case to get measurable photocurrent. As the phosphor regains its colloid water, the photocurrent decreases. (8). (Tables II., III. and IV.).

The photocurrent is increasing with the increase of concentration (Table V.) under every voltage but the percentage, comparing the photocurrent with the dark current, decreases. This may be explained in the following way. The conductivity of phosphor is

Table V.

	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage
Outer voltage Unit: Volt	10			50			100			150			200			250			300		
—1·0	6	6	100	19	16·5	87	35	30	86	51	43	84	67	56	83	83	70	83	99	83	84
—2·0	not measurable	5	—	7·5	14	187	18	25	139	28·5	36	126	39	47	120	49	59	120	60	70	116
—3·0	2	3·5	175	8	12	150	15	21	140	22	31	140	29	40	138	36	50	139	42	59	138
Pure gelatine	1·5	3·5	230	5	8·5	170	10	16	160	15	24	160	20	31	155	25	30	120	30	37	123

log conc. gr dyestuff/cm³ dry gelatine

increasing more rapidly with the increase of concentration than the photocurrent. Presumably the splitting of electrons is increasing with the increase of concentration (just as it has been found in the case of outer photoelectric effect), but the secondary currents are greater compared with the primary current in cases of smaller concentration than in cases of greater concentration. It may also be explained by supposing smaller secondary currents in plates of greater conductivity (greater concentration).

Summary.

I have measured the inner photoelectric effect of rigid gelatineous dyestuffs. The results are:

1. The photocurrent decreases and reaches a constant value in time. The decrease is proportional with outer voltage in absolute value. The percentage is also decreasing. The absolute value of photocurrent is increasing when outer voltage is increased, but its percentage, calculated according to dark current, is diminishing.

2. The photocurrent is increasing protortionally to outer voltage. The greater the loss of colloid water of phosphor, the greater the photocurrent at every outer voltage. There is not to be found a photocurrent on plates exposed to humidity of room.

3. When increasing the concentration of dye, the absolute value of photocurrent is increasing under every outer voltage but its percentage, calculated according to dark current, is diminishing.

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