# A STUDY ON THE SURFACE PROCESSES
# OF THE ELECTRIC CONTACT BY MEANS
# OF THERMOANALYTICAL AND SPECTROCHEMICAL
# METHODS

By

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## Introduction

The lifetime of the power-current electric switches greatly depends on the material of the discs applied in the process. The application of silver contacts containing cadmium has come lately increasingly into prominence [1]. On the surface of the contacts physical and chemical processes take place upon arc discharge generated by the interruption of current. The quantity and composition of the arising metal vapors have an influence on the duration, and current intensity of the arc discharge when breaking the circuit and therefore on the consumption of the contacts. On the other hand the quality of the electric contact depends considerably on the reaction products forming on the surface of the contacts.

The determination of the lifetime of the contacts fitted into a magnetic switch is generally carried on by a long test [2]. This way of examination, however, does not give the possibility of following the consumption process. On the other hand, technological investigations dealing with producing contacts demand the shortening of the examination time. To solve these problems, thermogravimetric and spectrographic processes have been elaborated. According to these methods, arc discharge sequence with adjustable frequency and current intensity is produced between the contacts by means of an arc generator manufactured for spectrochemical analysis.

The silver-cadmium contacts are produced by alloying or powder technique. The evaporation (consumption) characteristics of the following three materials were studied:

  *a)* silver-cadmium alloy without previous oxidization,
  *b)* previously oxidized silver-cadmium alloy,
  *c)* silver-cadmium oxide disc made by powder technique.

Spectrographic examination of the composition of arising vapours and

the examination of the surface reaction products by thermoanalytical methods are expected to explain the behaviour of the three materials. The factors influencing the previous oxidization and the depth of the oxidized layer have been studied. The depth examinations were carried out by electron micro-sonde.

## Experimental

Thermogravimetric and spectrographic examinations were made by means of an electronically controlled a.c. arc generator type RO-202, with the following data:

voltage: 220 V,

frequency: 45 a.c. discharge $min^{-1}$,

current intensity (in short circuit)

*a)* 10 A (discs of 6 mm dia.),

*b)* 40 A (discs of 12 mm dia.),

duration of discharges: 7 ms.

The samples were examined as described in Table 1. The cadmium content of the samples was approximately similar. The discs of different size were used for medium or high-power switches. The smaller discs were examined for an arc discharge of 10 A, while the larger ones for an arc discharge of 40 A.

### Table 1

Data of the examined contacts of disc form

| Mark | Denomination | Additive | Diameter mm | Thickness mm |
|------|--------------|----------|-------------|--------------|
| A | Ag—Cd alloy (non-oxidized) | 10% Cd | 12.5 | 2.5 |
| B | oxidized Ag—Cd alloy | 10% Cd | 12.5 | 2.5 |
| C | oxidized Ag—Cd alloy | 10% Cd | 6.0 | 2.0 |
| D | powder technique product | 11% CdO | 6.0 | 2.0 |

*Continuous measurement of the consumption rate with*
*a thermobalance*

The measurements with thermobalance were carried out according to the experimental arrangements in Fig. 1. Two discs were spot welded [3] and a hole was made for the thermocouple [2]. The auxiliary electrodes [4] were made of discs identical to the sample, the centres of the discs were drilled to one half of the wall thickness. A copper rod was fitted into the hole and fixed
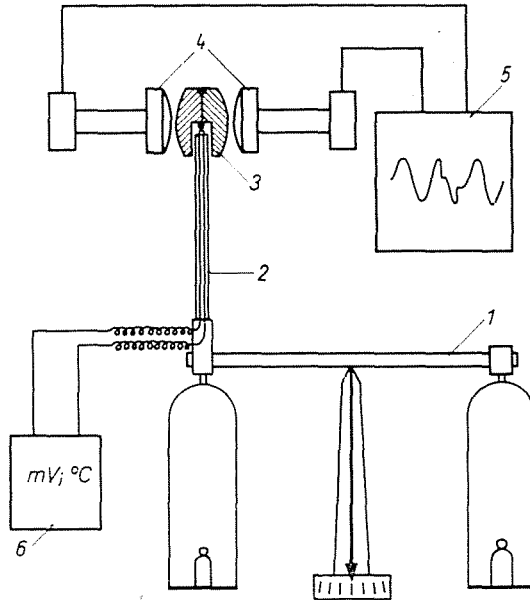
*Fig. 1.* Weight loss measurement with thermobalance. 1. analytical balance; 2. thermocouple fitted into a ceramic tube; 3. sample; 4. auxiliary electrodes; 5. a.c. arc generator; 6. mV-meter calibrated for temperature

by beading. Between the auxiliary electrodes and the sample material a gap of 2 mm was managed.

The balance was counterbalanced before measuring [1]. After switching on the arc generator (5) the temperature of the sample (6) was read off each 20 sec in the first period and later each 20 min. The sample was weighed about hour by hour, gradually decreasing the weight on the balance arm, to keep the deviation of the balance as little as possible. In Fig. 2 the temperature change of the samples types B and D is plotted against the arcing time.
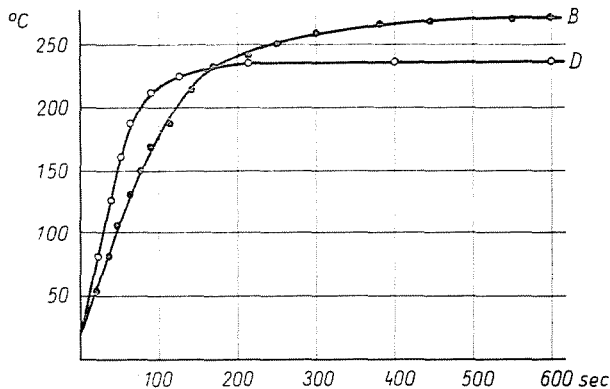


*Fig. 2.* Temperature change of the contacts during arcing. B — oxidized Ag—Cd alloy, 40 A; D — powder technique disc 10 A

Equilibrium temperatures are seen to be reached after 400 and 200 sec, respectively. In case of the larger disc (B) arc current of 40 A, while in case of the smaller disc (D) only 10 A was applied. The two equilibrium temperatures differ only by 40 °C.

In Fig. 3 the weight losses of discs A and B (alloys) were plotted against arcing time (30 hours). The weight loss of the previously oxidized disc type B is found to be smoother and smaller.

In Fig. 4 the weight loss of discs C (oxidized alloy) and D (powder technique disc) is seen during 30 hours of arcing. The decrease of the discs produced by powder technique appears to be much less.
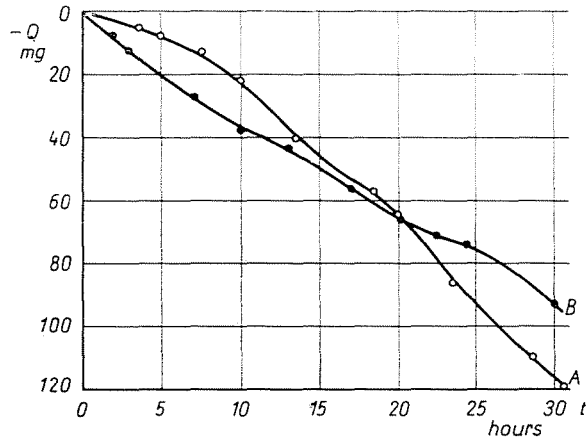


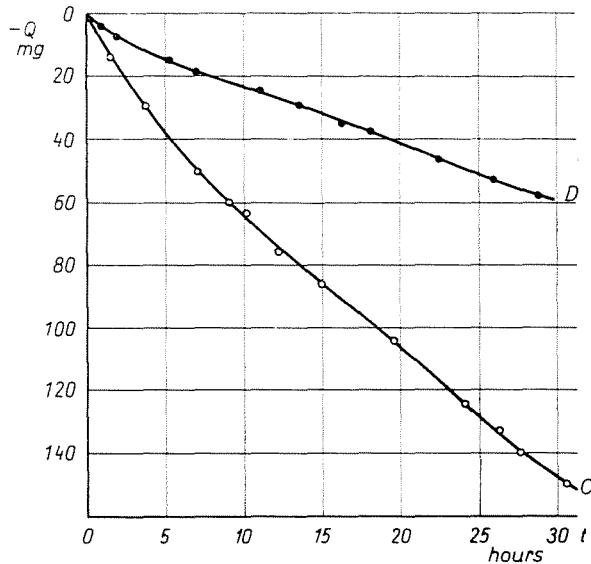Fig. 3. Weight loss of contacts A and B upon arcing (Table 1)



Fig. 4. Weight loss of contacts C and D upon arcing (Table 1)

### *Determination of metallic concentration ratio*
### *of arc discharge by spectrographic method*

For the spectroscopic calculation of the atomic concentration in arc plasma a local thermal equilibrium is supposed. Concerning the detailed expounding of this question and calculation we refer to BOUMANS' general work [3].

The calculations in question were used mainly for theoretical purposes and technical application is only found in a few papers. Therefore a more detailed discussion of these calculations seems to be desirable. ACINGER carried out calculations of the same principle for the welding arc of steels [4].

The silver-cadmium system is relatively easy to treat from the point of view of spectroscopic calculations. The ionization potentials of the two elements are relatively high ($V_{i(Ag)} = 7.57$V, $V_{i(Cd)} = 8.99$ V) and in consequence the two elements are little ionized in the arc discharge. It can be calculated by Saha's relationship (3) that in the arc between the copper electrodes (5170°K, see below) the ionization of the silver introduced into the arc plasma is 1.9% and that of cadmium is 0.8%. Consequently the ionization of both silver and cadmium vapours in the arc plasma is negligible. Besides also the oxidization of silver and cadmium vapours is negligible. A further possibility for simplification in case of cadmium and silver is that partition functions involved in the Boltzmann equation can be substituted by appropriate statistical weights.

Hence:

$$\frac{I^\circ_{Cd}}{I^\circ_{Ag}} = \frac{N_{Cd}}{N_{Ag}} \; \frac{A_{Cd}(g_q/g_0)_{Cd}}{A_{Ag}(g_q/g_0)_{Ag}} \exp \frac{V_{Ag} - V_{Cd}}{kT} \tag{1}$$

where $I^\circ$ (photons sec$^{-1}$) is the absolute intensity of the spectral line used, $N$ is the number of atoms in the light source, $A$ is the transition probability, $g_q$ is the statistical weight of the excitation level, $g_0$ is the statistical weight in the basic condition, $V$ (Volt) is excitation potential, $k$ is Boltzmann constant, $T$ (°K) is the absolute temperature.

From Eq. (1) it appears that the closer are the excitation potentials of the two lines, the less the influence of the temperature variation on the intensity ratio. Therefore this is an important criterion in choosing the lines. It is also very important to have negligible self-absorption of the applied lines under the given circumstances. For this reason no ground lines are to be applied. Further, from practical point of view it is advantageous to have similar instrumental factors valid for the wave length of both lines (speed of emulsion, optical conductivity). In this case the absolute ratio of intensity can be substituted by the intensity ratio measured in an arbitrary scale. For this purpose it is advisable to use two spectral lines of similar wave lengths. In selecting the lines, their spectroscopic constants are, of course, of decisive importance.

Under the given experimental circumstances, these requirements are relatively well satisfied by the following lines:

| wave length | excitation potential |
|---|---|
| (Å) | (V) |
| Cd I  3133.17 | 7.76 |
| Ag I  2721.77 | 6.05 |

Eq. (1) shows that the determination of the temperature of the arc plasma is also necessary for calculating the atom concentration ratio, if the difference between excitation potentials is not negligible. This determination is possible also by spectroscopic method. It should be noted, however that (1) is strictly valid only for a very small volume element, within which the plasma temperature and the metallic concentration are constant. For calculating the concentration ratio integrated over the whole plasma volume, the temperature distribution of the arc plasma should also be taken into consideration, making the calculation rather complicated.

For practical purposes the process where the absolute intensity of spectral lines and the average temperature of the arc discharge are determined under well defined conditions, is more successful. From these data the "experimental" transition probability of lines and their ratio, are to be calculated using (1).

The characteristics of arc discharge between silver-cadmium electrodes are similar to those of copper arc and there are published data on characteristics of the copper arc. The temperature and the electron pressure of the arc plasma is determined by the constituent of the smallest ionization potential being present in a suitable concentration. Since the silver of smaller ionization potential is present in a high concentration in the examined arc discharge, silver vapours define the fundamental parameters of the plasma. The ionization potential of the silver is near to that of copper ($V_{i(Cu)} = 7.72$ V, $V_{i(Ag)} = 7.57$ V) therefore the electron pressure and temperature of silver arc and copper arc are similar. MEGGERS, CORLISS and SCRIBNER [5] gave a detailed survey of the characteristics of copper arc and the absolute intensity of lines of 70 elements evaporated into the copper arc. An average temperature of 5170 °K was found in the copper arc of 10 A using the multi-line spectroscopic method. The absolute intensity of line Cd I 3133.17 is $I^\circ_{Cd} = 5$, that of Ag I 2721.77 is $I^\circ_{Ag} = 6$, provided that $N_{Cd} = N_{Ag}$. Consequently for the lines chosen:

$$\frac{N_{Cd}}{N_{Ag}} = 1.2 \, \frac{I^\circ_{Cd}}{I^\circ_{Ag}} \tag{2}$$

Eq. (2) contains absolute intensities ($I^\circ$). In photographic photometry applied in analytical practice intensities are, however, measured only on an arbitrary

scale. The two kinds of intensities are related as:

$$I = \varphi I^\circ \tag{3}$$

where $\varphi$ is the instrumental factor to be determined by means of a light source with known spectral radiance. In the above mentioned work the data of the absolute intensities of copper lines are tabulated and lend themselves for such calibration purposes, too.

Two copper lines were selected, approaching wavelengths of cadmium line (Cu I 3194.10), and silver line (Cu I 2766.37), respectively. A separate spectrum was recorded of the copper arc and the intensity ratio between the two copper lines was determined under the same circumstances. The absolute intensities of the two copper lines were found to be equal by authors referred to. Therefore our intensity ratio gives directly the ratio of the instrumental factor:

$$\frac{I \text{ Cu } 3194}{I \text{ Cu } 2766} = \varphi \,\text{Cd}/\varphi \,\text{Ag} = 1.1 \tag{4}$$

Thus Eq. (2) can be rewritten for our conditions of intensity measurement using (3) and (4):

$$N_{Cd}/N_{Ag} = 0.91 \cdot 1.2 \, I_{Cd}/I_{Ag} \tag{5}$$

For practical purposes it is advisable to replace the ratio of atoms valid in the arc plasma (vapour phase) by the concentration ratio calculated from atomic weights:

$$c_{Cd}/c_{Ag} = 1.042 \cdot 0.91 \cdot 1.2 \, I_{Cd}/I_{Ag} = 1.14 \, I_{Cd}/I_{Ag} \tag{6}$$

Eq. (6) delivers the instantaneous concentration ratio and the concentration ratio vs. time curves can be determined for the arcing process. For our examination it is, however more suitable to relate the quantity of the cadmium vapour ($q_{Cd}$) to that of silver ($q_{Ag}$), both evaporated to time $t$. The ratio $q_{Cd}/q_{Ag}$ determined by spectroscopic way can easily be compared to the weight loss ($q_{Cd} + q_{Ag}$) determined thermogravimetrically. The desired variable can be calculated by integrating Eq. (6):

$$\frac{q_{Cd}}{q_{Ag}} = \frac{\int_0^t c_{Cd}(t)\,dt}{\int_0^t c_{Ag}(t)\,dt} = 1.14 \frac{\int_0^t I_{Cd}(t)\,dt}{\int_0^t I_{Ag}(t)\,dt} \tag{7}$$

## Experimental conditions

Spectrograph: Zeiss, Jena Q-24 quartz spectrograph, slit width 0.015 mm, internal focusing, without blending.

The spectrum of the light source was recorded each quarter of an hour, furthering the plate holder. Photographic conditions: Ilford N 30 emulsion, 1 min exposure time, Kodak D 19 developer, 20 °C, 4 min.

Evaluation: The blackening of the spectral lines was measured by a Zeiss Jena microphotometer. The blackening curves of each plate were determined and the measured blackenings were converted to intensities. The line intensities were corrected for background.

## Results

In Fig. 5, the ratio of the vapour concentration is plotted against time (30 hours) in case of discs types A and B (alloys). It can be stated that the vaporization of the previously oxidized disc type B is less selective and the concentration ratio of the components more uniform in vapour phase.
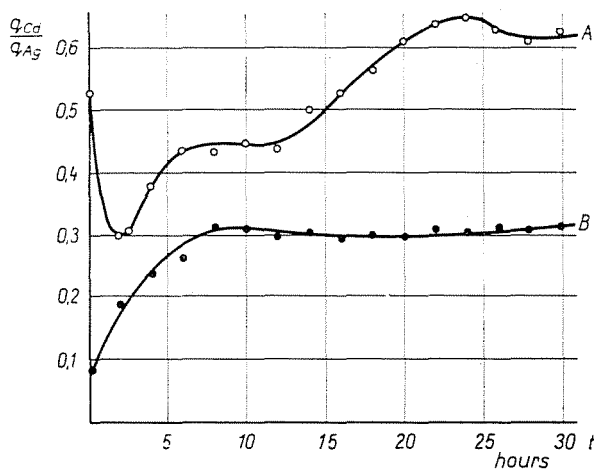


*Fig. 5.* Change in the vapour concentration ratio in the evaporated material (Discs A and B; Table 1)

In Fig. 6, the change of the composition in vapour phase of the disc type D produced by powder technique and type C (oxidized alloy) is seen during 30 hours of arcing. Comparing these curves the powder technique disc shows an essentially lower selective evaporization.
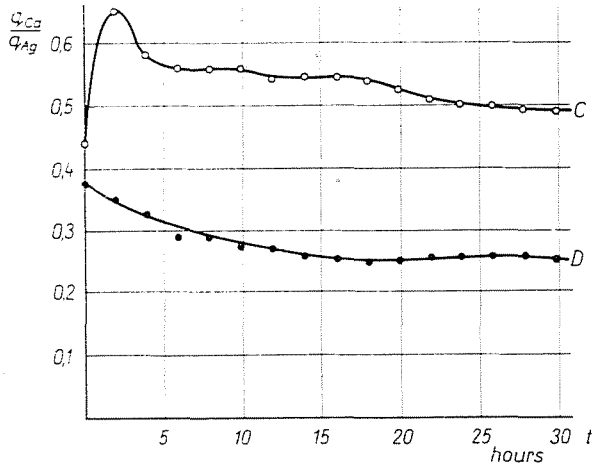
*Fig. 6.* Change in the vapour concentration ratio in the evaporated material (Discs C and D; Table 1)

## Derivatographic analysis of the contacts used for a longer period

We carried out our measurements by means of a Paulik—Paulik—Erdey derivatograph made by MOM [6], suitable for the simultaneous measurement of the change of weight (TG) the rate of the weight change (DTG) and the change of enthalpy (DTA) vs. increasing temperature.
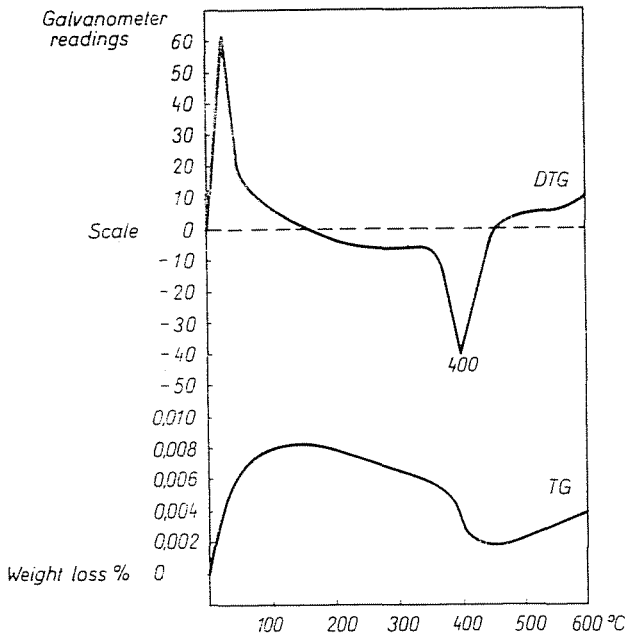


*Fig. 7.* Derivatographic recordings of a disc arced for 30 hours. Weight change %; galvanometer deflection scale
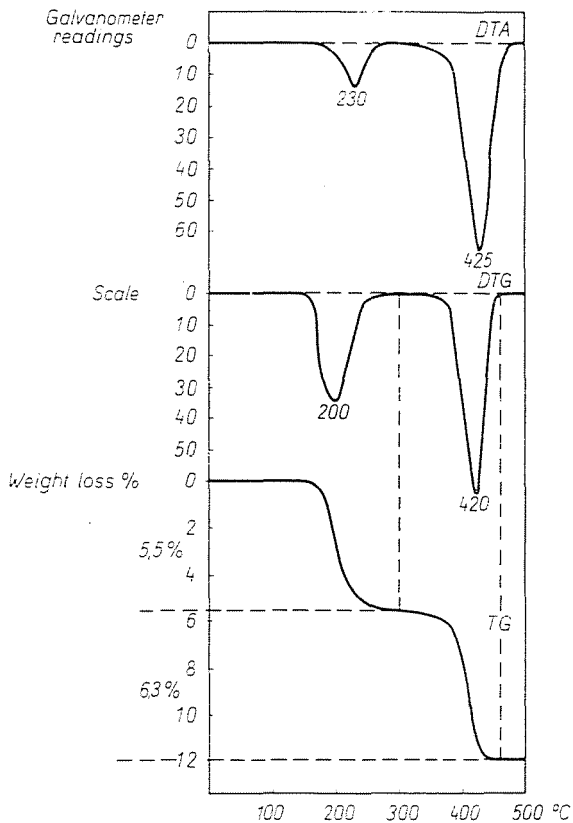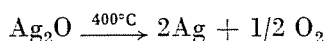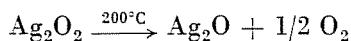
*Fig. 8.* Derivatographic recordings of silver oxidized electrolytically. Weight change %
Galvanometer deflection scale

The examination was carried out on 4 previously non-oxidized discs (type A) arced for 30 hours. The surfaces of the discs got a brown-grey layer. The total weight of the sample was 17.9077 g.

DTG and TG curves in Fig. 7 show an increase of weight to 150 °C, then a weight loss to 400 °C and over it again an increase of weight. The initial increase of weight is attributed to the oxidization of the silver particles of microscopic size on the sample surface. The weight loss was supposed to be due to the decomposition of the silver peroxide starting at 150 °C, then to that of silver oxide at about 400 °C at a maximum rate. The increase of weight over 450 °C could be explained by the oxidization of the metallic cadmium.

To verify our assumptions, a layer of silver, silver peroxide and silver oxide was prepared by electrolytical oxidization on a sintered silver sheet [7]. This layer was investigated by the same derivatograph under the same conditions. The experimental curves obtained are shown in Fig. 8. For the two TG steps the following equations of decomposition can be written:

$$Ag_2O_2 \xrightarrow{200°C} Ag_2O + 1/2\ O_2$$

$$Ag_2O \xrightarrow{400°C} 2Ag + 1/2\ O_2$$

Comparing the curves in Figs 7 and 8 it can be established that the decomposition (weight loss) of the surface layer resulting from the arc discharges is similar to the decomposition of the layer prepared electrolytically. Consequently as an effect of the arc discharge $Ag_2O_2$ and $Ag_2O$ are formed on the surface. The following examinations give the interpretation of the increase of weight above 450 °C.

### The study of the previous oxidization of the Ag/Cd alloy by derivatograph and electron microsonde

The disc (type A) prepared of alloy containing 90% silver and 10% cadmium was placed onto the sample holder of the derivatograph, and 10°C/min heating rate was applied. An oxygen flow with a rate of 20 lit/hour was passed through the furnace. The furnace temperature was increased up to 750 °C, then kept constant with the help of an electronic temperature regulator (18) at an accuracy of $\pm 1$ °C upto constant weight.

In Fig. 9 the weight increase of the disc at 750 °C in oxygene athmosphere was plotted against time. The weight increase results from the cadmium oxidization taking place in the disc. After 80 hours the rate of oxidization is found to slow down and the further heating is inefficient.

The depth of the oxidization and the resulting structural change were examined with an electron microsonde Type JKA 6. The disc preoxidized under optimal conditions was cut in half perpendicularly to its surface and the sections recorded. The entire section picture showed the inner part (some 30%)
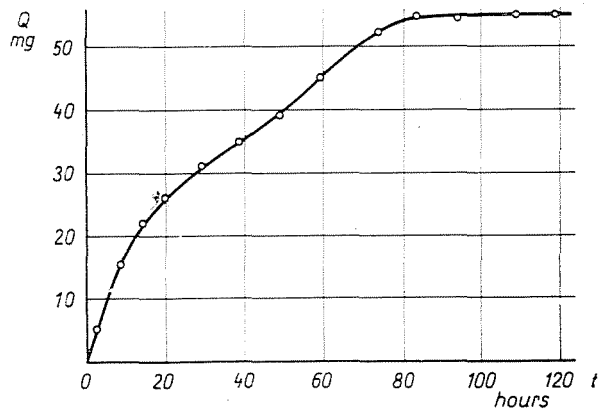


*Fig. 9.* Oxidization of the Ag—Cd alloy vs. time (oxygen atmosphere, 750 °C)

2*

of the disc not to be oxidized. Fig. 10 shows pictures taken by electron micro-
sonde of the surroundings of the oxidization border line.

On the left side of the electron reflexion image the oxidized layer, while
on the right side the non-oxidized layer is seen. The reflectivity of the cadmium
oxide is lower than that of involved metals, so the more covered black parts
show an enrichment in cadmium oxide on the positive picture. The picture
makes it likely that the oxidization is accompanied by local enrichment of
cadmium and to this effect the outside layer was transformed to macro-
crystalline structure.

These phenomena are supported also by pictures of characteristic X-rays
due to the electron beam. In picture (b) the radiation distribution of $Cd_{La}$,
in picture (c) that of $Ag_{La}$ is seen. Increasing cadmium concentration is evi-
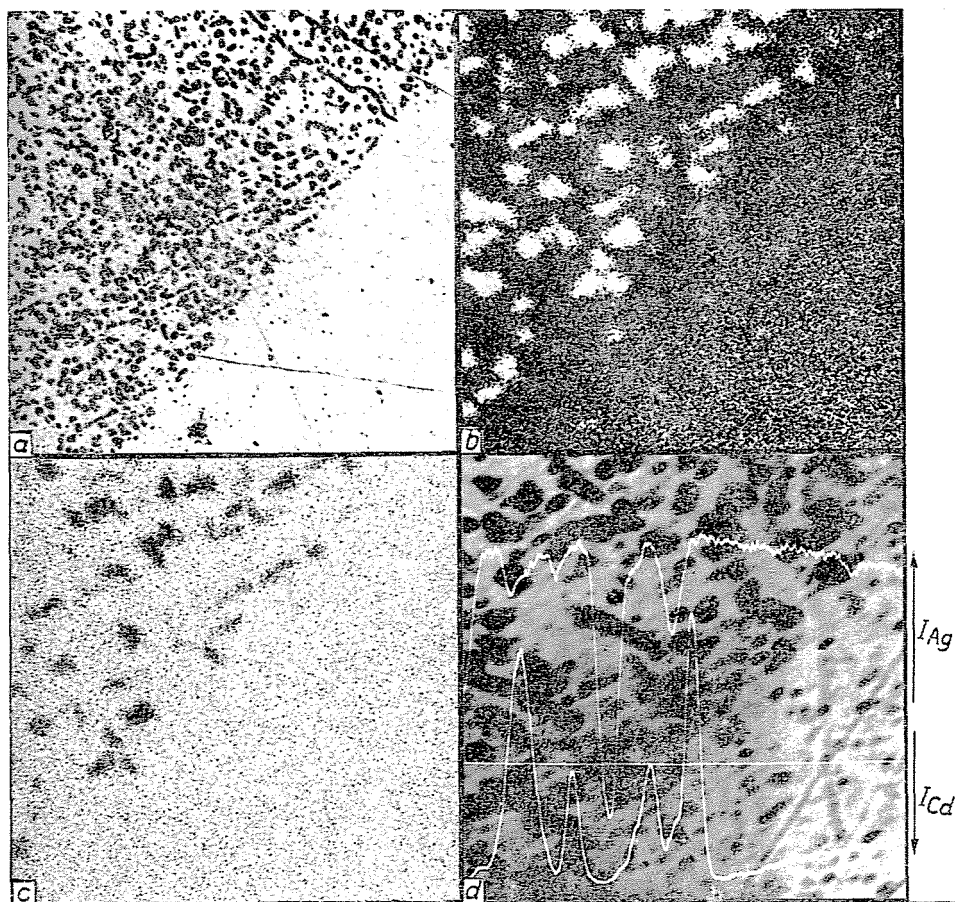


Fig. 10. Recordings made by electron microsonde. a) composition picture 20 kV, Enl. $= 160 \times$;
b) $Cd_{Lx}$-line profile 20 kV, Enl. $= 640 \times$; c) $Ag_{Lx}$-line profile 20 kV, Enl. $= 640 \times$; d) compo-
sition and characteristic picture $Ag_{Lx}$-line profile (upper) and $Cd_{Lx}$-line profile (lower) along
the white straight line (20 kV, Enl. $= 540 \times$)

dent by white tint and black tint, respectively. The composition picture (d) shows the recorded intensities of $Ag_{La}$ (upper) and $Cd_{La}$ (lower) radiations along horizontal white line. The intensity axes have inverse directions. The dark parts show the spots of higher cadmium oxide content similarly to the picture of moderate enlargement (a) discussed. The intensity of the $Cd_{La}$ radiation is seen to be high, while that of $Ag_{La}$ radiation to be low at the dark spots. Thus a heterogeneous distribution is likely to develop both for cadmium and silver at the oxidization zone. On the right side of the picture, in the non-oxidized zone the concentration of the two metals shows a small random deviation, characteristic of the homogeneous alloys.

## Discussion

The thermogravimetric and spectrographic data used for characterizing the life time of the contacting discs of different types were summarized in Table 2.

### Table 2

Thermogravimetric and spectrographic data

| Symbol | Arc current A | Equilibrium temperature °C | Weight 1 loss mg* $q_{Cd} + q_{Ag}$ | Vapour concentration ratio* $q_{Cd} + q_{Ag}$ |
|--------|------|------|------|------|
| A | 40 | 310 | 120 | 0.63 |
| B | 40 | 270 | 95 | 0.32 |
| C | 10 | 350 | 151 | 0.49 |
| D | 10 | 240 | 60 | 0.26 |

* Remark: average values of arcing for 30 hours (2700 interruption per hours).

From thermogravimetric data it appears that among alloys (A and B) the weight loss of the previously oxidized contact B is less. As for the smaller discs C and D, the powder technique product D is even more constant than the previously oxidized contact C. According to spectrographic data, the vapour concentration ratio $q_{Cd}/q_{Ag}$ decreases at the same rate. The latter data give informations regarding to the later period of the consumption, too.

The cadmium/silver concentration ratio in the original discs is about 0.11. According to Table 2, this ratio is 2 to 6 times greater in the vapour phase due to the selective evaporation. (The boiling point of the cadmium is at 765 °C, and that of silver at 2212 °C.) According to Figs 5 and 6 the vapour concentration ratio $q_{Cd}/q_{Ag}$ does not decrease essentially during arcing time in spite of the selective evaporation. It is explained by the known fact that a fast diffusion process takes place in the high-temperature surface layer, likely to com-

pensate the cadmium loss for a relatively long time. Obviously, however, the higher is the ratio of $q_{Cd}/q_{Ag}$ in the first period of arcing, the sooner the disc cadmium is consumed. The cadmium vapour is less ionized in the arc plasma than silver vapour (see above) and this is why the electrical conductivity of the arc column containing cadmium is smaller. Thus, the presence of cadmium vapour helps the break-down of the arc created by switching off the current. After cadmium is lost, the consumption of the contact grows on account of decreasing the effect of breaking down. According to data in Table 2, the consumption of the contacts B and D is probably smaller throughout the life time.

As a conclusion it can be stated that according to our measurements and order of life times of the contacts is as follows:

1. Ag—Cd alloy without previous oxidization,
2. Ag—Cd alloy preoxidized,
3. Ag—CdO disc produced by powder technique.

It is to be noted, however, that the powder technique product is the best only if it is of a suitable strength, which characteristic was realized by the producer only in case of discs of small size. According to our derivatographic examinations the previous oxidization of the Ag—Cd alloy can be carried out properly at 750 °C and for 80 hours in oxygen atmosphere.

On the surface of the contacts a layer containing $Ag_2O_2$, $Ag_2O$ and CdO is formed in the surroundings of the arc crater. The $Ag_2O_2$ decomposes at 200 °C, the $Ag_2O$ at 400 °C, and CdO at 1500 °C, so the metallic surface is renewed by the effect of further discharges. This ensures that the contacting resistance does not increase in the course of application.

According to our investigations carried out by means of an electron microsonde, the Ag—Cd alloy oxidizes up to a sharp border line and only to 70% even under optimal conditions. The CdO distribution in the outside oxidization zone is heterogeneous just like the whole section of the powder technique product.

## Summary

Processes influencing the life time of electric contacts containing silver-cadmium were studied under simulated operating conditions. Between the contacts pulsing arc discharge was used.

For the continuous measurement of the weight loss due to discharge a thermobalance was constructed. Spectrograms were recorded from the arc discharges and by measuring the intensity of spectral lines the cadmium/silver concentration ratio was determined in the arc discharge. Our measurements yielded conclusions on the expected lifetime of the three types of contacts investigated.

The composition of the surface layer formed during arc discharge was studied by derivatographic method. Optimum temperature and duration of the previous oxidization of the silver-cadmium alloy were determined. The depth of the previous oxidization and the structure of the oxidized layer were investigated by means of an electron microsonde.

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