

THE GERMAN METAL RECTIFIER INDUSTRY.

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BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

REPORT ON

THE GERMAN METAL RECTIFIER INDUSTRY

REPORTED BY

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Personnel of Team

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THE GERMAN METAL RECTIFIER INDUSTRY

1. INTRODUCTION

The manufacture of selenium and copper-oxide rectifiers was established in Germany long before the war, the principal manufacturers being The Sueddeutsche Apparate-Fabrik (S.A.F.) of Nuremberg for selenium rectifiers, and Siemens-Schuckert-Werke (S.S.W.) for copper-oxide rectifiers.

Owing to the importance of rectifiers to the war effort, the output of these manufacturers was greatly increased and other firms were brought in to work under the instructions of S.A.F.

In addition, the Allgemeine Elektrostats Gessellschaft (A.E.G.) brought into operation a new process which had been developed before the war, and they also made a considerable contribution to the supplies.

No developments which were not already known in this country were introduced, the main emphasis being upon the production of the maximum quantities of the existing types. Many difficulties were experienced in obtaining raw materials of sufficient purity and major breakdowns were experienced at times from this cause.

A considerable amount of research work was carried out, but although this provided some explanations for the complicated physical phenomena underlying the operation of metal rectifiers, it tended to confirm the suitability of the materials and processes already in use and did not lead to the development of any new types of rectifier.

This report gives a description of the manufacturing methods of the various firms engaged in the industry, and a resume of the theoretical conclusions on which there appeared to be a measure of mutual agreement.

2. COMPOSITION OF THE INDUSTRY

The firms engaged in the industry during the war, and their outputs were as follows :-

| <u>Firm</u> | <u>Type Manufactured</u> | <u>Approximate number of discs manufactured per annum.</u> |
|--------------|--------------------------|--|
| S.A.F. | Selenium | 36,000,000 |
| S.S.W. | Selenium | 6,000,000 |
| | Copper Oxide | 6,000,000 |
| Mix & Genest | Selenium | 6,000,000 |
| T.K.D. | Copper Oxide | 200,000 |
| A.E.G. | Selenium | 10,000,000 |

In order to assist the manufacturers of dry rectifiers, a Committee known as the "Rectifier Ring" was formed. All the principal

→ gleichrichter Ring
- 3 -

manufacturers were represented on this Committee, and a number of scientific workers engaged on research in this field co-operated.

The main functions of this Committee were to consider

- (a) the relative merits of the systems of production adopted by the various manufacturers :
- (b) the physical basis of dry rectifiers - particularly as applied to Selenium Rectifiers :
- (c) alternative types of rectifier :
- (d) proposals for future research.

The views expressed by members of this Committee represented the most advanced opinions concerning metal rectifiers, and a summary of its conclusions is given later in this report.

3. USES OF RECTIFIERS

The demands for metal rectifiers appear to have been much the same in Germany as in the Allied countries. Stationary and portable battery charging equipments for use at bases and in the field required a great number of discs of the larger sizes, but the heaviest demand was for the smaller sizes, which were used in vast quantities to provide power supplies for field radio equipment, radar and miscellaneous aircraft equipment.

In addition to the above, which were mainly of the selenium type, copper oxide rectifiers were used for small power equipment and, in the miniature sizes, for detectors in radio apparatus and modulators and demodulators in the communication field. No new uses for rectifiers were discovered.

4. SELENIUM RECTIFIERS. PROCESSES OF MANUFACTURE.

4.1. Suddeutsche Apparate-Fabrik

The principal manufacture of metal rectifiers was in the hands of the S.A.F. concern of Nuremberg. During the war, they opened another factory at Weissenberg in which was installed the newest equipment. The factory at Nuremberg was considerably damaged by bombing, but the Weissenberg plant was completely undamaged. They used two distinct processes, which are described separately.

4.1.1. Personnel interviewed

Herr Hermann
Dr. Kippham
Dr. Lauckner

4.1.2. The Hand-coating Process

The Nuremberg plant produced discs of 18, 25, 35, 45, 67, 84 and 112 mm. diameter by the following method.

Discs were blanked from sheet steel and pierced with a centre hole in the same operation.

The blanks were then sand-blasted to roughen the surface and electro-plated with a thin coat of nickel.

The plated discs were then coated with selenium in fume cupboards. The discs were placed on hot plates heated to 350°C and pellets of selenium containing the correct amount for each size of disc were melted on the disc and the molten selenium was spread by an operator using a glass tool.

The coated discs were then arranged in stacks with a mica disc in contact with each selenium surface. Rubber discs with a thin nickelled brass washer on each side were sandwiched between the discs. A suitable number of discs was arranged in a stack with a central spindle and clamped to produce a pressure of approximately 10 Kg/Cm². Springs were included to take up any variations during heating.

The stacks were then heated in an oven at 110°C for 5 - 6 hours. Owing to shortages of materials, the mica washers were replaced by aluminium foil and the rubber washers were dispensed with, at some sacrifice of quality.

After the preliminary heat treatment, the stacks were dis-assembled and the discs were passed through a belt oven maintained at a temperature of about 216°C. This treatment took approximately half an hour.

The discs were held by an operator in the fumes from heated selenium dioxide for a few seconds and then placed in a mask and sprayed with the eutectic alloy of tin, cadmium and bismuth containing 0.003 - 0.005% of thallium. The actual manufacture was then complete. but the discs had still to be electro-formed. To achieve this, the discs were placed in clips and connected in parallel to the output of a single-phase rectifier arranged to pass a pulsating current through the rectifiers in the blocking direction. As the resistance of the rectifiers increased, the voltage was raised until the full value was reached. The whole forming process occupied from 14 to 20 hours.

The discs were then tested individually in the forward and reverse direction and graded according to their quality. A model of an automatic grading machine was seen in which relays controlled gates to allow the discs to pass into boxes according to their grades, but it is uncertain whether this was ever in operation.

Further details of this process are given in C.I.O.S. Report, Item 1. File No. XXVII - 45. Sudddeutsche Apparate-Fabrik.

4.1.3. The pressed-powder process.

The method described above was used throughout the war on discs of 67, 84 and 112 mm., but the smaller discs of 18, 25 and 35 mm. diameter were made by a mechanised method in order to increase output. This mechanised plant was installed in the Weissenberg factory.

The discs were sandblasted and plated as before, and were then placed on a hot plate at 350°C and given a thin coating of selenium in the shortest possible time, no care being exercised to make this coating particularly smooth. The discs so coated were taken to the automatic line where the following processes took place.

The discs were placed with the coated side uppermost on a circular plate of approximately 120 mm. diameter and located by dropping the discs into recesses formed in a template pressed against the plate. A circular hopper containing selenium powder was fitted over the discs and template and a handle was rotated to agitate the selenium and cause a measured quantity of powder to be deposited on each disc.

The hopper and template were removed and the plate carrying, for example, 22 - 18 mm. discs covered with the requisite amount of powder was placed upon an endless steel belt. The operator pressed a button and the belt moved forward and stopped with the plate in position between the platens of an electrically heated hydraulic press. This operated and applied the necessary heat and pressure to soften and consolidate the selenium. The pressure was about 50 Kg/Cms² and the temperature 150°C. The time of operation was one minute, and during this time the operator was preparing the next plate, so that the operation proceeded regularly but intermittently. The belt carried the discs through a long tunnel oven heated to 216°C, in which the crystallization of the selenium was completed, the length of the oven being so designed that the discs occupied about half an hour in passing through it.

At the other end of the oven, the plates and discs were removed by an operator who cleared the flash from the edges and centre holes and put the individual discs back on the belt which at this point was provided with guides to maintain the correct spatial relation between the discs. After a further short travel, they reached the end of the belt and slid down guides in readiness for the fuming process. Here they were picked up in groups of three by electro-magnetic fingers which lifted them and held them over the fumes from heated selenium dioxide for a few seconds.

Whilst in this position, they were taken over by a second set of magnetic fingers, which transferred them to a further set of guides,

down which they passed to the metal spray position. Here they were clamped under a mask whilst the spray gun moved backwards and forwards above the selenium surface. They were then ejected and were ready for electro-forming.

The whole process from the hot pressing of the powder to the spraying of the counter-electrode was thus entirely automatic except for the removal of the flash and rearrangement of the discs on the belt, carried out by the intermediate operator. Another operator attended to the spray gun and removed surplus metal from the mask when necessary. The mechanical construction of the rectifiers was then complete and the electro-forming and testing of the discs was carried out in the manner previously described for the other process.

The completed discs were assembled on spindles insulated by a bakelised paper tube in the normal manner. Contact was made to the surface of the counter-electrode by a thin metal leaf washer or spider insulated by a bakelite washer at the centre. Cellulose acetate lacquer embodying a red pigment was sprayed on the assembled unit to provide a certain amount of protection against moisture.

4.2. Mix & Genest

This was merely a replica of the S.A.F. equipment which manufactured selenium discs by the hand-coated process. A certain number of discs were also made by the S.S.W. process described below. All the plant was destroyed by bombing and was out of action in the later stages of the war.

4.2.1. Personnel interviewed.

Dr. Kauffmann
Dr. Mehliß

4.3. Siemens-Schuckert-Werke.

It was not possible to see any of the plant used for the manufacture of selenium discs, since it had been destroyed by bombing, but the following description was given by Herr Tschermak and Dr. Nietsche.

4.3.1. Personnel interviewed.

Herr Tschermak
Dr. Nietsche

4.3.2. The Siemens-Schuckert-Werke Process.

S.S.W. made discs of 18, 25, 35, 45 and 112 mm. diameter. They used steel baseplates which were roughened by blasting with quartz and nickel plated. The 18 mm. discs were coated with selenium on a hot plate by the S.A.F. method.

The larger discs were placed on a rotating plate heated to 350°C and powdered selenium was sprinkled on the surface. The molten selenium was then spread over the disc by applying a stainless steel plate similar to a table knife to the rotating surface.

The discs were stacked with interleaved aluminium foil and compressed to a pressure of 15 Kg per Cm². They were then placed in an oven at 110°C for 5 hours. After removal from the oven and disassembly of the stacks, the discs were passed through a belt oven maintained at a temperature of 216°C, with the faces freely exposed. The time of travel through the oven was about half an hour.

The discs were then placed individually on a rotating mandrel and the selenium surfaces were painted with a solution of sulphur in carbon bisulphide. The solution contained 65 grammes of sulphur in one litre of carbon bisulphide. It was brushed lightly over the surface with a marten-hair brush about 0.5 cms. wide. It was understood that this process was a very critical one for the production of good rectifiers. The discs were then placed in a mask and sprayed with an alloy of cadmium and tin, having a melting point of 177°C. No thallium was included in the counter electrode because it had been found that even 0.001% caused increased ageing.

The discs were electro-formed by connecting them individually to a rectified D.C. supply at 65 volts in series with a resistance. A voltage relay was connected across each disc, which was set to cut off the current at 45 volts. If the discs did not form properly, the surface of the counter electrode became oxydized and the discs were rejected. This short forming process was adopted to save time and space, but it was understood that rejections were very high amounting to as much as 35% on the larger sizes, mainly due to high reverse current.

4.4. Allgemeine Elektrostats Gesellschaft.

During the war A.E.G. rectifiers were manufactured in Berlin, but on visiting the factory it was found that all the plant had been removed. It was understood that the personnel and the plant had been transferred by the Russian authorities to Reschen, between Berlin and Dresden and that at this newly established factory there was some production of selenium rectifiers.

The following description of the A.E.G. process was therefore obtained from the personnel at S.A.F. and S.S.W. and not by direct contact with the persons engaged in the manufacture.

4.4.1. The Allgemeine Elektrostats Gesellschaft Process.

The essential difference between the A.F.G. and the other methods is that the selenium was evaporated onto the surface of the

base plate in a high vacuum. It was understood that aluminium plates of about 40 x 20 cms. were roughened by sand blasting and then coated with a thin layer of bismuth by the evaporation method.

The plates so prepared were then placed in a vacuum chamber and maintained at a temperature of about 120°C, whilst being subjected to the vapour from selenium to which a small percentage of bromine had been added. The thickness of the layer so produced was about 0.002 to 0.003 cms. The plates were passed through a tunnel oven at 210°C for one hour. They were then fumed in air for one minute with the vapour from heated selenium dioxide.

The counter electrode was then sprayed on to the selenium surface. It consisted of the eutectic alloy of cadmium, tin and bismuth with a melting point of 103°C. No additions were made to the alloy.

At some stage in the process, the initial plate was cut into squares of dimensions to give equivalent areas to the S.A.F. discs, and centre holes were punched for mounting purposes. It is probable that this operation was carried out immediately after the heat treatment at 210°C.

The electrical forming was carried out by connecting pairs of plates back-to-back in series with a resistance, and applying an alternating potential which was raised from 20 volts R.M.S. to 30 volts in about one hour. The voltage was measured across the individual plates.

5. SUPPLY OF SELENIUM

The selenium used for the manufacture of rectifiers in Germany was prepared by purification of raw materials supplied by Bolidens, Sweden and since it was necessary to import this material, considerable attention was paid to conserving it. Purification was carried out by Merck - Darmstadt, and Riedel de Haen, but the purified material was supplied to the manufacturers of rectifiers either in the form of selenous acid from which the manufacturer precipitated selenium or as selenium slab.

To render the powdered selenium suitable for the manufacture of rectifiers the following principal additions were made :-

1. S.A.F. added iodine :
2. A.E.G. added bromine :
3. S.S.W. received selenium which had been precipitated in the presence of hydrochloric acid and contained a pre-determined amount of chlorine.

5.1. A visit was paid to Merck and Dr. Wallstein was interviewed. The following information was obtained.

Merck had supplied pure selenium dioxide to S.A.F. and selenium containing chlorine to Siemens. They had not supplied any material to A.E.G. The raw selenium used for the manufacture of these materials was obtained from Bolidens - Sweden, and was in a black pulverised form having a purity of 99.5% and as free from tellurium as possible.

Some investigation had been conducted by Merck and Riedel de Haen Hanover as to the most suitable source of selenium. An extract of a report of a meeting was as follows.

Discussions on Selenium for Rectifiers
10th and 11th August, 1942.

Investigations by H. Nietsche (S. and H.) had shown that the pure selenium supplied by Merck differed from that supplied by Riedel and by S.A.F. in regard to its electrical conductivities. These differences could be attributed either to the raw material or to the method of preparation of the seleneous acid. For this reason tests had been conducted on various raw materials, and this meeting was called to discuss the origin and treatment of the raw material used for rectifier selenium and also the methods of purification. The gentlemen present were :-

| | | |
|------------|-------|---------|
| Baudisch | Hoppe | S.S.W. |
| Nietsche | | S. & H. |
| Geissler | | S.A.F. |
| Dr. Psille | | M. & G. |

Both firms had collaborated in work designed to clarify the situation. It had been shown quantitatively that the quality of natural selenium depended upon the soil from which it was obtained and this had been investigated by both firms.

Dr. Theile (Fiedel) had made experiments on the composition of a diversity of seleniums.

| | Residue | Selenium | Iron | Copper | Tellur |
|--|---------|----------|----------|----------|-----------------|
| | % | % | % | % | % |
| <u>Japanese</u> Selenium (yellow sample) | 0.83 | 98.7 | 0.05 | 0.02) | Not measured |
| Selenium (white sample) | 0.08 | 99.8 | 0.0007 | 0.005) | |
| <u>Canadian</u> Selenium I | 0.62 | 99.1 | 0.05 | 0.05) | Not measured |
| " II | 0.79 | 99.0 | 0.03 | 0.01) | |
| <u>Swedish</u> Selenium 1934 | 0.19 | 99.7 | 0.008 | 0.35 | 0.05 |
| " 1942 | 0.06 | 99.6 | Not | Not | 0.06 |
| | 0.04 | 99.6 | measured | measured | |

The Swedish raw material has been prepared to the highest degree of purity and is already used exclusively. From this raw material Riedel prepares for A.E.G. a pure selenium having an ash residue of 0.004 to 0.005% and this material shows unwanted impurities of the following upper values.

| | |
|---------|--------------|
| 0.0002% | Iron |
| 0.001% | Copper |
| 0.005% | Silicic Acid |

Riedel have sublimed seleneous acid several times and obtained the following data :-

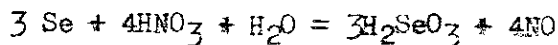
| | Ash Residue % | Iron % | Copper % |
|----------------------|------------------|-----------|-------------|
| Once Sublimed | 0.0008 | 0.00015 | 0.0002 |
| Twice " | ditto | 0.00007 | 0.00005 |
| Three times sublimed | ditto | 0.00009 | 0.00005 |

A second sublimation considerably reduces the iron and copper content but no further improvement is obtained by a third sublimation. The residual ash remains at the same value ; this is due to the calcium sulphate introduced by the enamel of the subliming apparatus."

5.2. Manufacture of Seleneous Acid

The method of manufacturing seleneous acid from the Bolidens selenium was as follows.

Seleneous acid, H_2SeO_3 has a molecular weight of 129.2 and contains 81% Se. It may be produced by treating selenium with nitric acid.



Apparatus 2 - 550 litre steam pressure boilers mounted on a gantry and connected to a plant for the absorption of NO

1 - 550 litre steam pressure boiler.

2 - 1,000 litre troughs.

1 - 500 litre trough, transportable and fitted with a cooling jacket.

(Disc filter - rubber connection to Membrane Pump)
Rubber centrifuge-capacity 150 kg.

Raw Material Black selenium - finely powdered commercial -
obtained from Bolidens.

Nitric acid 1 : 3 as free of chlorine as possible.
(2.4 kg. HNO_3 (1:3) for 1 kg. selenium).

Process

Into a 550 litre steam pressure boiler mounted on a gantry 1.6 metres high and connected to a plant for the absorption of NO pour 360 kgms. of commercial nitric acid and then over a period of $2\frac{1}{2}$ - 3 hours add 150 kgms. of commercial selenium by means of a "cradle shovel". The reaction mixture is heated until it begins to froth and in this manner the selenium excess is kept active. Stir vigorously with a "spatula" and moderate the reaction by the addition of cold water. At the end of the reaction the boiler is heated and evaporated until no more NO escapes and the solution shows only a small trace of nitric acid by the "Nitron" reaction. The volume of liquid left at this stage should be about 150 litres and then 500 litres of distilled water is added and the solution allowed to stand overnight. The next day the solution of selenous acid (about 45 Be) is syphoned into another vessel, passed through a rubber disc filter (PeCe Beutel) into a second 550 litre vessel and evaporated until crystallisation occurs. When it is observed that a crystalline skin is forming and the thickness has reached about 2.5 cms. the solution is ladled into a transportable 500 litre trough fitted with a cooling jacket. Whilst the concentrated solution is being water cooled, it is stirred with a large spatula until the temperature has fallen to 20°C . The next day the crystals are extracted in a rubber centrifuge (150 Kgm. capacity) (Pe-Ce unstitched cloth) and washed with 1-2 litres of cold water.

The crystals are stored in stoneware jars or wooden barrels protected against organic dusts.

Output. About 200 kgms. selenous acid for manufacture with 61%
Se (compared with 80% by theory).

The mother liquor is collected in a large bath. By the addition of an excess of Barium nitrate solution the SO_4 concentration is reduced and then the liquor is concentrated by evaporation as described above. More nitric acid is given off. While the oxydisation of the selenium is proceeding, it is necessary to wear a gas mask anywhere in the room as large quantities of gas are released. When handling the strongly corrosive selenous acid protective goggles and rubber gloves must be worn.

The remaining liquor from the crystallisation of selenous acid contains mostly the impurities iron, copper, sulphate, chlorine and tellurium. One can prepare from this liquor technical sodium selenite or one can precipitate the selenium with sulphur dioxide and

add the product to the raw selenium to be used in manufacture.

In order to prepare selenium dioxide of the highest purity for S.A.F. the seleneous acid described above was twice sublimed. This sublimation was carried out in a special apparatus, constructed of enamelled iron. Nitric acid is added to prevent the reduction of the selenium dioxide to selenium, i.e. to keep the crystals white. The apparatus is heated by gas to approximately 400°C and a quantity of 25 - 30 Kgs. takes 3 - 4 hours to sublime.

5.3. Precipitation of selenium from selenium dioxide.

Merck have precipitated some selenium for S.A.F. and have always precipitated selenium for Siemens. For S.A.F. it was important that the selenium should be entirely free from halide. For Siemens the precipitation was carried out in the presence of H.Cl in order that the resultant precipitate should have a chlorine content. Two chlorine bearing seleniums were supplied to Siemens :-

| | |
|------------------------|---------------------|
| (a) high concentration | 0.070% Cl \pm 10% |
| (b) low " | 0.020% Cl \pm 10% |

For S.A.F. the concentration had to be less than 0.004 to 0.005%.

The selenium was prepared by dissolving the selenium dioxide in water in large glass vessels. Sulphur dioxide was passed first through one solution and then through another to increase its action. During the reaction heat was generated and the vessels were allowed to rise to a temperature of 80 - 100°C which caused coagulation of the selenium. In order to ensure that this temperature was reached the vessels were frequently lagged with wood. The selenium is washed until free of H₂SO₄ and then dried in a centrifuge. The selenium is melted in a porcelain vessel at 380 - 400°C, the surface scum removed and then poured into slabs.

A chlorine content check of 100 gms. of the final material was made.

5 gms. of powdered selenium was dissolved in 20 ccs. of concd HNO₃ (S.G. 1.4) as free from chlorine as possible (a blank check of the nitric acid was conducted). It took approximately 2 hours to dissolve all the selenium.

25 ccs. of silver nitrate $\frac{(N)}{(10)}$ was added to precipitate the chloride and the excess of silver nitrate was estimated by adding an excess of ammonium sulpho-cyanide $\frac{(N)}{(100)}$ and titrating the excess ammonium sulpho-cyanide with $\frac{(N)}{(100)}$ silver nitrate using ferric ammonium sulphide and toluol to determine end point.

S.A.F. had developed a method to check the iodine content of prepared selenium mixtures :-

5 gms. of powdered selenium was dissolved in NaOH and the selenium precipitated with CO_2 . $\text{Fe}_2(\text{SO}_4)_3$ was added and then an excess of AgNO_3 . The precipitate of silver iodide was estimated gravimetrically.

All the plant used for selenium production by Merck had been entirely destroyed.

6. THEORETICAL CONCLUSIONS CONCERNING SELENIUM RECTIFIERS.

A meeting of the "^{gleichschichten}Rectifier Ring" was called in Prague on November 24th and 25th, 1944, by the Ministries concerned to discuss the production position of selenium rectifiers, and the physical basis of dry rectifiers. The meeting was attended by representatives of the Ministries and the manufacturers, and also by scientists who had undertaken investigations in this field. A full report of this meeting is given in F.I.A.T. Final Report No. 706 dated 26th January, 1946.

6.1. Relative Merits of Various Manufacturing Methods.

Each manufacturer presented an account of his particular method of manufacture, the various methods described being in accordance with the information given earlier in this report.

In spite of the differences in detail which appeared, there was no agreement on a most favourable method of manufacture. Each firm had developed independently balanced methods which produced rectifiers of comparable characteristics.

6.2. The physical basis of the Selenium Rectifier.

The following conclusions appear to have emerged from the discussion of the Committee.

6.2.1. The electrical conductivity of selenium.

Conduction in selenium is by electron deficiency. The addition of halogen whether Iodine, Bromine or Chlorine, greatly increases the conductivity. Additions of oxygen also increase the conductivity, while the presence of metal atoms may increase or decrease it, depending upon their nature and concentration. The conductivity is determined not only by the concentration of those chemical additions, but also the structure of the selenium layers formed.

It was the opinion of the majority of investigators that the resistance of selenium does not obey Ohms Law and that its value is strongly dependent upon frequency, i.e. the specific resistance of

various seleniums measured with direct voltage was found to vary between 300 ohms/cm and 100 megohms/cm, while with high frequency the specific resistance for all types approximated to 300 ohms/cm.

The temperature coefficient of resistance is dependent on the specific resistance and its value and possibly its sign is dependent upon the state of crystallisation, additions and temperature. The temperature coefficient is not reproducible and is dependent upon the previous thermal and electrical history of the sample.

6.2.2. The contact-resistance between selenium and counter-electrode.

The rectifying action takes place at the junction between the selenium and the counter electrode metal. It is dependent on the character of the surface of the selenium layer and the metal, or metals, of which the counter electrode is composed.

It is probable that the surface film of the selenium layer becomes poorer in the conductivity-providing disturbance centres, during the various heat treatments.

It was suggested that the various chemical treatments applied to the selenium surface, e.g. fuming with selenium dioxide, sulphurisation etc. have the effect of :-

- (a) still further impoverishing the surface film ; or
- (b) providing the necessary chemical material to assist in building up the barrier layer during electrical forming ; or
- (c) closing minute holes in the surface film and minimising the effect of weak spots in the selenium layer.

6.3. The Counter-electrode.

Investigations of the counter electrode were primarily directed to the three technically important metals, Bismuth, Cadmium and Tin. These metals, either pure or combined as eutectic alloys, were applied as counter electrodes either by the usual manufacturing technique of metal spraying or by vaporization.

Invariably, the alloys gave superior results to the pure metals themselves. Experiments have been conducted with small percentages of thallium added to the counter electrode which has the power of greatly increasing the resistance in the blocking direction, and the use of this addition has been adopted by some manufacturers.

6.4. Electrical Forming.

During electrical forming, metal ions diffuse from the counter-electrode to the selenium, forming metal selenide compounds and simultaneously reinforcing the barrier layer. Increase of temperature favours this migration.

Electrical forming also produces an equalisation of the barrier film resistance, either due to high temperature at weak points, favouring migration, or due to high electrical stress at such points.

6.5. Ageing.

Ageing in selenium rectifiers is due to the continuation under service conditions of the conditions which lead to the initial setting up of the barrier layer, i.e. the impoverishment of disturbance centres resulting in poorer conductivity in the selenium layer and the diffusion of metal ions into the selenium layer.

6.6. General Conclusions.

An intensive study of the selenium rectifier by Koch and Paganski with particular regard to the variations of self capacity has led to the following conclusions :-

6.6.1. That the simple theory of a metal rectifier consisting of a good conductor (counter electrode metal) in contact with a semiconductor (selenium) is not applicable to the selenium type of rectifier.

6.6.2. This rectifier fails to obey anticipated laws, particularly at high reverse voltages.

6.6.3. The departure is probably due to marked lack of homogeneities at the contact, since a metal selenide layer is formed on the metal and there is a diffusion of metal into surface films of the selenium layer. It is in this chemically complex zone that the space charge effects leading to the rectifier action take place.

6.6.4. The effective surface area of the selenium layer is 1.5 to 2 times the nominal area of the rectifier, but it cannot be assumed that the counter-electrode makes contact everywhere.

6.6.5. The special processes which lead to substantial improvements in the blocking voltage are

- (a) chemical treatment of selenium surface to cause a preferential impoverishment of disturbance centres in the surface films :
- (b) the application of lacquer films :
- (c) the use of small additions of thallium in the counter-electrode.

6.6.6. To improve the rectifier in the conducting direction, it is necessary to increase the number of disturbance centres in the selenium layer by the addition of halogen and possibly certain metals, and the formation of a structurally perfect layer.

6.7. Alternative types of metal rectifier.

Owing to difficulties in obtaining supplies of raw material in the later stages of the war, and to the high demand for metal rectifiers, serious consideration was given to providing an alternative to the selenium rectifier. The obvious first choice was the copper-oxide rectifier, which was already established in manufacture. The difficulties involved were twofold.

- (a) It was necessary to produce a German copper at least comparable to the American C.C.C. copper, which was being used for production and was already in short supply.
- (b) In order that the copper oxide rectifier could be substituted for the selenium rectifier in the space provided in existing designs, it was necessary to increase the rated output of copper oxide assemblies, and this could only be achieved by producing a German copper with rectifying qualities even better than the American supplies hitherto available, or devising processes to apply to existing supplies of copper which would permit of increased ratings.

It was decided to pursue research to obtain such a material, but it is unlikely that any further work was carried out owing to the conditions obtaining in Germany at the time.

With regard to other possible alternatives, it was considered that as the search for a new rectifier had been going on in Germany for 15 years without result, it was useless to hope for any alleviation of the existing difficulties from this source.

6.8. Proposals for future research.

The directions in which improvements were desired by the manufacturers were as follows :-

- Reduction of the forward resistance.
- Increase of the reverse resistance.
- Reduction of time of electrical forming.
- Reduction of sensitivity to temperature and humidity.
- Increase of life.

In order to achieve these objects, the following programme of research was suggested. It is practically certain that none of this work was carried out.

- (a) Forming and ageing experiments on all manufactured products.
(Dr. H. Schmidt).
- (b) Influence of different lacquer layers (Dr. Koch and Dr. Poganski).
- (c) Extension of the experiments on the influence of the temperatures of evaporation of electrodes on A.C. voltages (Dr. van Dingenen).
- (d) Researches on the selenium itself, particularly on single crystals. Radiographic and ultramicroscopic research of single crystals.
(Dr. Lehovec).
- (e) The conductivity of selenium in relation to the structure of the crystal (Dr. Krebs).
- (f) Metal-selenides : conductivity, work function vers. vacuum. Investigation of the contact selenium-metal selenide (Dr. van Dingenen).
- (g) X-Ray analysis of the selenide layers on the front-electrode (Dr. Krebs together with the A.E.G.).
- (h) Method of analysis for very small quantities of bromine (Inquiries to be made to Merck).
- (i) Ultramicroscopic investigations to find whether there exist precipitations of halogen-selenium compounds.
- (j) Determination of the equilibrium concentration of the halogen in the interior of the selenium by measuring vapor pressure.
- (k) Investigations of halogen-selenium compounds.
- (l) Clarification of the mechanism of the increase in the blocking voltage due to metal-traces.

7. COPPER OXIDE RECTIFIERS. PROCESSES OF MANUFACTURE.

During the period of the war, two German companies, Siemens Schuckertwerk A.G., Siemensstadt, Berlin, and Te.Ka.De.A.G., Nuremberg manufactured copper oxide rectifiers. The peak production figures for this type of rectifier which were reached during 1943 were :-

| | | | | |
|------------------|-----------|-------|-----|-------|
| Siemens, approx. | 6,000,000 | discs | per | annum |
| TeKaDe, approx. | 200,000 | " | " | " |

and the total of 6,200,000 represented approximately 10% of the output of selenium rectifiers produced in Germany.

The majority of these copper oxide rectifiers were used in special applications such as modulators, high frequency rectifiers and measuring instruments.

7.1. Suddutsche Telefon-Aparate-Kabel Und Drahtwerke A.G.
(Te.Ka.De.).

Rectifier Personnel : Dr. Baum
Dr. Muschweck

7.1.1. Plant

The copper oxide plant is relatively small. It was originally installed at Nuremberg and during the war moved to Schwarzenback (near Hof). In March 1946 the plant was dismantled and brought back to Nuremberg.

7.1.2. Copper

Te.Ka.De. had no supplies of American Copper but used a German electrolytic copper prepared by

Felten & Guilleame Carlswerk A.C. Koln-Mulheim and
Wieland-Werke Ulm.

This copper was specified as 99.998% purity and according to Te.Ka.De. gave excellent results.

7.1.3. Sizes of Rectifiers Manufactured.

The following sizes of discs were manufactured :-

2 mm. dia. disc for Sirutors (Siemens H.F. detectors)

3 mm. dia. disc)

7 mm. dia. disc) for modulators

20 mm. dia. washer)

40 mm. dia. washers and 81 x 300 mm. double sided plates were built experimentally.

7.1.4. Process Details

1. The discs are punched and rumbled with iron balls to remove burrs and polish.
2. Washed in pure acetone and dried.
3. Loaded on aluminium oxide plate and preheated at 500°C for 30 mins.
4. Oxydized for 8 mins. at 1020°C with steady stream of oxygen through oven.

5. Quickly transferred to low temperature furnace set at 560°C, where they remain for 20 mins.
6. Quenched without delay in distilled water contained in glass bath.
7. The backs of the discs are treated with sulphuric acid and polished.
8. The black oxide is removed from front face with potassium cyanide and after washing and drying the oxide surface is roughened by gently rubbing with No.0 glass paper.
9. Powdered graphite is rubbed into the cuprous oxide surface with a leather pad.
10. The discs are mounted in a mask and a silver front electrode deposited by vaporisation in high vacuum.
11. The rectifiers were tested to the following limits :-
 - 2 mm.dia. Forward current at 0.5 volts must exceed 0.8 mA
Reverse current at 6.0 volts must be less than 20 microamps.
 - 20 mm.dia. Forward current at 0.5 volts must exceed 175 mA.
Reverse current at 6.0 volts must be less than 2 milliamps.
12. The 2 mm. discs were assembled in moulded bakelite bodies with brass screw on end caps and soldered wire end connections.
13. The modulator rectifiers 3 and 7 mm. dia. were assembled in ceramic tubes with soldered end caps.

7.2. Manufacturing Details - Siemens Schuckertwerke.

7.2.1. Rectifier Personnel : Herr Tschermak
Dr. Nietsche

7.2.2. Plant

Until 1945 all rectifiers were manufactured at Siemensstadt, but in that year production was commenced at dispersal plants at Soenerwitz (Dresden) and at Hoff. The plant at Siemensstadt was largely destroyed but it has been rebuilt and manufacture is recommencing.

7.2.3. Copper

At the outbreak of war Siemens had approximately 700 tons of

American C.C.C. copper and during the war they have used approximately 500 tons. Siemens rolled their own copper strip and considered it of great importance to keep the copper free from oil, thus no oil was used during rolling or punching.

Attempts had been made to use German electrolytically refined copper, but it was found that rectifiers made with this type of copper had forward resistances twice as high as those made with American copper.

7.2.4. Sizes of Rectifiers Manufactured.

- 2 mm. dia. disc for Sirutor (Siemens H.F. detector)
- 3 mm. " ")
- 4 mm. " ") for modulators,
- 7 mm. " ") instrument purposes.

- 20 mm. " washers for modulators or small power requirements.

- 40 mm. " washers) for power requirements, e.g.
- 300 x 81 mm. double sided plate) battery charging, etc.

7.2.5. Process Details

1. The discs or washers are punched flat.
2. The discs are placed on copper sheets which have been rejected for rectifier manufacture.
3. The washers are mounted on rods in pairs.
4. The charge of discs or washers is preheated for 5 to 15 minutes at 520°C.
5. Oxydized at 1000 - 1020°C for 8 to 12 minutes.
6. Annealed for 15 to 30 minutes at 520°C.
7. For low resistance rectifiers the charge is quenched in water.
8. For medium resistance rectifiers the charge is quenched in oil.
9. For high resistance rectifiers the charge is either cooled in air or after the 520°C anneal is further annealed at 365°C for 15 minutes and then quenched in water.
10. The chemical treatment for the removal of black oxide varied with size of element : thus for small discs (2, 3 and 4 mm. dia.) 30% nitric acid was used, while for large discs, washers and plates 46.9% nitric acid with an addition of 6.2% sulphuric acid was favoured.

11. The front contact electrode consisted of a vaporised silver contact direct on the oxide for 2, 3, 4, 7 mm. dia. discs, and for certain special (modulator type) 20 mm. dia. washers. For all other elements, i.e. washers and plates, an aquadag contact was prepared.
12. The following figures are typical of the limits to which rectifiers were tested.
- | | |
|---------------------------------|--|
| 2 mm. dia. discs | Forward current greater than 0.2 mA at 2 volts Reverse current less than 3.5 uA. at 2 volts. |
| 3 mm. " " | Forward current greater than 0.8 mA at 0.4 volt Reverse current less than 8 uA at 2 volts. |
| 5 mm. " " | Forward current greater than 3 mA. at 0.4 volts Reverse current less than 20 uA. at 2 volts. |
| 7 mm. " " | Forward current greater than 5 mA. at 0.4 volts Reverse current less than 40 uA. at 2 volts. |
| 20 mm. " " | Forward current greater than 0.100 amp. at 0.5 volts Reverse current less than 3 mA. at 6 volts. |
| 40 mm. " " | Forward current greater than 0.7 A. at 0.5 volts Reverse current less than 7 mA at 6 volts. |
| 300 x 81 mm. plates Grade I. | Forward current greater than 25 A. at 0.48 volts Reverse current less than 70 mA. at 6 volts. |
13. For the manufacture of HOKO (highly stable) discs, a "pre-ageing" treatment of 48 hours at 90°C. was applied to the completed disc.

8. THEORETICAL CONCLUSIONS CONCERNING COPPER OXIDE RECTIFIERS

Very little advance in the technique of manufacturing copper oxide rectifiers has been made during the war period. The work of developing the copper oxide rectifier was left entirely to the Siemens organisation and Dr. Waibel of the Siemens Halske Laboratories carried out various researches, particularly in regard to the purity of copper for rectifier purposes. This work had been conducted primarily with a view to substituting German Electrolytic Copper for American C.C.C. A study of the effect of impurities in rectifier copper had enabled Siemens to state why certain German

Electrolytic Coppers were inferior, but it could not be proved that any of the impurities in American C.C.C. were decisive. In general, the result of deliberately adding impurities to "good" rectifier copper was to increase the forward and reverse resistances, and no improvement in the fundamental rectifier could be effected. Only specially selected German coppers subjected to careful refinement could yield rectifiers approaching those made from American C.C.C.

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