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PRODUCTION OF LUMINOUS COMPOUNDS AT THE WORKS OF AUER GESELLSCHAFT A.G.

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PRODUCTION OF LUMINOUS COMPOUNDS AT THE WORKS OF AUER GESELLSCHAFT A.G.

Reported by:

E.R. OWEN, AIRCRAFT BRANCH, ECONOMIC DIVISION
C.C. FOR GERMANY (B.E.)

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE
32 Bryanston Square, London, W.1.

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Report on the Production of Luminous Compounds at the Works of Auer Gesellschaft A.G. Berlin

Investigator: E.R. Owen, Asst Controller, Aircraft Branch, Control Commission for Germany (B.E.)

Object of Investigation: To obtain information on the production and application of luminous compounds, particularly for aircraft purposes, and on the materials used in production.

Summary

The Auer Gesellschaft A.G. was one of four firms forming the German Radium Syndicate which handled all the supplies of radioactive materials in Germany during the war. Auer was also the principal producer of luminous compounds or paints and the only firm in Germany making incandescent gas mantles. There were two plants concerned with the production of luminous paints; one at Oranienburg where radioactive materials were extracted from ores, residues, etc and the other in Berlin for the further treatment of the products from Oranienburg and the manufacture of radioactive preparations and appliances generally. This report describes the methods employed for the production of luminous compounds at the Berlin plant, to which visits were paid, and gives some information, obtained during these visits, about the Company's activities at Oranienburg.

General Position

During the war the distribution of radioactive compounds for:-

(i) production of luminous compounds for instruments;
(ii) medical and surgical applications;
(iii) scientific and technical applications
e.g. materials testing;

was under the control of the Reichsstelle für Metalle of the Reichswirtschaftsministerium. The manufacture of compounds, equipment, etc., for the above three purposes was in the hands of four firms who together with the Auer formed the Radium Syndicate. The Reichsstelle issued radioactive compounds to the Syndicate who, in turn, distributed them to its four members. The four firms and the percentage of the total material issued to each were as follows:-

(1) Auer Gesellschaft A.G. Berlin 27%
(2) Chininfabrik Buchler and Co. Brunswick 27%
(3) Treibacher Chemische Werke 27%
Treibach - Karnten - Oesterreich
(4) Radium - Chemie, Frankfurt/Main 19%

The managing director of the Syndicate was Herr Rabbe, who is at present in Hamburg (address - c/o Messrs. Stortlander & Co. Hamburg, Chile - Haus). The principals in charge of the Reichstelle Chemie at the Reichswirtschaftsministerium were Dr. Hoffmann and Dr. Kraft.

Stocks

The total stock of radioactive materials held by Auer Gesellschaft during recent years averaged about 10 grams, inclusive of radium, mesothorium and radio thorium compounds. An inventory was made last on February 28th, 1945, and was as follows:-

	Milligrams
Radium	4,120
Mesothorium	6,042
Radiothorium	120

Radium: Of the 4120 mg., 2240 mg. did not belong to Auer, consisting of materials which they had on hand from hospitals and other sources for reclamation. About 1200 mg. was lent or hired out to medical and chemical establishments and to other firms for treatment for which Auer paid a fee.

Mesothorium: 1253 mg. of the 6042 mg. was hired out chiefly to medical establishments and to Treibacher Chemical Works for treatment. The main part of the stock was contained in raw material, monazite sand, held at St. Joachimsthal Czechoslovakia, the remainder comprised finished material held in Berlin.

Radiothorium: Owing to the short life of this material, only a small stock was kept (120 mg). This was held partly in Berlin and partly as raw material at St. Joachimsthal.

Sources of Supply

The sources of the radioactive materials handled by Auer were:-

Radium One source was the pitchblende ore obtained from St. Joachimsthal. Further supplies were derived from the large stock of radium held by the Reichswirtschaftministerium, from the reclamation of old medical preparations obtained in Germany and from abroad, particularly France and Belgium.

Mesothorium. The main source was monazite sand stocks held at Oranienburg: the remainder came from various materials obtained through the firm Société Products Chimique des Terres Rares Paris.

Radiothorium. All the radiothorium delivered in recent years was obtained from the reclamation of old mesothorium preparations which the firm had supplied to various medical institutions.

Uses

During the war radioactive materials were used almost exclusively for the manufacture of radioactive luminous paints, very little being used for medical and scientific purposes.

The plants of the Auer Gesellschaft

Auer has a plant for the extraction of radioactive materials from ore, scrap etc., at Oranienburg about 20 miles north of Berlin, and a chemical plant for the manufacture of luminous compounds and other products at Berlin Friedrich-Krause-Ufer 24. The former is in the Russian sector and the latter in the British sector of the city. Visits were paid to the Berlin works but not to the Oranienburg works.

The Auer Gesellschaft A.G. Works, Berlin

Location. This is situated in the British Sector of Berlin at Friedrich-Krause Ufer 24, near the Thyssen Eisen-und Stahl - A.G. on the south bank of the Hohenzollern Kanal. It is rather difficult to locate and about the most direct route from the Kaiserdamm is to cross the Bridge by the Schloss Brucke, then follow Kaiserin Augusta Allee, Alt Moabit, Stroms Strasse and Putlitz Strasse to the junction of the latter with the Friedrich-Krause Ufer.

Map Reference. Berlin Sheet 1 (N.W) or Sheet 5 (Central) 1:11

Visits: On October 12th, 16th

Personnel Interviewed:

Mr. Pautsch	President
Dr. Iwen	Technical Director
Mr. W. Woltje	Technical Assistant
Dr. Wolf	Technical Director

All were co-operative and appeared to be reliable.

Condition of Works. The works had suffered little damage from bombing or shelling and at the time of the visits was in condition for production again. Production of gas mantles and radioactive preparations and appliances was, however, at a standstill because of lack of materials. There was a small production of simple textile goods and ornaments which involved a great deal of hand sewing by female labour. It was stated that the object of this activity was to try to keep the firm's trained labour on the company's books.

Production

Manufacture of radioactive luminous paints

Luminous paints were manufactured from a base of zinc sulphide with additions of radioactive material, mainly radium and radiothorium in the form of bromide solutions. The degree of luminosity was controlled by the quantity of radioactive material added. For the usual grades of paints for war purposes an intensity lying in the range 20-200 millispestilb (masb.) was required

(1 millispestilb = $\frac{1 \text{ candle} \times 10^{-3}}{10\pi}$) per sq. cm.

For the production of these average grades the zinc sulphide was first moistened with distilled water and the bromide solution usually containing 1 mg. of radium element per 10 c.c. added and the whole mixed thoroughly in a porcelain evaporating dish. To make 1 Kilogram of paint giving an intensity of 150 millispestilb (No. 8) 15 mg. of radioactive substance comprising a mixture of radium and radiothorium in 150 c.c. bromide solution was added to approximately 1 Kilogram of zinc sulphide. This paint had a brightness of 150 masb two months after production.

Radioactive luminous paint was largely used with nitrocellulose lacquers, in the proportions of luminous powder to lacquer of 1 to 1 or ½ to ½, according to the purpose for which the paint was required.

Luminous films were also produced with intensities of about 22-30 mesb.

The production of radioactive luminous compounds was about 50Kg. per month in terms of No. 8 compound (15-18 mgm. radium per Kilogram). The plant at Berlin could produce this quantity now if the materials were available.

Manufacture of Zinc Sulphide

Zinc sulphide for the base material in luminous paints was produced by precipitation from a solution of zinc sulphate by means of sulphuretted hydrogen, followed by purification, drying and activation. The process of manufacture comprises the following stages:-

(i) Preparation of zinc sulphate solution;
(ii) Manufacture of sulphuretted hydrogen;
(iii) Precipitation of zinc sulphide, washing and drying precipitate;
(iv) Preparation of wash water.
(v) Activation of zinc sulphide;

(i) Preparation of zinc sulphate solution.

In a cylindrical vat capacity 500 litres, 180 Kg. of zinc sulphate is placed and dissolved in 450 litres of distilled water vat is provided with a mechanical stirrer and the solution is stirred for 5 minutes while 5 litres of a solution of ammonium sulphide is added gradually. This latter solution is made up from 1335 c.c. of a 10 per cent. ammonium sulphide solution (as generally used for analytical purposes) and diluting with water to 5 litres. Sulphuretted hydrogen is passed into the vat for 15 minutes followed by an addition of 250 c.c. of a solution of hydrogen peroxide containing 75 c.c. of perhydrol. Finally 5 litres of ammonia solution (25 per cent. of .88 ammonia) is added and the whole contents of the vat are stirred for 10 to 15 minutes. Experience has shown that most grades of zinc sulphate are too acidic and must be neutralised before starting with the precipitation proper.

After standing for several days to allow the precipitate to settle completely, the solution is drained off on to a membrane filter held in a porcelain funnel or cylinder.

(ii) Manufacture of Sulphuretted Hydrogen

In a stoneware holding pot, capacity 1000 litres 120 Kg. of sodium sulphide, Na_2S, is dissolved in about 800 litres of hot water

water while stirring. The solution is allowed to stand for 1 day and is then transferred into a preliminary saturation pot in which sodium sulphide changes into NaHS. All waste H_2S in the whole plant is led into this pot where it is absorbed and becomes available for further use.

The NaHS solution from this pot is pumped or sucked into the main H_2S generator pot which contains dilute hydrochloric acid (30 per cent Hcl). H_2S contained in solution in the generator pot can be recovered by the addition of 15 litres of NaOH solution (45 per cent NaOH) and stirring to convert the H_2S into NaHS for further use.

(iii) Precipitation of zinc sulphide.

250 litres of the filtered solution from operation (i) are placed in a porcelain vessel, diluted with "double" distilled water 450 litres, and then transferred into the main precipitating vessel which consists of a porcelain pot with a lid with an airtight joint. The pot is evacuated down to a pressure of 360 m.m. mercury and H_2S is introduced while stirring the solution and keeping the pump running to reduce the pressure inside the vessel to 280 m.m. It is important to control the pressure closely and keep it at this level.

The gas is passed into the solution for 47 minutes at the end of which time the solution and precipitate are transferred into a porcelain settling vessel where they are allowed to settle for 1 hour. The overlying solution containing sulphuric acid is run off after a sample has been taken and the sulphuric acid content ascertained by titration.

In the meantime a second lot of 250 litres of preliminary precipitated solution (para (i)) diluted with 200 litres of double distilled water is treated in the same way as the first lot and the whole of the zinc sulphide precipitate and solution are added to the zinc sulphide in the porcelain settling vessel. After standing for 2 hours, the solution in this vessel is siphoned off and 50 litres of double distilled water is added to the zinc sulphide precipitate. The zinc sulphide and water are now transferred to a large filter and washed on the filter five times with 100 litres of double distilled water.

The washed sulphide is dried in porcelain evaporating dishes on a water bath or in glass dishes inside a drying oven with hot air circulation. The output of sulphide from each precipitation is 48-52 Kilograms. It was found in practice that sulphide dried over a water bath had superior physical properties to sulphide dried in an oven.

(iv) Preparation of the wash-water.

Formerly the washing of the zinc sulphide on the filter was done by double distilled water kept in quartz containers. In recent practice the wash water was prepared by the following process:-

100 litres of distilled water is heated in a boiler to 50°C and transferred into a procelain vessel, capacity 600 litres. After warming the vessel, another 400 litres of distilled water at 80°-90°C is added to the first 100 litres. About 30 grams of precipitated zinc sulphide is poured into the water while stirring, and the whole is then stirred for an hour by means of filtered air. After being allowed to rest for 24 hours the solution is passed through a membrane filter and transferred into stock vessels.

(v) Activation of zinc sulphide.

(a) Preparation. The dried sulphide is mixed with flux and activating matter for the production of Clarophan. For the production of 100 Kg. of Clarophan, zinc sulphide is mixed with 750 grams of powdered sulphur and the following quantities of flux ingredients:-

	Grams
$BaCl2\ 2H_2O$	3,125.0
Na Cl	469.0
$Mg\ Cl_2\ 6H_2O$	156.5
$Zn\ Cl_2$ (dry)	156.5
$Cu\ SO4\ 2H_2O$	39.3
	3,946.3

The sulphide, sulphur and flux make up a total of 100 Kg. The sulphide which has been dried over a water bath is mixed with the sulphur, and is then mixed with the flux in portions of 10 Kg. at a time in a porcelain bowl or mortar. The 10 Kg. of mixture is charged into a quartz crucible with double covers. The first or inner cover just fits the inside of the crucible and rests on the charge. As the charge shrinks on ignition the cover sinks with it and protects it from gases. The second cover has the same diameter as the crucible and closes it hermetically.

(b) Ignition. The crucibles with their charge are first placed in a drier at 100°C for an initial warming and then in a stove or furnace for igniting.

The practice was to heat the crucibles in a gas heated stove or electric furnace. In the former the temperature was slowly brought up to 1200°C (as measured on the outside of the crucible by a thermocouple) over 3 hours and then maintain it for another 2 hours at this temperature.

When using a larger electric furnace the temperature was brought up to 1200°C over 4 hours and then held at 1200°C for another 4 hours. At the end of this period the furnace was switched off and the crucibles cooled slowly in the furnace, the door of the furnace being opened after 4 hours to expedite the cooling.

(c) Washing. When thoroughly cool the contents of the crucible is tipped out - generally it falls out quite easily as in the igniting process the charge sinters strongly. It is washed with water and screened to remove the rough melted and unusable portions. The screened material is washed thoroughly again to remove chlorine, dried, and screened.

(d) Further treatment. To improve the steadiness of the luminescence, the sulphide is further treated with sodium hydroxide and waterglass. Two stock solutions are made by dissolving 100 grams of Na_2O in 5 litres of water and 600 c.c. of waterglass (40° Baume) in 5 litres of water. To each Kilogram of sulphide 50 c.c. of each of these stock solutions are added together with sufficient distilled water to allow the mixture to be well stirred. The mixture is dried over a water bath while stirring thoroughly.

Production of radium compounds for luminous paints

(a) The raw material was pitchblende obtained from St. Joachimsthal Czechoslovakia. The ore was brought to the Company's works at Oranienburg in the form of a concentrate, finely ground, and free from barren gangue material. At Oranienburg the concentrate was smelted with caustic soda and after cooling the product was washed with water and digested with dilute hydrochloric acid containing some sulphuric acid. The uranium in the product went into solution leaving the radium in the residue. The residue was boiled several times with sodium carbonate and caustic soda, washed out with water, and then dissolved in pure hydrochloric acid. The hydrochloric acid dissolved the insoluble carbonates, and the solution contained radium and barium chlorides.

By fractional crystallization a material was obtained containing 100 mg. of radium to 5 Kg. of barium chloride and this material was sent to the Berlin works for further treatment.

The Radium Department of the Oranienburg Works is shown in the photographs in the Appendix hereto.

(b) At the Berlin plant the material was further concentrated by fractionating to a product containing 100 mg. radium in 100 to 250 grams. Eventually the radium and barium were precipitated as bromides which were separated as far as possible by fractional crystallization. After the final concentration a product was obtained consisting of radium and barium bromides containing approximately 50-55 mg. radium per 100 mg.

During these concentrating processes the product at each stage was always tested for its content of radium by means of the electroscope. The final bromide product was packed in small glass tubes, and was supplied from these tubes for making solutions for luminous paints. For medical applications this concentrated bromide product was first converted into sulphate and then filled into small tubes, needles or similar containers.

The Auer Adaptometer

This Adaptometer, manufactured by Auer Berlin, is a device for testing the adaptation of the eyes to darkness.

It consists of a box-shaped frame about 15 x 5 x 5 cm., the front and back sides being missing, and the upper and lower sides are transparent. In this frame are several cylindrical stampers or tubes about 4 cm. long and 1 cm. diameter with their axes at right angles to the longitudinal side of the frame, and easily movable into any position along the length of the frame. These stampers show at one end a large luminous disc of equal diameter for each stamper but with the degree of brightness varying for each stamper. The other ends of the stampers have a luminous disc of different diameter for each stamper but of the same degree of brightness for all. All the luminous surfaces at both ends of the stampers are produced of radioactive paint the illuminating power of which is of a high degree of constancy and is not affected by daylight.

To test the adaptation of the sight to darkness the subject is first made to stare at a large plain white surface for at least 10 minutes. He is then given the adaptometer in which the stampers have been mixed and arranged irregularly in order of brightness, and in the dark, has to arrange the stampers in increasing order of brightness by looking only at the ends which have the discs of equal diameter but varying brightness. When these ends of the stampers are arranged in regularly increasing order of brightness, on turning the frame round to show the other ends of the stampers, the latter will show their luminous discs ranging evenly from the smallest diameter to the largest diameter discs.

The time taken by the subject to arrange the ends with discs of varying brightness in the correct order of increasing brightness is a measure of the speed of adaptation to darkness.

Manufacture. The frame of the adaptometer is made of aluminium, the upper and lower sides are made of normal glass and the sides of sheet aluminium.

The stampers or cylinders are tubes made of plastic with inlaid radioactive films at each end. This luminous film contains 3.4 gram of paint powder per 100 sq. cm. made from zinc silicate with an addition of radium bromide.

There are seven stampers or cylinders and the luminous discs at the ends of the stampers are made with paints with the following radium content:-

(a) Discs of equal diameter at front end of stampers

Stamper No.	Radium Element in mg. per 1000 gram paint
1	50
2	35
3	24.5
4	17.1
5	12.0
6	8.4
7	5.9

(b) Discs of different diameter at back or control end of stampers.

Stamper No.	Diameter of disc cm.	Radium Element in mg. per 1000 gram. paint
1	1	150
2	0.8	150
3	0.6	150
4	0.5	150
5	0.4	150
7	0.2	150

Stocks. On 15th October 1945 the firm had 68 of these adaptometers in stock. They were inspected by R...F. Air Disarmament Flight, Berlin who gave the firm instructions that the stock was not to be removed.

Conclusions [redacted]

1. According to information obtained from principals of the Auer Gesellschaft A.G. Berlin the radioactive materials available in Germany during the war appear to have been used almost exclusively for the preparation of luminous paints for use in mechanical instruments, equipment, etc.

2. In luminous compounds radium was mainly used with some radiothorium. Very little mesothorium appears to have been used no doubt due to the fact that no source of the raw material (monagite sand) was open to Germany during hostilities, whereas radium could be obtained from pitchblende obtained from St. Joachimsthal Czechoslovakia.

3. The Auer Gesellschaft has at Berlin a very modern and efficient plant for the production of luminous compounds, particularly for the production of zinc sulphide. This plant could produce from 30-50 Kg. per month of luminous compounds depending on the strength of the compound produced. At present, however, the firm has no supply or source of supply of radioactive material and without this material, the plant could only be used for the manufacture of high grade activated zinc sulphide.

4. The firm has no plant, outside their Oranienburg works in the Russian zone, for the production of radioactive material either from ore or from scrap. They are anxious to set up an extraction plant in the British sector of Berlin. On the most conservative estimate having regard to the present industrial situation in Germany, such a plant could not be in production in less than 12 months. Unless therefore it is supplied with radioactive compounds in a pure form there is no prospect of obtaining luminous compounds from the Berlin plant. In this connection it is interesting to note that the Military Government Berlin has already granted the firm a permit to start production again.

5. The Auer Gesellschaft has a very wide technical knowledge and experience of radioactive materials and their industrial and technical applications and played an important role in the production of weapons of war.

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