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GERMAN PHOTOCONDUCTING CELLS FOR THE DETECTION OF INFRA-RED RADIATION

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE.

GERMAN PHOTOCONDUCTING CELLS FOR THE DETECTION OF INFRA-RED RADIATION

Reported by
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BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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Investigator

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1. Object of Visit

From the interrogation of Dr. Kutzscher of the Electro-Acustic Kommanditgesellschaft, Kiel, in London some weeks ago, it was apparent that a considerable amount of work has been done in Germany since 1939 on the development of photoconducting cells for the detection of infra-red radiation. Development work on such cells had been done principally by Dr. Kutscher's organisation - they had produced very sensitive lead sulphide cells which had been used operationally in various forms of detecting apparatus. Research work had been done mainly at Prague under Prof. Gudden, and at Göttingen under Prof. Pohl.

This visit was made with the object of obtaining as much information as possible about the method of manufacture and properties of these photo-counducting cells.

2. Targets Visited

The following targets were investigated:-

(a) Electro-Acustic Kommanditgesellschaft,
Weddigenring 73-83,
Kiel.

(b) Physikalischen Institut Der
Universitat Göttingen
(Göttingen, Bunsenstrasse, 9)

The following persons were interrogated:-

Dr. Kutzscher Dr. Sommer Mr. Nickerson Dr. Hecht	At Kiel
Prof. Pohl Dr. Krenzien	At Göttingen

3. Outline of the Work Done in Germany

Dr. Kutzscher of "ELAC", while working at the Berlin Technical High School, discovered that some lead sulphide ores showed the properties of photoconductivity. In the years following 1930 tests were made on some 100 available lead sulphide ores, about two-thirds of which, however, showed no sensitivity in the infra-red region. The ore

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found to be the most sensitive was the original Galena ore from the place of that name. The individual crystals were found to have sensitive spots, and great sensitivity was obtained if by a complicated optical system light were focussed on to such a sensitive spot. Alternatively, a cell could be made up of 40 or 50 such crystals, with the disadvantage of having insensitive areas in the cell. The first cells of this type were made by Dr. Sommer.

Later Dr. Sommer discovered that chemically deposited lead sulphide layers, if properly tempered, showed the property of photoconductivity. By a process of trial and error, ELAC have developed cells (in which the lead sulphide is chemically-deposited) which are very sensitive. These cells have found a number of wartime applications, which have already been described in A.D.I.K. Report No. 350/1945.

The photoconductivity of lead sulphide was discovered independently by Prof. Gudden, who apparently also discovered the photoconducting properties of lead selenide and lead telluride. Gudden's films were made by an evaporation process, and some commercial cells of this type were made by Zeiss-Ikon. A comparison of the two types of cell by Prof. Karolus, of the Phys. Inst., Leipzig, gave the following results. At room temperature there was little difference in the sensitivity of the two types, but when cooled to -80°C, the sensitivity of the sublimated type increased three or four times, while that of the chemical type increased 30 to 40 times. The latter was therefore used in application work.

Lead sulphide cells have a maximum sensitivity at about 2 μ, and their spectral response curve normally extends up to about 3.5 μ. The spectral response curves of lead selenide and lead telluride extend even further into the infra-red, and for this reason experimental work had been done on them by Prof. Gudden. These cells had, however, not reached the production stage.

No theory has so far been put forward which adequately explains the dependance of the properties of these photoconducting cells on temperature and on the method of preparing the layer. Experiments have been made at Göttingen University by Dr. Krenzien, working under Prof. Pohl, with the object of obtaining more precise information on these points. These experiments have not been completed, and the University have now been told that they must not do any more work of this type in the infra-red region (above 1 μ).

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The information obtained from "ELAC" and from Göttingen is described in greater detail in the following paragraphs.

4. Manufacture of the "ELAC" Lead Sulphide Cells

The following information regarding the manufacture of the "Technical" lead sulphide cells by the Electro-Acustic Kommanditgesellschaft was obtained from the following members of that firm:

Mr. Nickerson,
Dr. Hecht,
Dr. Kutscher,
and Dr. Sommer.

Dr. Sommer gave most of the details.

4.1 General Assembly

The cell consists of a vessel of the shape shown in Fig. 1. The cell is made of Duren-glass, which is transparent to infra-red radiation of wavelength up to about 3.5 µ. The sensitive lead sulphide film is deposited in the manner described below on the front surfaces of the inner cylinder.

The inside cylinder is filled with solid carbon dioxide, which keeps the temperature of the lead sulphide film at about -80°C. The space between the two cylinders is evacuated, and a "Getter" is inserted to absorb any gas given off by the lead sulphide film. As a result there is very little conduction of heat from the outer cylinder to the inner one, and the outer cylinder is not cooled appreciably (this avoids condensation of water on the outer cell). As a further precaution against condensation of water on the outer cylinder, this is heated electrically by a small heating element H.

4.2 The Electrodes.

The electrodes are situated at EE. Contact is made with the lead sulphide film by means of conducting films on the sides of the inner cylinder. After manufacture the cell is split at A. Then a film of fine pure platinum is put on the sides of the inner cylinder in several thin layers; this film is burnt in by heating in an electric oven at about 700°C. Then a layer of fine pure gold is similarly burnt on, over the platinum.

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These layers are so put on that they form leads underneath the lead sulphide film (which is deposited after the layers have been burnt on). These layers are connected with the outside leads EE by means of a special solder consisting of a mixture of tin, aluminium and cadmium.

4.3 Depositing of the Lead Sulphide Film.

The following solutions are required:-

(a) An aqueous solution of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, containing 400 gms. in 1000 ccs. water.

(b) An aqueous solution of thio-urea, $CH_4 \cdot N_2S$, containing 118 gms. in 1000 ccs. water.

(c) A solution of caustic soda, NaOH, containing 666 gms. in 1000 ccs. water.

To a vessel containing 40 ccs. of water at 45°C are added 10 ccs. of the thio-urea solution, 30 ccs. of the lead acetate solution, and 10 ccs. of the caustic soda solution, in that order. The cell is immersed in the water before these solutions are added, in the manner shown in Fig. 2. The mixture is stirred quickly at first, and then more slowly. After a few seconds the lead sulphide begins to precipitate. The cell is removed from the solution after exactly 100 secs., and the lead sulphide film is almost immediately washed and cleaned with a soft brush.

4.4 Tempering the Film

After deposition, the film is tempered at 100°C for about 3/4 hour. This can be done either in air or in a vacuum, but ELAC have generally done it in vacuum. This heat treatment causes a very considerable increase in the sensitivity of the cell, but at the same time causes an increase in the resistance of the cell.

The outer cylinder is then again sealed on to the inner one, and the space between them is evacuated by means of a high-speed pump. A Getter material in the vacuum is heated to 300°C during this process, so that on cooling it absorbs some of the remaining gases.

5. Properties of the "ELAC" Cell

5.1 Sensitivity

The sensitivity of the cell is such that a signal-to-noise ratio of 1 is obtained when

$$50 - 500 \times 10^{-11} \quad \text{watts/sq. cm.}$$

of radiation from a black body at 500°K fall on the cell. This figure apparently applies when an amplifier having a constant response between 10 and 10,000 cycles per second is used, in conjunction with a shutter rotating at 800 revs./sec.

Unfortunately, details regarding the electrical and other apparatus used in measuring the sensitivity could not be obtained. The sensitivity measurements were made by Dr. Mangold of the Phys. Inst., Leipzig, Linestrasse, 4 (Director Prof. Karolus) and by Dr. Treu, Phys. Inst., Prague, 11 (Director Prof. Gudden) at the Phys. Inst., Prague.

5.2 Noise Level

Clearly the signal-to-noise ratio is one of the most important characteristics of the cell. The signal voltage must be as high as possible, and the noise voltage must be as low as possible. The first condition depends on using the methods of deposition and tempering of the lead sulphide layer already described.

The condition of low noise level is mainly dependent on having the proper contacts. Since the cell works as a resistance cell, through which a current is passed, the noise is made up of two parts.

(a) The noise potential in the contacts by means of which the current is led into the photosensitive film, and

(b) The noise potential in the layer itself.

The latter potential depends on the structure of the layer. It is greater in thin layers than in thick ones. The noise potential in the contacts depends on the method of making these contacts and can be made very small. Pressure contacts on to the layer itself give poor results,

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but the method, already described, of depositing the lead sulphide on a film of platinum and gold, gives very good results - the noise potential in the contacts can be reduced to about 2 microvolts for an applied potential of about 200 volts.

The layer giving the actual resistance is approximately square (and so its resistance is independent of size). The smaller the cell, the better - the smaller the threshold sensitivity value. However, the smaller the cell, the smaller the exciting voltage which can be allowed. The exciting voltage is limited to about 60 volts for small cells, and 200 volts for large ones; larger voltages cause the layer to get hot, so that the noise level increases, and the threshold sensitivity falls off.

5.3 Resistance

The resistance of the finished cell (cooled to -80°C) lies between 50,000 and 500,000 ohms, depending on the tempering time. The resistance varies slightly in the days following manufacture, because of an ageing process. The most suitable resistance from the electrical point of view is 100,000 ohms. The maximum efficiency is obtained if the resistance R in the amplifying circuit (See Fig.3) is equal to the resistance Z of the cell, and in the ELAC apparatus R was made about 100,000 ohms.

5.4 Reproducibility

It is very difficult to mass-produce these lead sulphide cells. ELAC have found that they can obtain cells having reasonably similar characteristics if they make them singly, as described above, in exactly similar vessels. If different shapes of vessel are used, the properties of the cell are changed very greatly presumably because the effect of stirring is different. Similarly, if you try making a number of cells at a time in a large bath, the stirring rate will usually vary from one cell to another, and the finished cells will have different properties.

Similarly the cells are more sensitive when tempered in air, than when heated in a vacuum, but are less reproducible. In general a compromise has to be made between getting the highest sensitivity and the best reproducibility.

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5.5 Effect of Temperature

According to Dr. Sommer, the resistance of the cell increases continuously as the temperature is lowered, but the noise level decreases. He stated that the threshold sensitivity increases continuously as the temperature is lowered, though the increase in sensitivity on cooling to below -80°C is not great. I am, however, doubtful whether these statements are correct, as Dr. Sommer appeared to have very little evidence on which to base such statements.

5.6 Reason for Using Various Sizes of Cell

As stated above, the best results are obtained with small cells. However, the early ELAC cells were developed for use with very large receiving mirrors, and the optics of these was such that the radiation was focussed on an area about 3 cm. square. Consequently 30 mm. cells were made. When smaller receiving mirrors were used, however, it became advisable to use smaller cells, and eventually a 3 mm. one was developed.

6. Lead Telluride Cells

Dr. Krenzien has been doing some work on lead telluride cells, at the Physikalischen Institut Der Universtität, Göttingen (Director Prof. R. W. Pohl). This work has not been completed, but the following information has so far been obtained.

Dr. Krenzien states that the photoconduction is dependent on the presence of oxygen. If lead sulphide or lead telluride is evaporated in a vacuum, no photo-sensitivity is apparent. He states that if these substances are deposited chemically and then tempered in a vacuum, the absorbed oxygen is sufficient to cause the effect. In the case of lead telluride, the optimum sensitivity is obtained by tempering the film in oxygen at about 400-430°C. The cell is twice as sensitive if cooled to -190°C as at -80°C, but the greatest sensitivity (2 or 3 times that at -190°C) is obtained at some unknown intermediate temperature. Dr. Krenzien thinks that the effect of tempering in oxygen may be to produce lead tellurate, but there is no real evidence to support this theory.

6.1 The Electrodes

Platinum and gold are not suitable for the electrodes in the case of lead telluride cells, because they oxidise in the tempering process. For this reason carbon electrodes about 1/10 mm. thick have been used.

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6.2 Spectral Sensitivity Curve

The shape of the spectral sensitivity curve depends on the tempering temperature and on the temperature at which the cell is used. If the cell is tempered at about 410 - 420°C in oxygen, its spectral sensitivity curve when used at -190°C extends up to about 6 μ, and has a maximum at about 4.5 μ. However, such cells are very insensitive when used at (say) -80°C. Cells tempered at about 450 - 460°C have a spectral sensitivity curve extending up to only about 4 or 5 μ when used at -190°C; when they are used at -80°C, their sensitivity curve extends to 3 or 4 μ, and the peak sensitivity is about half the corresponding value for the same cell at -190°C. Typical spectral sensitivity curves are shown in Figs. 4 and 5.

6.3 Response Time

The response time of the lead telluride cells is of the order of 1/10 sec. at -190°C, but it falls off rapidly as the temperature is raised. It has been found that cells having a long response time are in general the most sensitive.

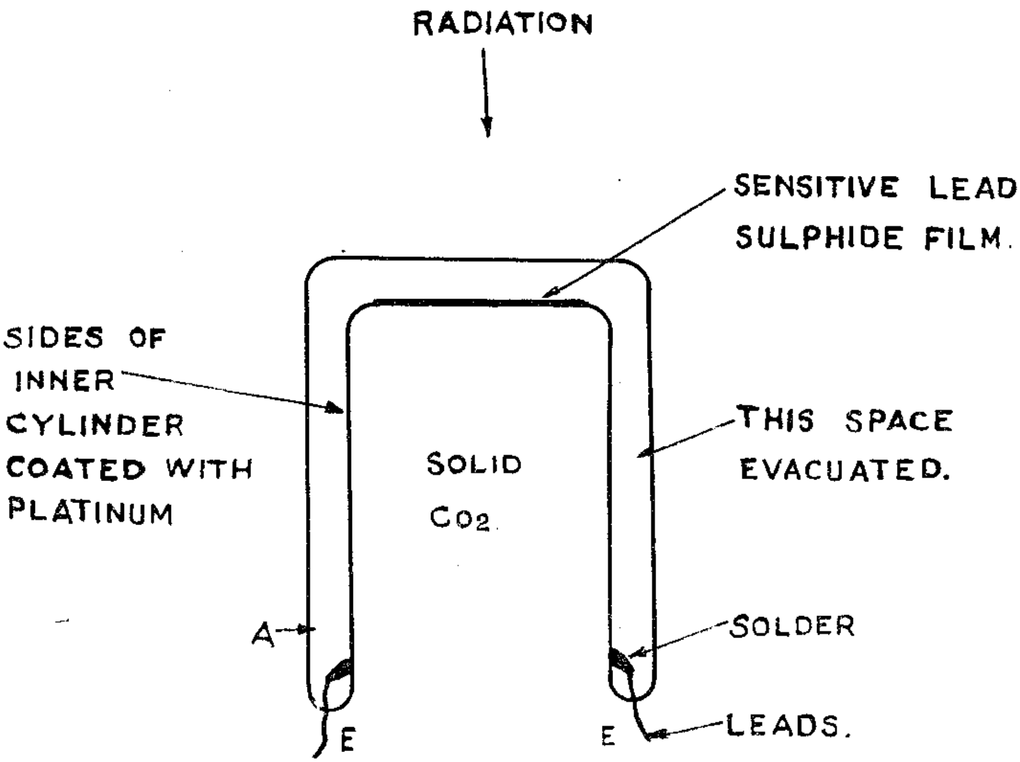
6.4 Windows

The most suitable substance for the windows in lead telluride cells is synthetic sapphire, which is transparent up to 6 μ. This substance was made by I.G. Farbenindustrie, Bitterfeld, and can be made by careful warming with molten molybdenum glass.

7. Condlusionz and Recommendations.

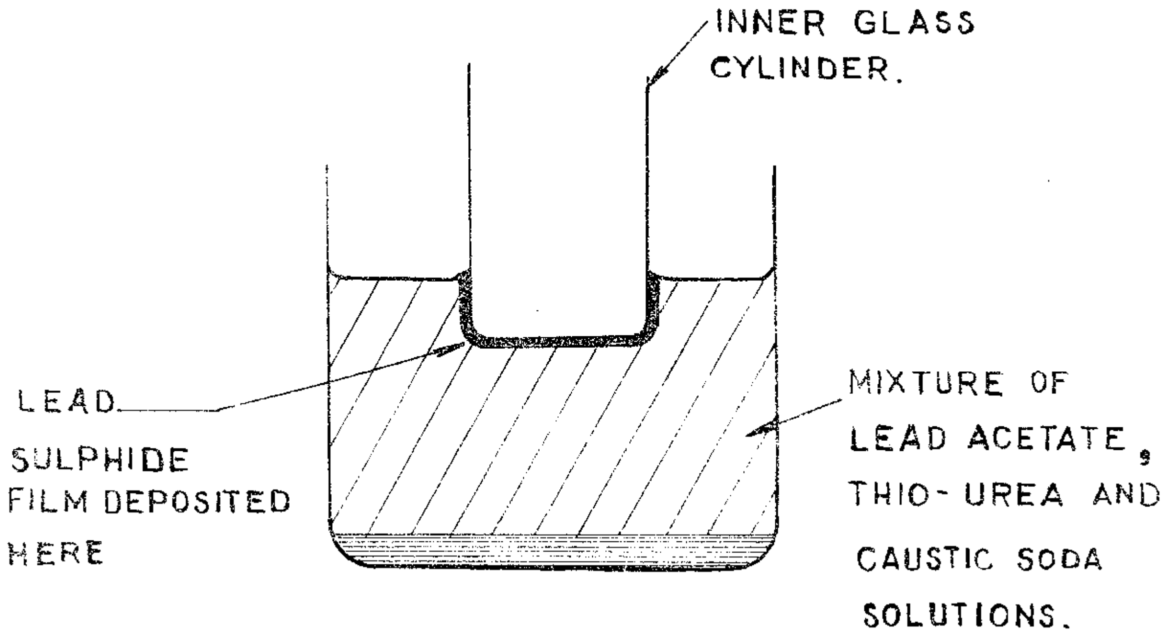
The Germans have developed very sensitive photoconducting cells for the detection of infra-red radiation, but clearly do not understand the physical basis of the photoconducting effect. It is suggested that some fundamental work on the behaviour of lead sulphide, lead selenide and lead telluride photoconducting films should be undertaken in this country.

FIG. 1.



"ELAC" LEAD SULPHIDE CELL.

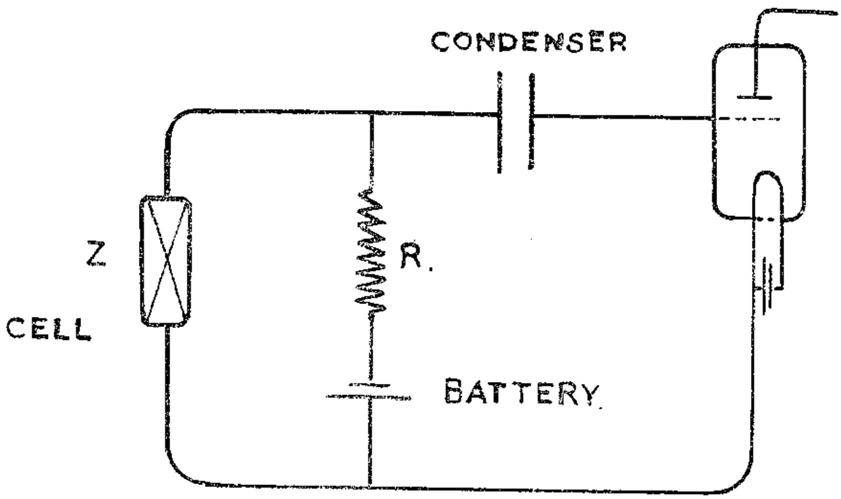
FIG. 2



METHOD OF DEPOSITING

LEAD SULPHIDE FILM.

FIG. 3



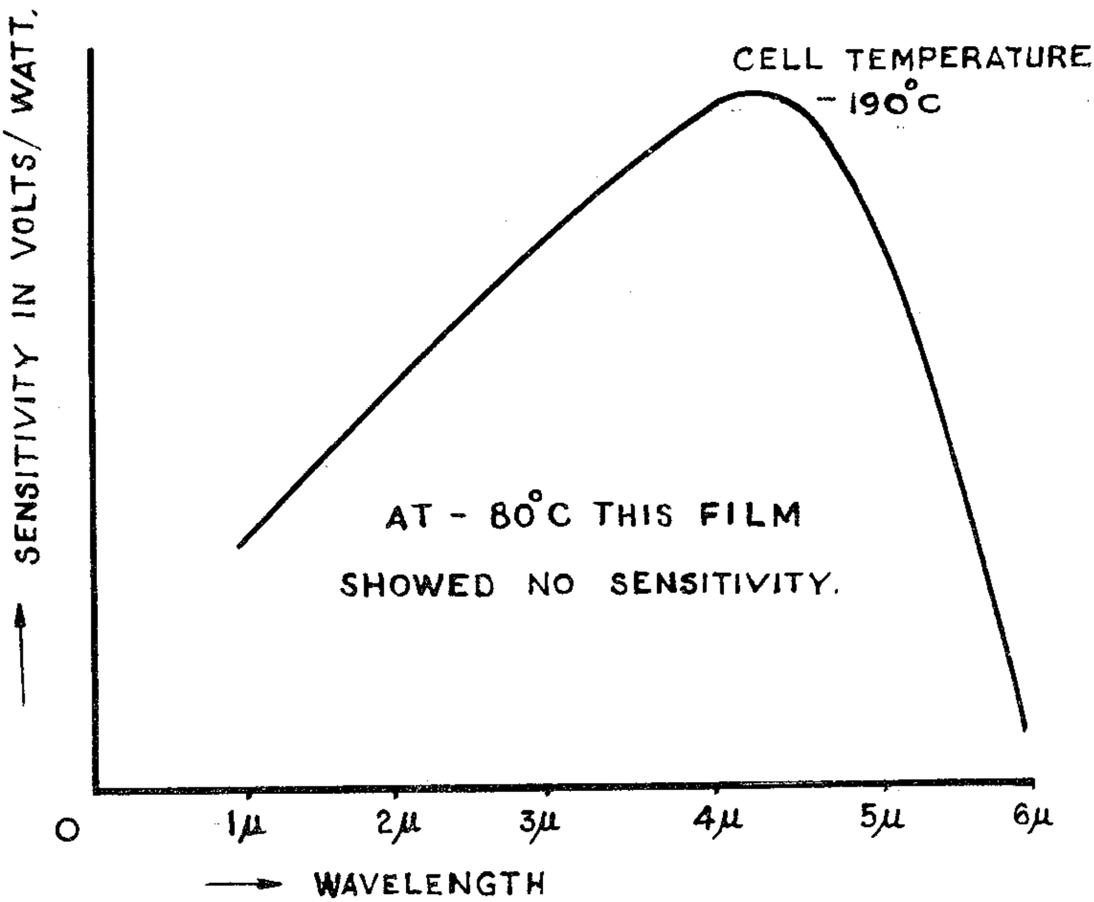
R = Z.

INSERTION OF CELL INTO AMPLIFYING CIRCUIT.

FIG. 4

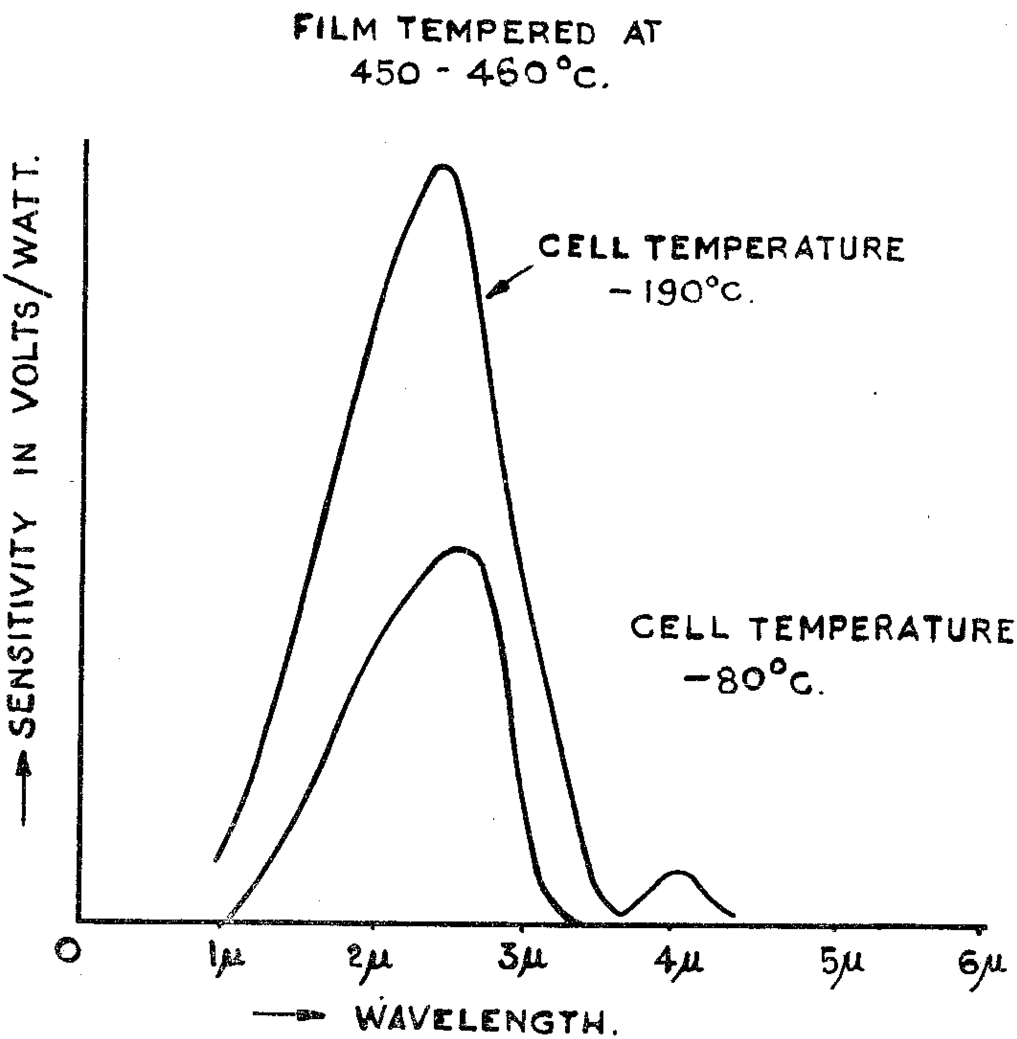
FILM TEMPERED AT

410 - 425 °C



SPECTRAL SENSITIVITY CURVE FOR

A LEAD TELLURIDE CELL. (1)



SPECTRAL SENSITIVITY CURVE FOR A LEAD TELLURIDE CELL. (2)