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TELEFUNKEN CATHODE RAY TUBE LABORATORIES AND LEUCHTSTOFFE, PHOSPHOR MANUFACTURE

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COMBINED INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

TELEFUNKEN CATHODE RAY TUBE LABORATORIES AND LEUCHTSTOFFE, PHOSPHOR MANUFACTURE.

Reported by

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CIOS TARGET NOS. 1/18P, 1/350 AND 9/359
RADAR
PHYSICAL AND OPTICAL INSTRUMENTS AND DEVICES

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413.

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1. Introduction

The Telefunken Laboratory at Bad Liebenstein and the neighbouring Leuchtstoff factory at Steinbach were investigated during the period 18th - 20th June, 1945. The investigation of the Telefunken laboratory led to further investigation at Göttingen University which was visited on 21st June, 1945.

At the Telefunken laboratory, which had been evacuated from Berlin in 1943, research was on television and electronic devices.

Leuchtstoff was a separate company formed for the production of phosphors for cathode ray tubes and fluorescent lighting. Telefunken, AEG, I.G.Farben and the German Post Office each have a 25% holding but AEG have delegated their control to Telefunken who are therefore the main controlling body.

1.1. The Telefunken laboratory at Bad Liebenstein

was under the direction of Prof.Schröter and work in progress consisted of investigations of electronic devices, mainly cathode ray tubes for radar and television, and iconoscopes. Some work had also been carried out on crystal detectors for 3 and 9 cm. wavelengths. In addition to Prof.Schröter the following personnel were also interrogated:-

Dr. Bartels: production of crystal detectors.

Dr. Gundert: cathode ray tube development.

Dr. Wendt: television cameras.

Dr. Theile who worked on iconoscopes had left to visit his family and then to proceed to Dr.Hachenberg's laboratory at Göttingen.

1.2. Leuchtstoff: Steinbach

This laboratory had been concerned with large scale production of phosphors for applications such as television, image converters, Radar and fluorescent lighting. Other activities of the laboratory were production of graphite wall coatings for cathode ray tubes and synthetic quartz crystals for frequency control.

Dr. Kamm and Dr. Funk were interrogated during the visit. Samples of fluorescent materials were obtained.

1.3. Physics Institute: University of Göttingen

This laboratory under the direction of Prof. R.W.Pohl included in its activities dark trace tubes and zinc oxide fluorescence cathode ray tube screens with extremely small grain size.

The following staff were interrogated:

Professor Kupfermann
Dr. Mollwo
Dr. Hachenberg

Prof. Hautermans acted as interpreter. Prof. Pohl was indisposed at the time of the visit.

2. Iconoscopes (Telefunken - Bad Liebenstein)

2.1. The work on iconoscopes was undertaken by Telefunken mainly for the purpose of television. It was also required for military use in connection with a guided projectile, the transmitter being placed in the nose of the projectile. This equipment was designed by the Reichpost at Klein Machnow (later evacuated to Ach near Bodensee). A model of the equipment had been made up and had been tried in an aircraft, a film being taken of the result as seen in the receiver. Professor Schröter had seen this film and he thought that Dr. Weiss of the Reichpost may have a copy of it. Samples of the tube used, which was a type of supericonoscope, were sent to the Reichpost at Ach in March, 1945. Professor Schröter thought that the transmission was by frequency modulation in the region of 50 cms., and the picture definition was 441 lines 50 frames interlaced.

Telefunken were asked by the German military authorities to attempt to push the photo-sensitivity of the super-iconoscope towards the infra red region, but little progress had been made and this requirement lapsed owing to pressure of other work.

The limit of resolution of present mosaics was of the order of 100 lines per cm.

2.2. The Standard Iconoscope

Three sizes of the standard iconoscope have been developed. The design calls for little comment, being in accordance with standard practice. The mosaic was caesium on silver oxide, and the photo-sensitivity was normal for this surface. An attempt had been made by Dr.Gold at Marburg University to prepare an antimony mosaic by decomposition of antimony hydride. (SbH_3). Professor Schröter stated that this work appeared to be promising, although definite results have not yet been achieved. Blowing particles of Ag oxide on to mica plates also looked promising.

In Paris (See section on orthicons) 3kV. had been used on iconoscopes for 1000 line definition. The French were also trying silver mosaics deposited on Al_2O_3 on an Al signal plate.

Figures 1 and 2 are photographs of the standard large and small size iconoscopes, and the arrangement of base connections is shown in figure 3.

2.3. Super Iconoscope

The work on this tube had been done by Dr.Pheile, but he was not available, and the following information was given by Prof. Schröter, who claimed that this tube had roughly 10 times as much sensitivity as the standard iconoscope, and attributed this mainly to the excellent storage properties of the mosaic used. Figure 4 shows a diagram of the super-iconoscope, and a photograph of the tube itself

is shown in figure 6. The tube uses an electrostatic image focussing system, and to compensate for the known curvature of the image surface in such an arrangement, the photocathode is deposited on a curved end plate of about 70 mm. radius of curvature.

The optical image is maintained in focus over this curved surface by a special optical arrangement devised by Telefunken, and Messrs. Leitz at Wetzlar. This is shown diagrammatically in figure 5. While this optical system corrects for focus erros it causes cushion distortion in the final image, and the correction of this effect has not yet been accomplished. Prof. Schröter suggested that it could be corrected either by an adjustment of the scanning waveform or perhaps by curvature of the mosaic surface, e.g. on glass or Al base.

Two forms of electron lens systems were used for reproducing the electron image on the tube mosaic. The first, which was identical with that used by the AEG in their "Bildwandler" tube, was not really suitable for the super-iconoscope because it was designed to operate at a much higher voltage (20,000V). A sketch of this system is shown in figure 7. The second arrangement, which had been employed was a simple two tube lens, and this was stated to be much more suitable for the super-iconoscope application. A high order of accuracy in alignment was required in order to obtain a good image.

The photo electric surface of the super-iconoscope was of semi-transparent antimony activated with caesium. This was usually deposited during the processing of the tube, although Prof. Schröter stated that it can be made before the processing by a separate operation.

The mosaic of the tube was made of magnesium oxide on mica, made by evaporating Magnesium on to the mica through a series of meshes to make the deposit uniform, andthen oxidising by an electric discharge in a few mm. of oxygen. This was done in a separate apparatus before assembly in the super-iconoscope. Prof. Schröter stated that this mosaic has very good storage and insulation properties, and can store up images for several seconds. He also stated that an attempt had been made to use aluminium oxide on aluminium instead of magnesium oxide on mica and that this appeared to be as good as mica providing the thickness was maintained very accurately. The thickness of the oxide should be about 15 to 16 μ in order to obtain the best results. He also stated that they had tried to use the Malter effect for picture storage, but that no success had been obtained.

2.4. Construction and Processing

The signal plate of the tube is made separately before processing, and all the silver surfaces in the iconoscope are produced by an evaporation technique. The electrode lens and mosaic are then assembled in the envelope and the electron gun, which is a simple magnetic focussing arrangement, is inserted. The antimony photo-cathode is generated from a mixture of caesium chromate and zirconium. After the photo-cathode has been sensitised, and while the tube is still on the pumps, it is tested roughly by throwing an image on to the photo-cathode and observing the resultant picture.

The processing has apparently not yet been standardised in any way, and Prof. Schröter stated that a number of variations were still being tried. After construction subsequent bake at 150-200°c for short time often effected improvement in performance.

2.5. The Orthicon

No work had been done at Bad Liebenstein on the orthicon, apart from some theoretical calculations on the quality of definition by Dr.Wendt. Prof. Schröter had, however, been in contact with M.Barthemlemy of the Compagnie des Compteurs in Paris, and the latter company had done a considerable amount of development work on the Orthicon which was called by them the Isoscope. This work was on similar lines to that done by R.C.A. and Prof. Schröter said that the device posessed good 441 line definition, and that tilt was absent. The picture geometry was not good, and a white spot was always present in the centre of the screen which changed size under different lighting conditions. This spot was never eliminated, and was thought to be due to the presence of caesium ions.

The original experiments used electrostatic deflection in the frame direction and electro-magnetic in the line direction, but smaller tubes were made eventually which used electro-magnetic deflection in both directions. The picture contract was said to be very good, and more or less linear.

2.6. Semi-conductive tube

Some experiments were done by Telefunken on a television transmitting tube using a semi-conductive layer of copper oxide, cadmium selenide or lead sulphide as a means of avoiding the tilt normally present in the iconoscope. The beam current in these tubes was of the order of 1 μ amp. and when operated under the correct conditions the tubes had very little tilt. They were, however, extremely difficult to operate since under conditions when tilt was absent the crystaline structure of the material was prone to appear in the picture with very detrimental results. No samples of these tubes were seen, and it was understood that the work was still in progress.

3. Crystal Valves (Telefunken - Bad Liebenstein)

Dr. Bartels described the work which he had been doing at Bad Liebenstein on the subject of crystal valves for rectification at centimetre wave lengths. These crystals were made by the deposition of silicon on to carbon rods about 3 to 4 mm. long and about 1½ mm. in diameter. The carbon rods were placed in a quartz tube and silicon was deposited on them by reduction of silicon tetrachloride by aluminium at a temperature of about 800°C. and a pressure of 10 mm. of mercury. The completed crystals were assembled in the mounting shown diagrammatically in figure 8.

The only test applied to these crystals at Bad Liebenstein was the measurement of the ratio of the front and back conductivity, using D.C. with about 100 m.v. potential across the crystal. More complete high frequency tests were done by Rothe's section at the high frequency laboratories which have been recently moved from Breslau to Stolberg near Chemnitz. It was thought that noise values at 9 and 3 cms. had been measured by Rothe.

No compalints had been received from the users on the burning out of crystals when used in high frequency equipments, and Dr. Bartels appeared to have little information on this subject, except that he considered that his crystals would stand 10V. of D.C. before burning out.

4. Dark Trace Tubes (Physical Institute - Göttingen University)

Dr. Hackenberg, who was formerly with Telefunken, gave an account of his experiments on the dark trace tube which is supplemented by information obtained from Prof. Schröter at Bad Liebenstein. The development of the dark trace tube has followed rather different lines in Germany from those pursued in England, mainly because the tube was used entirely for recording oscillographic patterns or P.P.I. displays and not for continuous observation of P.P.I. displays. Diascopic projection was employed instead of the episcopic projection used in England, and the removal of the dark trace from the screen was accomplished by heating up the screen material. To do this the screen was deposited by evaporation on a thin tungsten base which had been evaporated on a quartz or mica plate. The tungsten film was semi-transparent and had a resistance of between 1000 and 3000 ohms. Its thickness was controlled by optical transmission measurements. Contact was made to it by strips of chemically deposited platinum along opposite edges of the plate. The backing plate was about 6 cms. x 6 cms. in area. In manufacturing the tube, the tungsten film was first deposited on the backing plate and then the plate inserted in an apparatus for evaporating KCL on to the tungsten screen.

The KCL was in the form of single crystals which had been made at Göttingen from Kahlbaum material by the Kyropoulus method. The evaporation was done in a number of stages, sometimes as many as 4 in all, and took usually about 10 mins. The screens were always placed sufficiently far from this evaporating filament to ensure a reasonably homogeneous layer. The thickness of the layer was from 6 - 10 μ.

Nearly 180 different materials had been tried for the screens of the Dark Trace tubes, but KCL had been found to be the best. No impurity additions were tried but Prof.Schröter suggested that potasium hydride might perhaps be a useful material to add to KCL. Schröter claims that these tubes have extremely good definition; he estimated that it was equivalent to approximately 2000 lines on a 6 cm. x 6 cm. picture. The writing speed varies from about 20 up to 100 metres per second, and the operating voltage for the higher speed is about 20 K.V. with a beam current of 10 to 50 μ amps. The absorption spectrum of the dark trace is said to have a maximum at about 5,600 Å Units, and the screen is usually illuminated by sodium light or by a high pressure mercury 1-amp with the green lines filtered out leaving the yellow.

The proposed application for this tube was an intermittent radar transmitter for submarines, and it was also tried for recording supersonic echo sounding in U boats. The trace was cleared from the screen after a suitable period by heating the tungsten film, a power input of between 30 and 100 watts being required to clear the trace in a period of from 2 to 10 secs.

5. Cathode Ray Tubes (Telefunken - Bad Liebenstein)

5.1. General

Dr.Gundert said that instructions having been received to copy the Rotterdam Gerat equipment, they had commenced work on an electrostatic tube. Starting with a 7" blown bulb they had changed over to a 5" flat screen. An 80 mm. diameter neck was used to accommodate the large deflecting system. The A3 aperture was 2½-3 mm. An experimental tube 12½ cm. diameter, 41 cm. long, and 17 cm. on the flared part of the bulb, (Code Ref.FC17R) was superseded by the magnetic tube Type LB9, and did not go into production. A sample of the latter measured 26 cm. overall length, 11 cm. conical bulb length, flat screen diameter 13 cms., screen diameter 12 cms.,

The flat screen, which was in fairly universal use by Telefunken requires 10 minutes for the process of joining to the conical bulb and subsequent annealing.

5.2. Television Tubes

The impression was obtained that as much work as possible was being directed towards television tubes and that various specific requests from the Luftwaffe were dealt with as expeditiously as possible, so that work could be resumed on television.

5.2.1. Receiver Tubes

The rectangular bulb 1939 type television tube had been shortened by using electrostatic focus, and a pressed glass base. The essential dimensions of this tube were:- Screen end 10½" x 8¾" (giving a picture size about 9½" x 7½"); overall length 13½"; neck length 4¾"; front of gun to neck shoulder 2". The bulb was blown - there had been no suggestion of moulding apparently - and the samples seen were of exceedingly uniform glass distribition, about 8 mm. thick on the screen end, and 4-5 mm. on the sides. The corners were well blown up into the mould. A larger bulb was available, with a screen end of 13½" x 12" (for a picture about 12½" x 11"), the body being about 3¾" longer than the above bulb, giving a finished tube length of about 17". Both tubes had 35 mm. neck diameter. The characteristics of the smaller tube were 6 KV, 100 uA beam current for 20 V drive from -40 V cut-off. Beam diameter in the deflecting system was 2 mm. 8-10 KV would have been preferred for the accelerator, but 6 KV was the maximum available from the receiver. The white fluorescent material was a mixture of powders - no single material had yet been obtained. Cathodes were run at 900°C, giving 800 hours evaporation life. Ion burn had been the main cause of rejection pre-war, giving lives of 200-600 hours, with emission still good. No useful information about the prevention or cure of ion-burn was obtained.
Prof. Schröter warned against pumping a number of tubes on one manifold, as under these conditions, the ion burn would be different in degree between the first and last tubes sealed off the manifold.

5.2.2. Projection Tubes

Projection tubes for big screen (2-3 metres wide) projection, had been under development. Little work had been done on home receiver tubes. Bulb diameter, with flat face, was 6½"; neck diameter 9 mm. Gun operated at about 60 KV, 1 ma. A transparent layer of aluminium was deposited on the glass before putting down the screen. Two methods were used to prepare the glass before depositing the aluminium, to obtain a sufficiently conducting and transparent film. The glass was covered with either a thin film of collodion, or a solution of parrafin wax in benzene, and the benzene evaporated. The aluminium film was then evaporated on. A beaded aluminised paper projection screen was used, and a F1.6 40 cm. focal length projection lens. Oxide cathodes were used, and died of ion bombardment in about 200 hours. The zinc sulphide/zinc selenide powders had been used more recently. A hard glass similar to Pyrex was used for the tubes, and cerium oxide was added, in order to reduce the blackening by soft X Rays. The special glass was made by Osram at Weisswasser, Berlin. Untreated glass blackened to about 50% transmission in about 20-30 hours, and got steadily worse. The special glass blackened to about 75-80% transmission in a few hours, and then remained steady at this value for the rest of tube life.

5.3. Reduction of Astigmatism

Much work had been done on magnetic deflecting coils. Deflection astigmatism had been reduced by shaping the stray field by adjusting the coil spacings in the single way deflecting system used on the Radar PPI display, and by inserting shaped iron poles in the case of the television coils. Apparently high efficiency of deflection is not considered important in either application. For example, the television coils were only 40 mm. long overall. This allows generous tolerance between tube and coil, and does not put serious restrictions on coil design, making for a cheap commercial construction. The price appears to be 30-50% in deflecting power. On the normal 441 line television picture, the H.F. fly back time was 8% with coils of 52 milli-henrys. Time bases were of the resonant fly back type, and both time base and coil design was largely governed by the requirement of generating the tube H.T. on the fly back. A diode was used to damp the overshoot on the fly back. Linearity was good, no distortion being apparent on the picture. The fastest/slowest part of the stroke was 110/100. No correction of the focus field curvature had been found necessary with either the pre-war television tubes, or with the radar tubes, provided the deflection astigmatism was corrected, but recent investigations into wider angles of deflection (± 40-45°), had necessitated the use of a feed back circuit ("swinging-lens"), to keep the spot in focus all over the screen. With magnetic focus, the feed back control was applied to an auxiliary coil in the lens. This correction was found to be necessary with higher definition pictures (880 lines - Karolus). Two alternative methods of deriving the feed back control were favoured. The first method was to feed the time base voltage on to two non-

linear valves in opposition. This had its greatest use for very slow scanning speeds (about 2/sec) as used in facsimile transmission. The alternative, suitable for both H.F. and L.F. scans in normal television, was to feed the synchronising pulses on to the grid of a valve, with the anode tuned so that during the cut-off period its capacity is reduced and it resonates at half the period of the pulses, thus performing one half oscillation per pulse.

5.4. Monoscopes

Some samples of monoscopes were seen, using etched copper blocks as targets, graphite being rubbed into the etching, and then polished off.

5.5. Use of Secondary Emission Cathodes

Some work was proceeding on the use of secondary emission cathodes for cathode ray tubes. An experimental tube containing six small electron guns arranged symmetrically round a secondary emitting target had been made up. The secondary emitting target, formed the cathode of an electron optical system arranged inside the six auxiliary guns. The six guns were to be replaced by a circular cathode arranged round the main gun, to excite the secondary emitting cathode. Theoretically Dr.Gundert claimed an advantage for the secondary emitting cathode, but so far it had not been realised.

5.6. Miscellaneous Constructional Details

Normal valve coatings were used for cathodes. The use of Aluminates to give a harder coating more resistant to ion bombardment was under investigation.

Ceramic insulators were used for electrode alignment. These were produced to high accuracy. For example, the concentricity of the modulator and A1 apertures were within 2 - 5/100ths of a mm., according to tube type.

Work on the tone range reproducible on the screens of direct viewing C.R.T.'s such as the LB9, had established that 20 - 30 just visible steps of brightness could be distinguished. This was considered to be more than sufficient, and no work was in hand to improve on this.

For graphite suspension for wall coatings etc. carbon was obtained from Siemens in the form of animal charcoal. This was vac. cooked at 800°C to remove oil, then ball milled with sodium silicate. A solution of 50% was diluted to 15%, and 300 gms of this added to 1 litre of carbon. 300 kilos/month were manufactured. Keeping properties were variable - 6 weeks maximum guaranteed, after which the silicate is liable to crystallise.

6. Type of Screen and Processing (Telefunken - Bad Liebenstein)

6.1. Afterglow Screens

Originally a long afterglow screen was obtained from ZnS - Cu activated, supplied from Auer Geschellschaft, but later a change was made to a double layer screen, using ZnS - Ag activated for the blue layer, and ZnCdS - Ag activated for the long yellow afterglow. More recently ZnS-ZnSe materials had been developed, which were more resistant to both chemical and electron burning. Apparently Telefunken were merely provided with suitable powders for the various tube requirements, the choice being made by Prof. Schleede, who dictated which material was most suitable for each requirement (see also 2 colour tube below). Prof. Schröter could say nothing about testing screens for most desirable performance, methods of production test, etc. Work had started on these screens in the Spring of 1944.

6.2. Method of preparing Screens

Screens were settled by a process which was almost exactly that used in the U.S.A. for the P7 screens, even to details such as the method of sucking out the liquor after settling.

Suitable weights of phosphor were suspended in a 1% potassium silicate solution in distilled water and poured into a cleaned CRT bulb. After settling, the solution was siphoned off and the tube tilted gradually then inverted and dried out. For double layer screens the excited layer was added, after settling the afterglow layer, as a suspension in distilled water with no binder present. This was done by a tube immersed under the surface of solution already in the bulb and the dispersal of the suspension was by a deflection disc at the end of the tube.

Grain size was controlled in the powder manufacture and by sieving before screen deposition.

Copper was mentioned as a dangerous contaminant, but no test for copper was known, better than making tubes and observing the state of the screen.

6.3. Two colour Screens

The Luftwaffe directed Telefunken to investigate the possibility of using a 2 colour tube for moving target discrimination in the Autumn of 1944, but a satisfactory solution was not possible with the powders available. The better the colour discrimination obtained the lower was the brightness. Powders used were Green-Long afterglow, - pure ZnS-Cu activator; Orange-Red short afterglow, - ZnCdS-Cu activator. They had tried mixtures of powders, and separate layers, with the usual blue layer over the two. Results were generally worse than with a single colour tube.

Screens with a mixture of two materials having different spectral emissions were developed for a similar airborne equipment to the GL. set with rotating colour filters in front of the tube to distinguish signal echoes coming from above or below the aircraft. The screen mixture was usually ZnS.Cu and ZnS-CdS-Cu. The difference in afterglow characteristics was found troublesome and also the difficulty of sufficient separation of the two emission bands.

6.4. Other Screen Developments

A further development was the production of a tube and screen to record a single revolution of the PPI Scan for submarine work. The picture was required to last 30 seconds but the best obtained was 15 seconds, using 4,000 volts, 100 uA beam current in a 0.3 mm. spot, on P.R.F. of 1,500 and 2 seconds per rev. of the scanner (i.e. each screen element excited 10-20 times. Ranges available were 15, 30 and 60 Km.

7. Phosphors (Leuchtstoffe - Steinbach)

7.1. General

The range of materials manufactured by Leuchtsteffe included phosphors of particular interest namely zinc sulphide - zinc selenide phosphors and fluorescent zinc oxide.

7.2. Zinc sulphide - zinc selenide phosphors.

7.2.1. Preparation of basic materials

Zinc sulphide was prepared from zinc chloride containing small traces of iron. The sulphide was precipitated from a solution of the chloride by hydrogen sulphide prepared from ferrous sulphide and hydrochloric acid. Zinc selenide was prepared in a similar manner from zinc chloride by precipitation with hydrogen selenide. The hydrogen selenide was produced by action of hydrochloric acid on aluminium selenide.

In general, one part of zinc selenide was fired with three parts of zinc sulphide, together with either 10^{-5} or 10^{-6} copper impurity or 10^{-4} - 10^{-5} silver impurity at 900°C. For special applications such as image converter screens the powder was heated to 900°C at 200 - 300 atmospheres pressure. This improved the fluorescence efficiency and increased the afterglow. This technique was developed at Heidelburg by Prof.L.Wesch in collaboration with the Steinbach laboratory.

7.2.2. Properties of zinc sulphide - zinc selenide phosphors.

The sulphide-selenide materials are very resistant to subsequent heating and electron burn. The luminescence efficiency is about the same as that of zinc sulphide. The secondary emission characteristics are better than those of zinc sulphide and the electrical conductivity is higher. With copper impurity the emission is green and with silver shifts towards the blue. Increasing content of zinc selenide causes the emission to move to the red end of the spectrum as for addition of cadmium sulphide to zinc sulphide with Cu or Ag impurity. The afterglow is much shorter than that of a normal zinc sulphide - copper phosphor. The phosphor is excited by long wavelength ultra violet light and by electrons. For television tubes, in particular projection tubes, a mixture of this material with blue emitting zinc sulphide silver is used to produce a near white fluorescence. Zinc-cadmium sulphide is sometimes added to give more red component.

To suppress afterglow Nickel killer inclusions have been used with success.

7.3. Pure zinc sulphide phosphors

Leuchtstoffe has produced pure blue emitting zinc sulphide materials activated by zinc from the matrix material. The specimens

examined were free from green afterglow emission due to copper contamination.

7.4. Physical measurements on powders at Leuchtestoffe: Steinbach

Measurements of spectral emission of luminescent materials were carried out using ultra violet light and cathode ray excitation. For cathode ray excitation a demountable cathode ray tube was employed with tungsten cathode and bent neck to avoid light emission from the tungsten reaching the phosphor screen. The electron beam was deflected at the bend by a magnetic yoke. Spectral emission was photographed using a triple prism spectograph of high aperture and the resulting negatives examined by means of a non-recording microphotometer by Zeiss.

7.5. Zinc oxide phosphors (developed at Physics Institute - Göttingen University)

Zinc oxide has been heated without deliberate addition of impurity giving a pale green-white powder with green luminescence but having an efficiency of about 20% that of zinc sulphide. It has been used for high voltage cathode ray tubes being more resistant to destruction and having a higher electrical conductivity than zinc sulphide materials. The interesting use of this material has been in small scanning tubes where the phosphor is produced by evaporation of zinc in an oxy-coal gas flame.

This development is due to a demand for a CRT screen of small dimensions capable of giving good definition with television scans of 2000 lines. This necessitated a very fine grain screen which would be stable under high voltage conditions. Potentials of 10 - 20 k.v. were used in the finalised tube. The preparation of the screens was as follows:- Pure zinc metal was evaporated from a quartz crucible in an oxy-coal gas-air flame and converted to zinc oxide which was deposited on a glass disc 5 cms. diameter held in the upper part of the flame. The material was partially fused into the glass and provided a fine adhering layer of zinc oxide phosphor. No deliberate activators had been included. The position of the screen in the flame was at the intermediate position where the flame colour changed from blue to yellow. Adjustment of oxygen in the burner was very critical and determined the amount of excess zinc included in the zinc oxide screen. A sketch of the experimental arrangement is given in Fig. 9. The deposition time was about two to three minutes and the flame temperature at the screen position was estimated to be 1200°C before insertion of the screen. The glass disc was subsequently sealed to the end of the CRT bulb to form the screen. The screen properties were not affected by this sealing performed on a glass lathe.

7.5.1. Characteristics of zinc oxide Screens

The luminescence of zinc oxide was stated to be seated in zinc centres forming part of the matrix lattice. Although excess zinc was present interstitially it was said to give no contribution to the fluorescence. An excess zinc content up to a concentration of 10^{-3} per lattice atom was desirable to improve the electrical conductivity of the phosphor. There is negligible afterglow from this powder. Measurements showed the duration to be less than one microsecond but the type of afterglow had not been studied i.e. whether it was of exponential or hyperbolic form. In some cases compensation for this lack of afterglow was made by circuit methods.

Zinc oxide gives a creeam-yellow-green emission spectrum under ultra violet light or electron excitation. Its efficiency is 50-70% that of ZnS-Cu for u.v. excitation but is only 20% for 20 k.v. cathode ray excitation. The colour changes from white to yellow with increase of interstitial zinc.

7.5.2. Physical measurements on zinc oxide

Efficiency, photoconductivity, stability and absorption measurements have been made in the laboratory for this phosphor. Fig.9 shows absorption coefficient variation with wavelength. The usual difficulties of powder measurements had been recognized and the curves are only approximate because of light scattering by the particles.

For white zinc oxide (no interstitial zinc) the photoconductivity shows a maximum effect at 3950 A° and for yellow zinc oxide (interstitial zinc present) the maximum is at 4200 A°. Comparison figures for the absorption coefficient of pure zinc sulphide are given in the diagrams.

The secondary emission ratio of zinc oxide is unity at 3000 v. but the high electrical conductivity is an advantage which can compensate for low secondary emission ratio at high voltages.

8. Light Valves, Picture Storage tubes etc.

No work had been done on these at Bad Liebenstein, but Prof. Schröter gave the following resume of the situation in Germany, as he knew it.

Tubes employing the absorption properties of ZnS failed through poor contrast. The RCA "graphite cell" proved difficult owing to the high voltage required between adjacent picture points. Von Ardenne had been experimenting with the Kerr effect in ZnS crystals.

The Fischer-Amrein project in Switzerland, using a thin oil film deformed by charges produced by a scanning C.R. beam. and projected by a Schlieren optical system, was considered to be very promising. Fischer claimed a picture 10 metres wide of cinema brightness - 441 line television picture. Prof. Schröter had not seen this apparatus demonstrated, but had seen a film made by projection from it, and was impressed by the quality. He thought they were only able to use a portion of the scanning field at the moment, which limited the actual picture displayed to about 300 lines.

Dr. Krawinkel of the Reichpost, had been working at Hirschberg, Silesia (Sudetan Mountains), on a picture storage device. This consisted of an image converter with a controlled photocathode. A mosaic of minute insulating particles (quartz?) is deposited on a photocathode. These particles are charged up by a modulated scanning beam, with the photocathode in the dark. The photocathode is then illuminated with U.V. or blue light, and suitably imaged on a fluorescent screen. The scanning gun is run at about 10,000 V., giving a secondary emission coefficient less than 1, so that the resulting picture appears as a negative.

No practical solution of a single storage mosaic, for storing and wiping off a picture, has been attained.

9. Synthetic Quartz Crystals for frequency control

At Steinbach preparations for production of synthetic quartz crystals had been under way. These were developed by Prof. Nacken in Schramberg. A disc of quartz 1 cm. diameter and 2 mm. thick, was suspended in a solution of SiO_2, water and sodium bicarbonate in an autoclave. The apparatus was closed at atmospheric pressure and room temperature, and then heated to 400°C, which developed a pressure of about 375 atmospheres. This was maintained for 3-4 weeks, by which time a suitable growth (3-4 cms.) of synthetic material had taken place on the original specimen.

10. Materials Evacuated

Powder samples from Telefunken - Bad Liebenstein

Samples of screen materials were collected. A list of these samples with some comments is given below:-

(a) From Telefunken

Origin or manufacturer	Ref. Nos.	Fluorescence and comments.	Chemical Matrix	Composition Activator
Schleede	2028	Blue exciter for d.l. screens.	ZnS	Ag
"	2032	Yellow afterglow layer for d.l. screens	ZnS.CdS	Ag
"	1648/46/25	Green short afterglow.	ZnS.ZnSe	Cu
"	1867	Green long afterglow.	ZnS	Cu
"	3008	Yellow	ZnS.CdS	Ag or Cu?
"	MS2	Green - no afterglow.	MgS	Cu
I.G.Farben	0.12	Green - long afterglow.	ZnS	Cu
"	439	Green - long afterglow.	ZnS	Cu
"	110	Mixture for two colour tube (G.L. type).	ZnS ZnS.CdS	Cu Cu or Ag?
Rot Leuchte Farbe	-	Red	ZnS.CdS	Cu
Steinbach: Dr.Kamm	K12	White mixture for television.	ZnS	Various Activators
Steinbach	T1274	Blue - short afterglow.	ZnS	Zn
Phys.T.Reich-Posen	-	Leuchte F.Rot.	ZnS.CdS	Ag or Cu?
-	Z168	Green - no afterglow.	MgS	Cu

Origin or manufacturer	Ref. Nos.	Fluorescence and comments.	Chemical Composition Matrix	Activator
Made at Heidelburg Prof.Dr.Wesch Dr.Krappke	K70	High press. 200 at Near white for image converters etc.	ZnS-ZnSe + ZnS	Cu Ag
Inst.f.Org.Ch.u.	-	Yellow - no afterglow.	Al_2O_3	Mn?
Bioch.Reich.Univ.	-	Red - no afterglow	Al_2O_3	Cr
-	UV1	Blue - no afterglow.	$CaWO_4$	-
Steinbach	-	Blue - no afterglow.	$CaWO_4$	-
"	-	Green Willemite	$ZnSiO_3$	Mn
Telefunken	10/3/44	Green Willemite	$ZnSiO_3$	Mn
Auer:forschritt	-	Yellow	$ZnBeSiO_4$	Mn

(b) From Leuchtstoffe

Unheated basic materials

Zinc sulphide precipitate
Zinc selenide precipitate
Cadmium sulphide precipitate

Phosphor samples

Phosphor fluorescence and application.	Chemical Composition Matrix	Activator
Blue exciter layer for d.l. CRT screens.	ZnS	Ag
Green - long afterglow	ZnS	Cu
Green television screen powder	ZnS:ZnSe	Cu
Blue emission No.SV162	$CaWO_4$	-

	Chemical Composition	
	Matrix	Activator
High voltage proj. tubes screen material pale green emission for Telefunken.	ZnO	
Further sample.	ZnO	
Yellow emission for d.l. tube screens.	ZnS.CdS	Cu or Ag?
Green willemite with afterglow under u.v. exc.	Zn_2Si_4	Mn
Yellow emission no. a.g.	$Zn.Be.SiO_4$	Mn
Near White emission television powder.	ZnS-ZnSe- + ZnS	Ag
Television screen powder.	ZnS-ZnSe	Ag

Equipment (from Telefunken)

1 large iconoscope
1 small iconoscope
1 super iconoscope with AEG type lens
1 " " " Telefunken experimental lens
1 Magnetic deflection coil assembly for television tube
1 Electrostatic gun
1 Set of optical lenses for super iconoscope

All these materials were evacuated through Official Army channels.

11. Summary of other targets and personnel mentioned during the visits.

Dr.Theile - Telefunken. Visiting parents at Marburg then going to Dr.Hachenberg's laboratory at Göttingen.

Dr.Weiss - Reichpost Laboratory. Believed to be at Aoh near Swiss border. Has worked on television cameras in nose of projectiles - has a film of picture received. Work on thermionic multipliers.

Prof.Schleede - Director of Chem. Inst. of Polytechnik, Berlin. Believed to be at Castle of Czernin near Salzburg. Appeared to be director of fluorescent powder research for Luftwaffe - long afterglow and two colour powders etc.

Dr.Rothe - At Breslau; work on 3 and 9 cm. crystal detectors. Factory for crystal manufacture at Stolberg near Kemnitz. (Chemnitz)

Prof.Knoll - At Munch. Fluorescent materials and CRTs.

Osram, Weisswasser S.E. Berlin. - Special glass for projection tubes.

Telefunken factory, Berlin - Tungsten for CRT heaters and hard glass, pressed bases for CRTs.

Prof.Pohl at Göttingen University - Dark trace tubes. Theoretical work on alkali halide colour centres.

Prof.Karolus at Leipzig - Developed 880 line television film scanner.

Fernseh A.G. Possibly at Salzburg.

Manfred von Ardenne - Believed to be still in Berlin. CRTs.

Dr.Krawinkel of Reichpost at Hirschberg, Silesia - near Sudetan Mountains. Work on picture storage tubes and image converters with controlled photocathode.

Dr.Gold at Manburg (Marburg?) - Work on antimony mosaics for television cameras.

Prof.Nacken at Schramberg - Work on synthetic quartz crystals for frequency control.

Prof.Wesch - Institute fur Weltpost u.s.w. Heidelburg. Processing of fluorescent powders at high pressure particularly for image converters. Collaboration with Leuchtstoffe Steinbach.

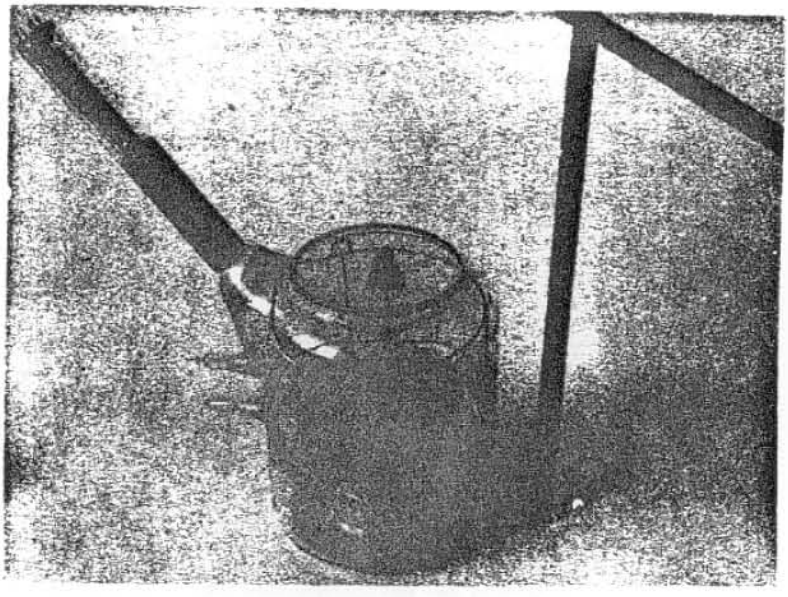


Fig. 1. Large Iconoscope.

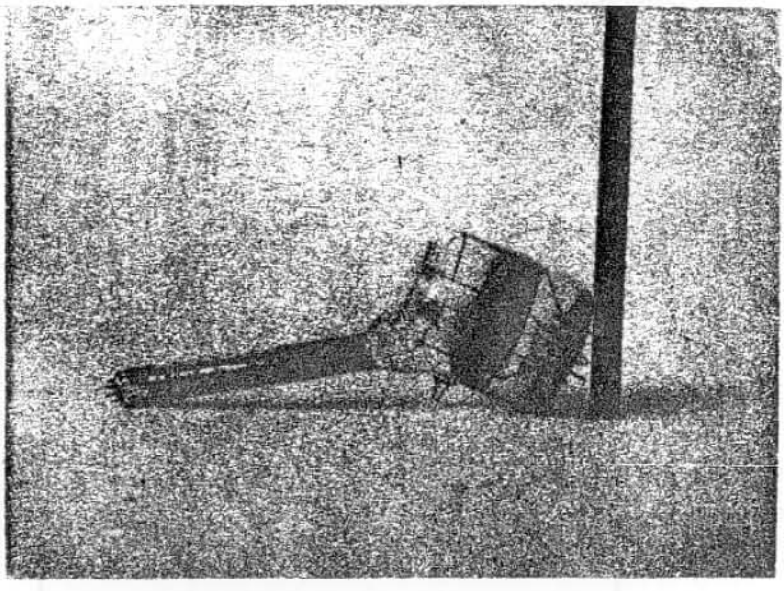
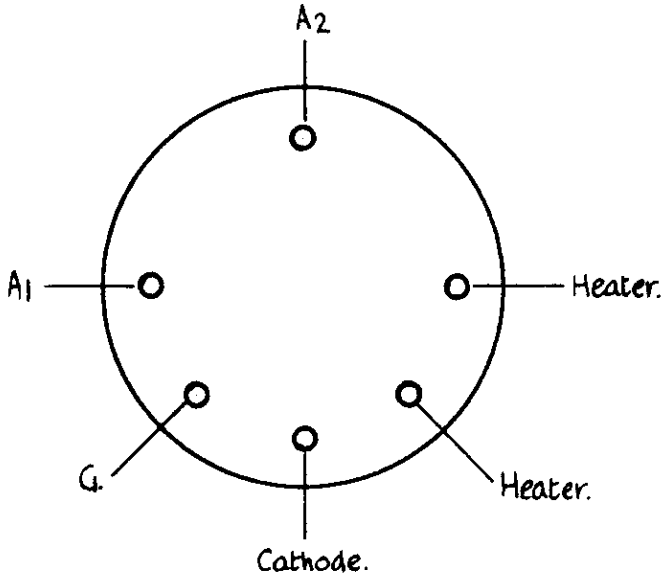
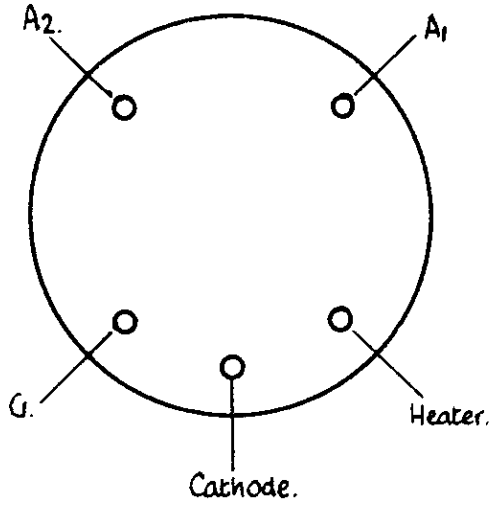


Fig. 2. Small Iconoscope.



Standard Iconoscope.



Small Iconoscope.

Fig. 3. Iconoscope Base Connections.

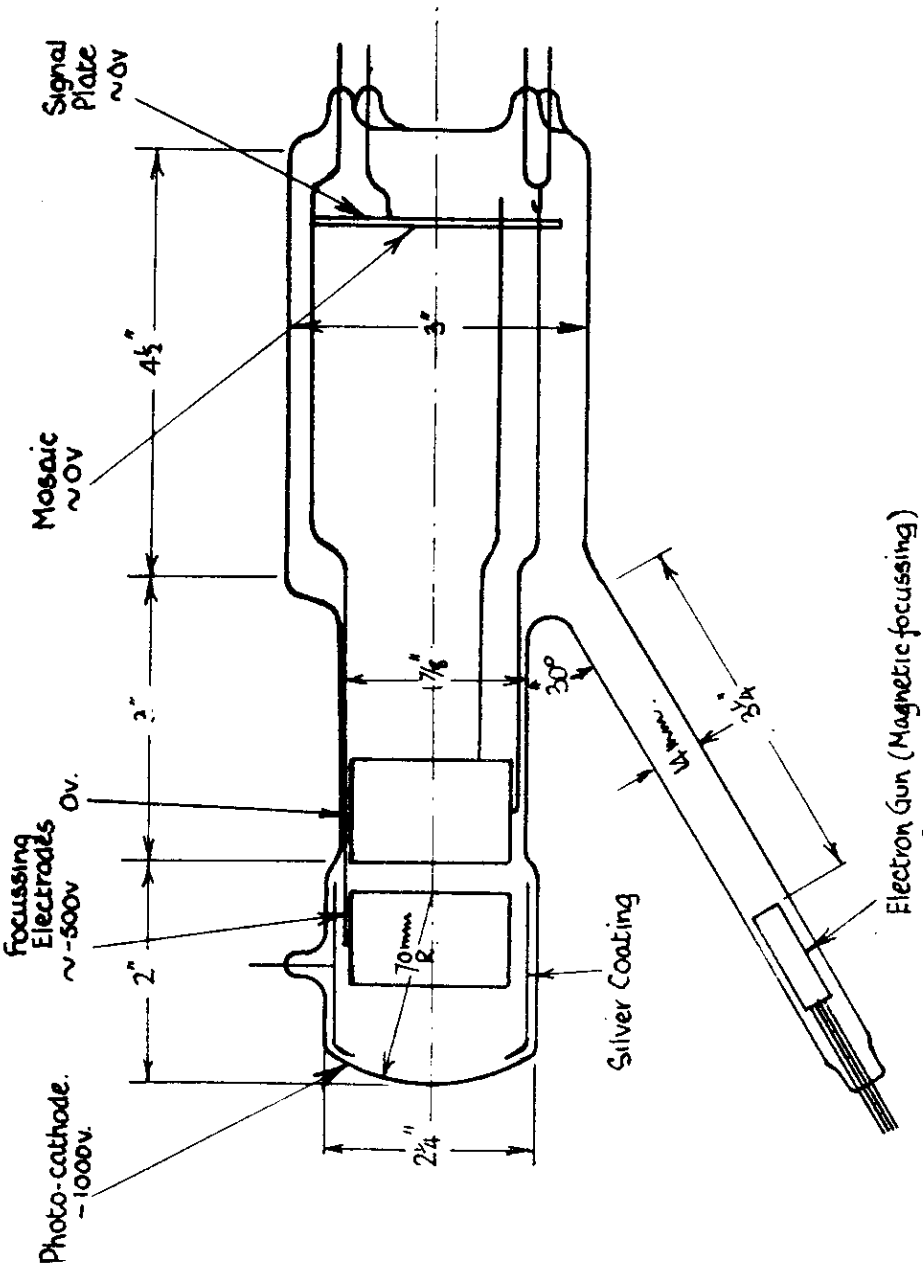


Fig.4. The Super Iconoscope.

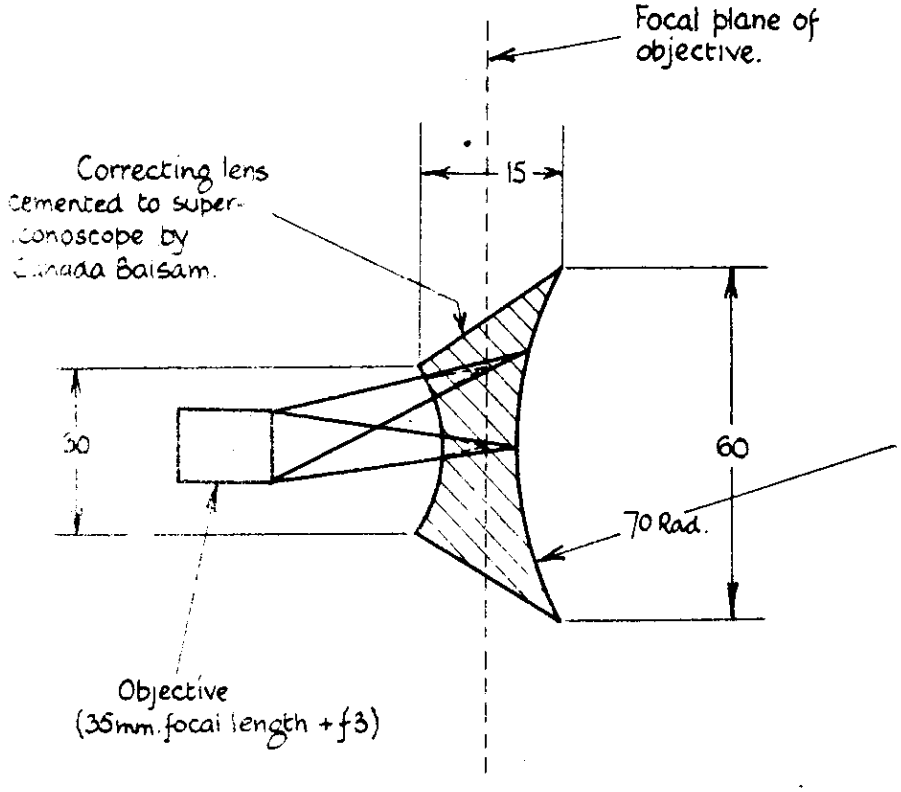


Fig.5. Optical System for Super Iconoscope. (Heitz)

Fig. 6. Super Iconoscope Telefunken Lens.

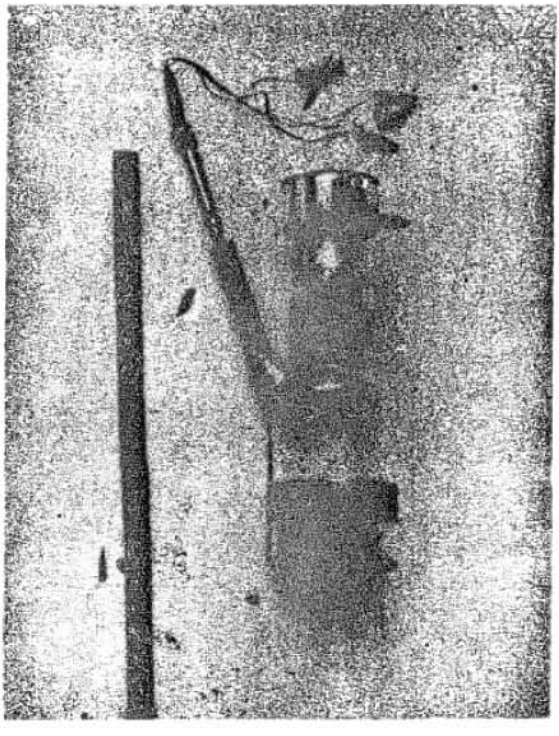


Fig.6a. Super Iconoscope AEG Lens.

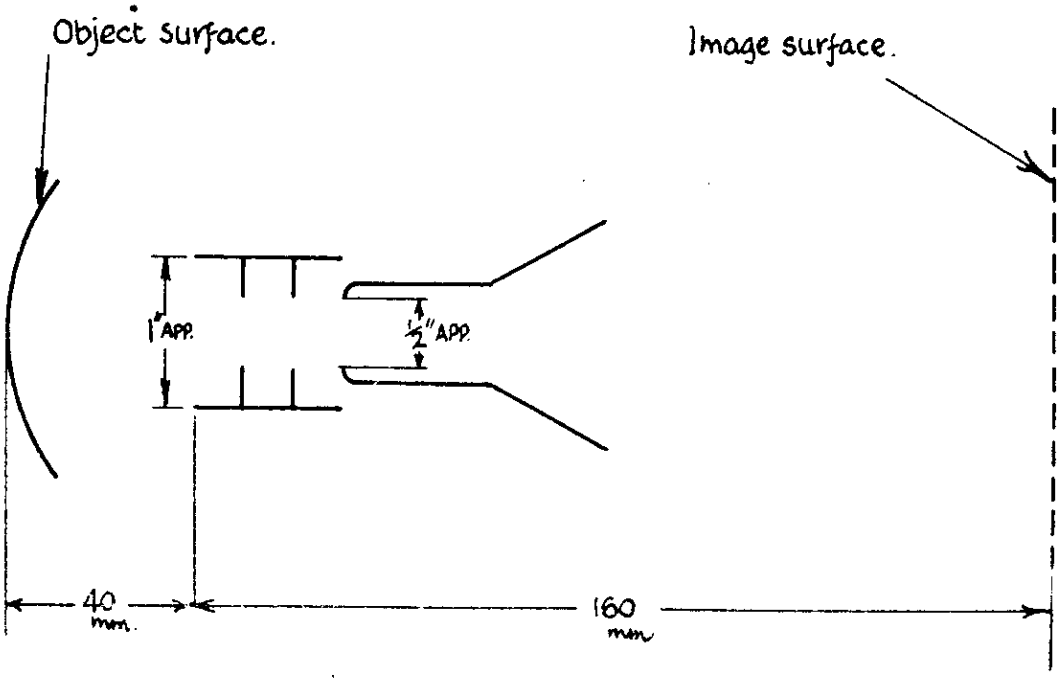


Fig.7. Focussing System of A.E.G. "Bildwandler" tube.

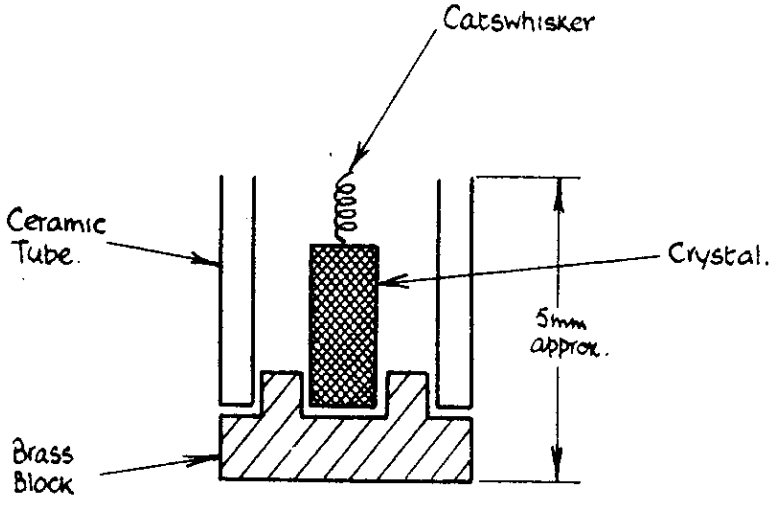


Fig.8. Method of mounting H.F. rectifier Silicon crystal.

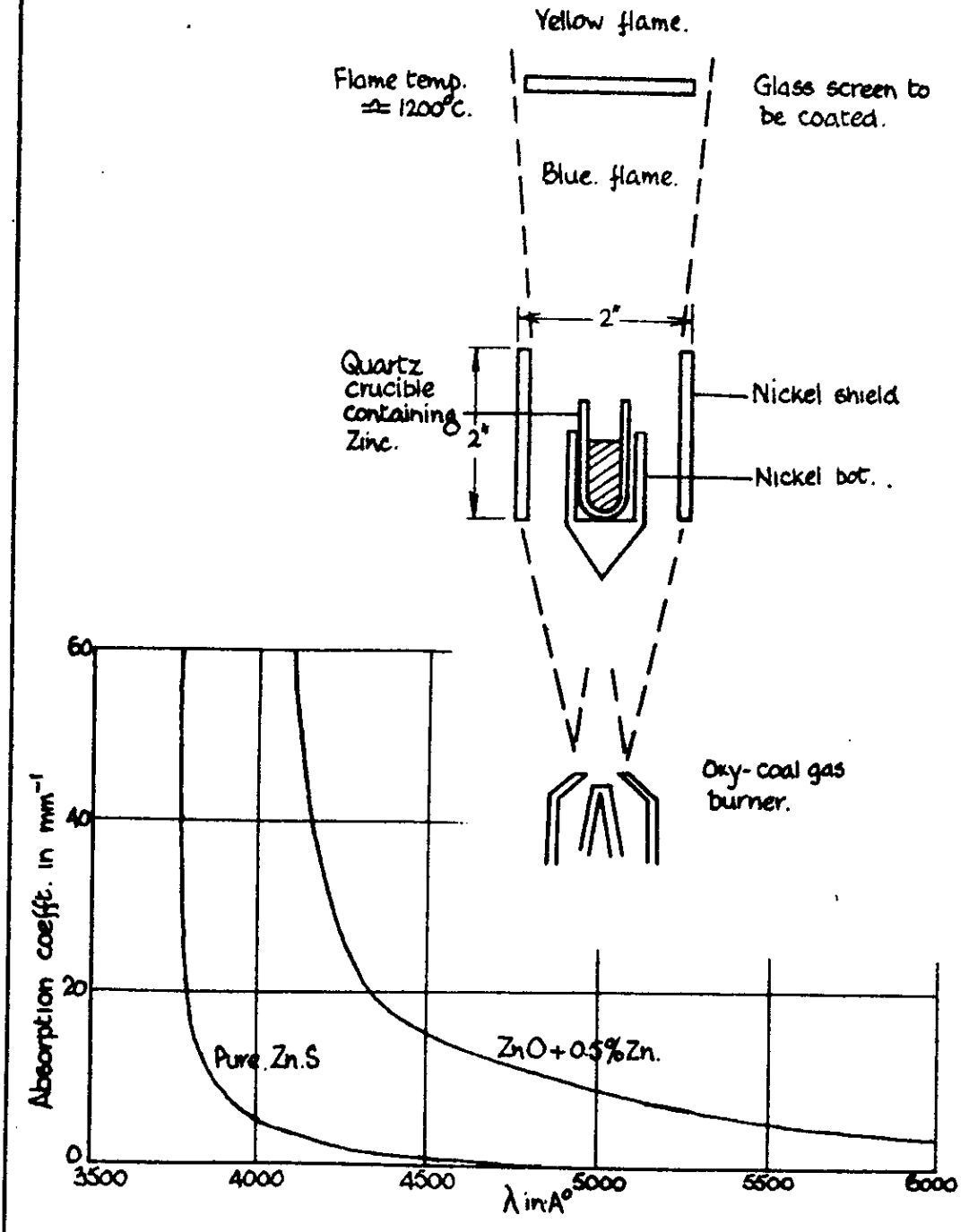


Fig.9. The preparation and properties of ZnO Screens.