THE DEVELOPMENT OF THE CATHODE RAY OSCILLOGRAPH



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# THE DEVELOPMENT OF THE CATHODE RAY OSCILLOGRAPH

by

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# INTRODUCTION

#### A. The Oscillograph

An oscillograph is an instrument which indicates, either visibly or photographically, the true wave form of a periodic or transient current or potential. The first instrument of this kind was invented by Blondel' in 1892 and called by him an "oscillograph". He had previously stated<sup>2</sup> the following requisites of an instrument capable of following rapid changes of current or potential:

(1) A natural frequency of oscillation at least fifty

times that of the phenomenon under investigation.

- (2) Damping such that the motion is exactly dead beat.
- (3) Low self induction.
- (4) Negligible hysteresis and eddy-current effects.
- (5) Suitable sensitivity.

He also shows that with such an instrument the indicated value for a sinusoidal periodic quantity of frequency f is  $\frac{1}{1 + (f/f_o)^2} \times$  the true value, where f<sub>o</sub> is the natural frequency of the oscillograph. For a transient quantity the formula applies to each individual sinusoidal component. Blondel's oscillograph was of the 'moving iron' type, but he also suggested the use of the 'moving coil' principle

which was applied by Duddell<sup>3</sup> with great success. The Duddell oscillograph was the first really practical oscillo-A single loop of thin phosphor-bronze strip is graph. stretched in the narrow air gap of a powerful electromagnet. The lower ends of the loop are fixed, and the tension of the The passage of a current causes a strip is adjustable. small mirror, attached to the loop, to deflect a beam of light across a falling photographic plate. Critical damping is obtained by immersing the whole loop and mirror in oil. The moving system is made very light, so that the instrument has a high natural frequency - about 10,000 cycles per second. It is useful for examining waves of frequencies up to 500 cycles per second, and it can be insulated for direct connection in circuits operating at 30,000 volts. For high tension work, where the potential may be as high as 250 kilovolts. electrostatic oscillographs have also been devised. The instrument developed by Ho and Koto<sup>4</sup> in 1913 is similar to the Duddell instrument in its damping characteristics and natural period (3,300 cycles per second), but being operated purely by electrostatic attraction it is more suitable for high voltage measurements.

With the development of radio communication and carrier wave telephony there has arisen the need for an oscillograph which can faithfully delineate high frequency wave forms. Carrier wave frequencies of 150 kilocycles are in common use today, so that this type of work is far beyond

the range of the mechanical oscillograph. A natural period of vibration is an inherent property of the mechanical oscillograph, as its operation depends on the motion of a finite mass controlled by an elastic constraining force. If we desire an instrument which shall be capable of indicating the magnitude of an electric variable, no matter how high the frequency may be, then we must seek some indicating device which does not contain a mechanical oscillatory sys-Such a device is found in a narrow beam of cathode tem. Since its inertia is quite negligible it will respond rays. instantaneously to changes in a deflecting field, and as it has no natural period it will have no frequency limitation. An oscillograph employing this device was first designed by Braun<sup>5</sup> in 1897 - the same year in which Thomson<sup>6</sup> employed a similar cathode ray apparatus for the determination of the physical constants of the electron. In the Braun tube cathode rays are produced by a p.d. of about 50,000 volts. Α narrow beam of cathode rays passes through a small hole in the anode and then between the poles of an electromagnet and a pair of electrostatic deflecting plates. Variations of the current through the magnet, or of the p.d. between the plates, produce a deflection of the cathode beam which is rendered visible where it impinges on a fluorescent screen. The Braun tube has been used by many workers and has been improved by them in various details. Ryan, in 1903. reported work on wave forms with a specially designed Braun tube built by Müller-Uri of Braunschweig. In 1905, Rankin<sup>8</sup>

used a similar tube with an axial focussing coil. In 1914, Dufour <sup>9</sup> proposed using the cathode ray tube for recording very rapid transient phenomena. This required a more powerful instrument, and he used a p.d. of 30 - 60 kilovolts. Dufour's oscillograph is at present the most successful instrument of the high voltage cold cathode type. With it he has obtained excellent photographic records of frequencies of the order of 10<sup>5</sup> cycles per second.<sup>(0, #.</sup>

Before discussing the desirable features of an oscillograph we must examine the properties of an electron beam passing through a magnetic or an electrostatic field. Consider an electron moving with velocity v at right angles to the direction of the field. The field will not have sharply defined boundaries, but for simplicity we may consider that the electron passes for a distance  $\ell$  through a uniform field. If f is the transverse acceleration of the electron in the field it will acquire a transverse velocity  $u = f \cdot \frac{\ell}{v}$ . The time to reach a screen or photographic plate at a distance D from the centre of the field is  $\frac{D}{v}$ , so that the deflection on the screen due to the field is given by

Deflection = 
$$\frac{f l D}{v^2}$$

If V is the potential difference between the cathode and the anode, we have for the velocity  $\mathbf{v}$  of the electron.

$$\mathbf{v}^2 = \frac{2 \, \mathrm{Ve}}{\mathrm{m}}$$

For an electrostatic field between two parallel plates, potential difference E, length  $\ell$ , distance d apart;

Electric field = 
$$\frac{E}{d}$$
  
Transverse acceleration =  $\frac{Ee}{md}$   
• Deflection on screen,  $y = \frac{Ee}{md} \cdot \frac{\ell D}{v^2}$   
=  $\frac{\ell D}{2d} \cdot \frac{E}{v}$ 

For a magnetic field H produced by an electromagnet or a solenoid, H is proportional to the number of ampere-turns, and we have:

Transverse acceleration = 
$$\frac{\text{Hev}}{\text{m}}$$
  
 $\therefore$  Deflection on screen  $x = \frac{\text{Hev}}{\text{m}} \cdot \frac{\ell D}{v^2}$   
 $= k \cdot \frac{\text{H}}{\sqrt{v}}$ 

(If H is measured in gauss, V in volts,  $\ell$  and D in cms., k = .298  $\ell$  D)

In the derivation of the above formulae the mass or inertia of the electron has been assumed constant, and the results obtained hold accurately for values of the accelerating voltage V up to 10 kilovolts. Above this value however the velocity of the electron begins to approach the velocity of light, and the transverse mass of the electron varies with its velocity according to Lorentz's formula

$$m_t = m_o \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}$$

We may now proceed to a study of the various factors affecting the use of an electron beam as an indicator. There are three types of cathode ray oscillograph in use today, and the most important point of difference between them is the order of magnitude of the accelerating voltage employed. Thus the Dufour oscillograph runs on 30 - 60 kilovolts, A.B.Wood's oscillograph on 3000 volts, and the Western Electric oscillograph on 300 As we have already shown, the electric and magnetic volts. sensitivities vary as  $\frac{1}{V}$  and  $\frac{1}{\sqrt{V}}$  respectively, so that there are strong reasons for the use of a low voltage instrument. As will be seen from the following considerations however, a high velocity beam is essential for work such as the recording of high frequency or transient phenomena. According to Whiddington<sup>12</sup> and Terrill<sup>13</sup> the penetration of cathode rays of velocity v into matter is given by  $t = v^4/a$ , where a is a constant proportional to the density of the absorbing matter. The depth of penetration is therefore proportional to the square of the accelerating voltage. By applying this, A.B. Wood<sup>14</sup> has shown that for an ordinary gelatine photographic emulsion the depth of penetration  $t = 1.25 V^2 \times 10^{-12} cms$ . approximately. Taking the thickness of the emulsion as about  $10^{-3}$  cms. we get complete penetration with 30,000 volts, 1% penetration with 3000 volts, and 0.01% penetration with 300 volts. Wood "5 describes various methods of increasing the sensitivity of the photographic plate to cathode rays. but however this may be done the advantage of the high

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velocity ray remains. Dufour has used his high voltage oscillograph for wireless oscillations up to frequencies of  $200 \times 10^6$  cycles per second. The velocity of the cathode ray spot in making such records is of the order of 10<sup>8</sup> cms. per second, so that no trace will be found on the plate unless the photographic efficiency of the cathode ray is very When examining very high frequencies there arises high. another factor calling for the use of a high voltage ray. As the electron takes a finite interval of time to pass through a deflecting field, its deflection will be a measure of the average strength of the field during that interval, and when the field is changing rapidly this mean strength will differ from the true instantaneous value at the middle of the interval. The error is shown by Mines '6 to be approximately .165  $\left(\frac{\pi f L}{\pi}\right)^2$ . Assuming a plate length of 5 cms. this gives

Error = 40 
$$\left(\frac{f}{v}\right)^2$$

The following table will give an indication of the %age error at high frequencies for various accelerating voltages

V	f	% Error
300	10 <sup>6</sup> 10 <sup>7</sup> 10 <sup>8</sup>	negligible 0.4 40.0
3,000	10 <sup>7</sup> 10 <sup>8</sup>	0.04 4.0
30,000	10 <sup>7</sup> 10 <sup>8</sup>	negligible 0.4

In making an accurate oscillographic record, the lines traced on the plate by the cathode beam must be narrow This is a difficult condition to fulfil, for a and sharp. beam of electrons is naturally divergent, owing to the mutual repulsive force between each electron and its neighbours. The motion of the electrons produces an electromagnetic field which tends to contract the beam, but no matter how fast the electrons move the convergent electromagnetic force can never be as great as the divergent electrostatic Consider an electron beam of radius r formed by the force. liberation of n electrons per second, moving with a velocity There will be n/v electrons in unit length of the ν. The radial electrostatic field E at the surface of beam. the beam is given by

$$\int_{c} E \, ds = 4\pi \cdot \frac{ne}{v}$$

$$E \cdot 2\pi r = 4\pi \frac{ne}{v}$$

$$\cdot \cdot E = \frac{2\pi e}{r \cdot v} e \cdot s \cdot u \cdot$$

. Radial electrostatic force on one electron = Ee e.s.u. =  $\frac{2ne^2c^2}{r.v}$  e.m.u. The electromagnetic field  $H = \frac{2I}{r} = \frac{2ne}{r} e \cdot m \cdot u$ . Radial electromagnetic force on one electron = -Hev $= -\frac{2ne^2v}{r}$ 

Resultant dispersive force on a boundary electron =  $\frac{2ne^2(c^2-v^2)}{rv}$ Let  $J = \frac{ne}{\pi r^2}$  be the initial current density of the beam. The radial dispersive force on a boundary electron, where the radius of the beam is y, is

$$Y = 2ne^{2} \cdot \frac{c^{2} - v}{v}^{2} \cdot \frac{1}{y}$$
$$= 2\pi r^{2} e J \cdot \frac{c^{2} - v}{v}^{2} \cdot \frac{1}{y} = \frac{k}{y}$$

If the electron beam is initially parallel and of radius r, we have for a boundary electron

$$\frac{1}{2} m \dot{y}^{2} = \int_{r}^{y} \frac{k}{y} dy$$

$$= k \log \frac{y}{r}$$

$$\cdot \sqrt{\frac{m}{2k}} \cdot dy = \sqrt{\log \frac{y}{r}} \cdot dt$$

$$\cdot t = \sqrt{\frac{m}{2k}} \int_{r}^{y} \frac{dy}{\log y/r}$$

Let the expansion ratio of the beam be R, so that  $R = \frac{y}{r}$ 

then 
$$\mathbf{x} = \mathbf{vt} = \frac{\mathbf{v}}{2} \sqrt{\frac{\mathbf{mv}}{\pi e J (c^2 - \mathbf{v}^2)}} \int_{1}^{R} \frac{d\mathbf{R}}{\sqrt{\log \mathbf{R}}}$$

Substituting for m, the transverse mass, its value  $m_o(1 - \frac{v}{c^2})^{-\frac{1}{2}}$ and denoting the integral by F(R):

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$$x = \sqrt{\frac{m_{o}}{4\pi e J}} \cdot \frac{v^{3/2}}{c} (1 - \frac{v^{2}}{c^{2}})^{-3/4} \cdot F(R)$$

Also let  $\oint(\mathbf{v}) = \frac{\mathbf{v}^{3/2}}{c} \left(1 - \frac{\mathbf{v}^2}{c^2}\right)^{-3/4}$ so that  $\mathbf{F}(\mathbf{R}) = \sqrt{\frac{4\pi\Theta}{m_o}} \cdot \mathbf{x} \frac{\sqrt{J}}{\phi(\mathbf{v})}$ 

or 
$$\mathbf{F} = a \mathbf{x} \sqrt{\frac{\mathbf{J}}{\Phi}}$$

where  $a = \sqrt{\frac{4\pi e}{m_o}} = 14920$ 

The value of  $\oint(\mathbf{v})$  for any value of  $\mathbf{v}$  may be obtained from the graph below. The above formula gives F, and the value of R corresponding to the value found for F(R) is also given by a graph. An empirical equation for the relation between R and F(R) is

or 
$$R = 1 = \frac{2F^2}{F + 6}$$
  
 $R = \frac{2F^2 + F + 6}{F + 6}$ 

Consider the energy T arriving per second per sq. cm. at the screen or photographic plate:

$$T = \frac{1}{2} mv^{2} \frac{n}{\pi R^{2} r^{2}} = \frac{m}{2} e \cdot \frac{v^{2} J}{R^{2}}$$
  

$$T = \frac{m}{2} e \cdot \frac{v^{2} J (F + 6)^{2}}{(2F^{2} + F + 6)^{2}}$$
  

$$\cdot \sqrt{T} \propto \frac{F(F + 6)}{2F^{2} + F + 6} \cdot \frac{v \phi}{x}$$

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By differentiation, we find that the maximum value of  

$$\frac{F(F+6)}{2F^2 + F+6}$$
 is given by  $F = 2.435$   
Results: -  
(i) The optimum value of J for any value of  $\Phi$  is given by  
 $\sqrt{J} = \frac{F\Phi}{ax} = \frac{2.435}{14920} \cdot \frac{\Phi}{x}$   
Thus the optimum value of J decreases as x is increased.  
(ii) When J is adjusted so that  $\frac{ax}{\Phi} \sqrt{J} = F = 2.435$ ,  
then the  
Energy  $T \propto \frac{v^2 \Phi^2}{x^2}$   
This explains the curious result of (1) : for as we  
increase x, T decreases, and we can not make up for  
increasing x by increasing J, but rather we must de-  
crease J according to (1).  
(iii)  $F(R) = 2.435$ .  $\therefore$  from the curve,  $R \neq 2.4$ 

(iii) F(R) = 2.435, . . from the curve,  $R \neq 2.4$ The value of R, corresponding to the optimum value of J, is R = 2.4. Hence J will satisfy (i) when it is adjusted so that R = 2.4.

These three results lead to the following method of procedure in designing and using an oscillograph. First we must plan to use the highest voltage available, so that v may be as great as possible. Then we choose the smallest value of xwhich will give the necessary sensitivity. To obtain the diameter of the pin-hole limiting the initial size of the electron beam, divide the maximum allowable diameter of the 'spot' by 2.4. The design and power of the source of electrons must be such that we can send through the pinhole a beam of electrons of current density J, where J has the value required by (i).

Owing to the practical difficulty of producing a parallel electron beam of high current density, attempts have been made to use a large beam of relatively low density and focus it in the plane of the photographic plate. The axial focussing coil is one of the earliest and most commonly used devices for this purpose. A short solenoid, about 6 inches in diameter, is mounted in front of the cathode so that the electron beam moves along the axis of the coil. The number of ampere-turns necessary is of the order of 1000. An electron moving at an angle 9 to the direction of a magnetic field H, with a velocity component v in the direction of the field, will have a component v tan 9 at right angles to the field. This component will produce motion in a circle of radius

$$\mathbf{r} = \frac{\mathbf{m}}{\mathbf{e}} \cdot \frac{\mathbf{v} \tan \theta}{\mathbf{H}}$$

Since its component v remains constant, the electron will move in a helix. The time for one revolution is

$$t = \frac{2\pi r}{v \tan \theta} = 2\pi \frac{m}{He}$$

so that the distance between two successive transits of the line through the initial position of the electron.

parallel to H, is

$$s = 2\pi \frac{m}{He} v$$

Since this distance is independent of 0, electrons diverging from a point in the field will be brought to a focus. It should be noted that the cylinders on which the helical electron paths lie are not coaxial, but have a common gener-In the case of a non-uniform field, such as ating line. that produced by a single coil, the radius of the helix will vary, but the focussing property of the field will be unaffected. The disadvantage of this method of focussing is that the spot produced is not uniform, but usually has a 'tail' which is troublesome. Also the use of a magnetic deflecting field complicates the effect of the focus sing field. A more direct method of focussing, in which the electrons are accelerated radially, is to be preferred. In a tube containing gas, focussing may be obtained by using a concave cathode, or, as in the Western Electric tube, the ionizing property of the moving electron may be used to focus the beam. Owing to the difference in mobility between the positive ions and the electrons, a radial field is built up aroung the electron beam. This keeps the beam from diverging, and with the correct gas pressure the beam may be focussed by regulating the current density. For high vacuum tubes a higher velocity beam is employed, and there is less need for focussing. To get a high current

density, however, the electron discharge from the hot filament cathode must be focussed on the pinhole in the anode. The most successful method of doing this was developed by Coolidge'' for his X-ray tube. The filament, wound in a flat spiral, is mounted coaxially with a cylindrical metal hood. The hood is negative with respect to the filament, and the amount it projects beyond the plane of the filament controls the focussing effect. This device was used in an oscillograph by Samson's in 1918, and later by Keys'<sup>9</sup> and Wood.'<sup>5</sup> Another method tried by Wood was to use a tubular anode with a wire mounted along its axis. The wire was charged positively with respect to the anode tube, so that the electrons passing through the amode were subjected to a radial field. The Coolidge type of cathode gave better results, but this idea seems theoretically sound and is worthy of further experimental investigation. Further work on the development of this part of the oscillograph is being done by the writer.

We have not yet considered the conditions imposed on the design of an oscillograph by the requirements of the deflecting systems. If the instrument is used to measufe potential variations the resistance between the electrostatic deflecting plates must be infinite, or serious errors may be introduced. This is especially so when examining transient electrostatic effects where the leakage current must be quite negligible. If there is to be no current

between the deflecting plates there must be no gas in the For the measurement of explosion pressure with a piezotube. electric crystal, Keys '9 used a gas free tube with a hot filament cathode. Whenever a tube containing gas is used it must be borne in mind that the electrostatic deflecting system is equivalent to a condenser and resistance in parallel. Before using such a tube this resistance must be determined. Dufour, who uses a tube containing gas, places his plates outside the tube. This prevents the passage of ions from one plate to the other, but the space charge produced between the plates is still an objectionable feature. The magnetic deflecting system presents no difficulty, except that the dimensions and design should be such as to confine the field to a sharply defined region.

A long paragraph might be devoted to a detailed description of the various types of oscillograph in use today, but as the outstanding features have been mentioned in the previous discussion it seems only necessary to give a brief classification of types. The cold cathode is always used in tubes containing gas and the hot filament cathode in high vacuum tubes. Wood<sup>14</sup> classifies modern oscillographs into three types, according to the accelerating voltage used. The high voltage oscillograph, as perfected by Dufour, uses up to 60 kilovolts. The advantages are high photographic sensitivity and ability to record very high frequencies by

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by a single transit. The medium voltage oscillograph as developed by Keys and Wood uses from 3000 to 5000 volts and combines photographic sensitivity with woltage and current sensitivity. The D.C. high voltage supply is taken from an Evershed 6000 volt generator - a simple and convenient unit. The high vacuum is easily obtained by means of a standard pump, such as the Cenco 'Hyvac'. The low voltage oscillograph, such as that developed by Johnson<sup>20</sup> and manufactured by the Western Electric Co., operates on 300 volts. It is very sensitive, and being sealed permanently it is portable and easily set up. The tube however contains gas, and this, together with the fact that it is not adapted for recording a single traverse of the spot, renders it quite unsuitable for examining transient electrostatic effects. It is very convenient for examining alternating current phenomena which can be reproduced on the screen as Lissajous' figures. In short, the low voltage tube is cheap, convenient, and easily operated, and is unexcelled for rough testing by visual observation. For giving permanent records of high frequency effects the higher voltage types of instrument are of greater value.

We are now in a position to show why the oscillograph, in its present state of development, is still regarded as an instrument which is more suitable to the research laboratory than to the engineer. Routine testing and commercial work require an instrument which is always ready for use, and which does not need frequent calibration. In this respect

the Western Electric tube is ideal - but its field is limited. The greatest difficulty in the development of the oscillograph lies in the recording part of the apparatus. As long as plates have to be put inside the tube it must frequently be opened and as often exhausted. If the recording of the spot could be achieved on a plate outside the tube, most of the disadvantages of the instrument would disappear. A highly exhausted well baked tube, with no internal sources of gas, would fulfil the conditions of constancy and simplicity. By using a tungsten filament rather than an oxide-coated platinum filament we would remove the only possible source of It remains to devise some method of recording the gas. Terroux<sup>21</sup> spot on a photographic plate outside the tube. suggests the use of a window of quartz, coated on the inside with calcium tungstate or other fluorescent material, and in contact with a photographic plate on the outside. Now calcium tungstate gives a fluorescent band which is almost entirely transmitted by glass, so that in this case there is little to be gained by the use of a quartz window. However. by coating the inside of a quartz window with some substance which gives out intense ultraviolet fluorescence under cathode rays, we can transform the energy of the electron beam into light energy of a wave length which is most efficient for affecting the photographic plate. A study of the ultraviolet light energy required to produce a photo image has been made by Helmick.<sup>22</sup> Owing to the thickness of the window

between the fluorescent screen and the photographic plate the spot will be somewhat diffused, but it is thought that this defect will prove to be of no great importance. The writer has consequently been making a study of the fluorescence of various materials under cathode rays, from the point of view of photographic efficiency. Since the behaviour of a panchromatic plate depends on the fluorescent properties of the dyes with which it is coated, it is obvious that the most efficient combination will consist of an uncoated rapid plate and a fluorescent screen giving out light to which the plate is most sensitive. Particular attention has therefore been paid to the ultraviolet region, and the investigation has been carried out almost entirely with a small Hilger quartz spectrograph. The problem of finding a suitable binder for the fluorescent material has also received considerable attention. Comparatively little is known about fluorescence, so that the problem of finding a suitable material for use in the oscillograph requires a rather wide study of the phenomenon.

# B. Fluorescence

According to the Wiedmann theory of fluorescence, it is an accompaniment of molecular change. An exciting agent falling on a substance changes it from a stable condition A to an unstable condition B. The light emitted while the substance is under excitation is called 'fluorescence'

and is given out during the A to B change. The light emitted when the excitation is discontinued is called 'phosphorescence', and is probably due to the return of the molecules to the stable state A. Experiments made with excitation by X-rays, by cathode rays, and by light of various wave lengths indicate that the distribution of energy in a fluorescence spectrum is independent of the mode of excitation. However, the material may possess several independent fluorescence bands, and the extent to which any one of these bands is excited will depend on the exciting agency. In general a particular material will only be sensitive to certain modes of excitation. It has been found that the fluorescence of a chemical substance is very greatly influenced by the presence of impurities. The most important of the early workers in this field were Sir W. Crookes,<sup>23</sup> Lecog de Boisbaudran<sup>24</sup> and E. Becquerel. Becquerel<sup>25</sup> in 1859 published an interesting account of his research on the luminous effects produced in substances by light stim-In 1888 he published a paper<sup>26</sup> on the preparation ulation. of phosphorescent sulphides of calcium and strontium in which he points out that the presence of a salt of an alkaline metal is necessary for marked luminescence. Thus calcium sulphide prepared by heating sulphur with calcium carbonate containing a trace of manganese or bismuth did not show much luminescence, but the addition of less than one percent of sodium carbonate produced brilliant yellow

or blue luminescence. On the other hand calcium carbonate containing a small percentage of lithium carbonate produced a sulphide with a strong green luminescence, without any further addition. If the sulphide is prepared by heating sulphur with calcined shells no sodium salt need be added, because the shells already contain sodium compounds. Lenard and Klatt<sup>27</sup> have made an extensive study of the preparation of luminescent sulphides. In 1909 Urbain<sup>28</sup> published his work on the cathodo-fluorescence of the rare earths. From his own work and that of previous investigators, notably Lecoq de Boisbaudran, he concluded that luminescent substances are a mixture of at least two bodies, a 'diluant' and the 'phosphorogène' or active matter. The substance forming the main portion of the mixture is the diluent, while the active matter is present in such a small proportion that it might be regarded as an impurity.

Lecoq de Boisbaudran, after a great deal of work on the fluorescence of both the rare earths and the commoner elements such as manganese and bismuth, formulated a number of laws on the subject. These laws are as follows:

(1) A material which strongly activates one body (the solid diluent) will not necessarily activate another body which has similar properties.

(2) A material may activate a particular compound of a metal and not its other compounds, and the fluorescence of different compounds of a metal may or may not be similar. (3) It is conceivable that coloured bodies will not make vary effective diluents, on account of the absorption of the exciting radiation. (Lecoq de Boisbaudran thought that luminescence was excited by the light from the discharge, whereas it is of course due to the cathode rays. The luminescence will, however, be somewhat diminished owing to the absorption within the body of the light emitted under the cathode ray bombardment.)

(4) A substance may behave as a diluent for certain active materials and as an active material for other substances.

(5) When two active substances are present in a solvent which is effective for each individually, the fluorescence due to each may be weakened, but not otherwise modified.

(6) Two materials which can more or less activate a diluent individually may sometimes neutralise each other so that there is no fluorescence at all.

(7) A material which is active under certain conditions, but inactive in a particular diluent, can by its presence weaken the effect of another active material on this diluent.

(8) The fluorescence in one diluent seems to be weakened by the addition of a second diluent which, though effective for some active materials, is not effective for the active material present. (9) An active material usually produces its double fluorescence in a mixture of two effective diluents, but, if they are in certain proportions, the ratio of the intensities of fluorescence may not be proportional to the ratio of the quantities of each diluent.

(10) With an active material in equivalent quantities of two effective diluents, the fluorescences may be of the same intensity; but the contrary is also observed.

(11) If two very unequally active materials are present in a diluent, and if the proportion of the active materials is kept constant while the proportion of the diluent is increased, then we will get: (a) only the effect of the less active material; (b) both effects, with a growing predominance of the effect of the more active material. On increasing the proportion of the more active material only the fluorescence due to it will be observed, no matter what quantity of diluent is used.

(12) Some fluorescence spectra may be hidden by others, but may be discovered on warming the tube, or on modifying the discharge.

These laws of Lecoq de Boisbaudran give some idea of the behaviour of fluorescent substances. Until fairly recently nothing further had been accomplished beyond the verification of his work.

An extensive research on the uranyl salts has been

made by Nichols<sup>29</sup> and Howes.<sup>30</sup> By using a spectrophotometer they showed that each broad luminescence band can be resolved into series of component bands. They also determined the spectral structure of the phosphorescence of certain sulphides.<sup>31</sup> In 1924 Tanaka<sup>32</sup> published the results of his work on the cathodo-luminescence of solid solutions of forty-two metals. He classifies luminescence spectra as follows:

Type I. Spectra containing fine line-like bands.

- Type II. Spectra containing one or more broad bands each of which is really composed of a group of bands.
- Type III. Spectra for which the envelope of the intensity curve has no distinct summit, and the luminescent colour is whitish.

He studied twenty-seven samples of Lenard and Klatt's sulphides spectro-photometrically and observed the following points:

(1) Just as in electrolytes, whatever bases (solvents) may be used, dissolved active metals show their characteristics. For each active metal there are characteristic series of constant frequency interval.

(2) The base seems to determine the colour of the luminescence.

(3) The flux has no important effect on the colour of the luminescence.

He then extended his research to thirty-six other metals. The

chief bases used were calcium carbonate, containing traces of manganese, and calcium fluoride, containing traces of man-The ratio between the number of atoms ganese and samarium. of the base and of the active metal was usually about 250:1, the ratio shown by Bruninghaus<sup>33</sup> to produce the maximum lumin-With regard to the preparation of his 'solid escence. solutions' Tanaka merely says that the calcination was usually done with a gas blowpipe, but that in some cases in which the luminescence was faint an oxyhydrogen flame As the bases used were certainly not melted was used. it is doubtful whether the resulting preparations were really solid solutions. His results may be summarised as follows:

(1) Whatever bases are used, each dissolved metal shows its characteristic luminescence, though this is often very faint.

(2) Each luminescence spectrum is composed of several series of overlapping bands, each series spaced equally in frequency units.

(3) Two characteristic frequency intervals, different or coincident, exist for each metal; these intervals are totally independent of the properties of the solvents.

Though ultraviolet light has frequently been used to excite fluorescence, little attention has been paid to the ultraviolet region of fluorescence spectra. Urbain, however,

used a tube with a quartz window, and obtained some interesting results. The spectrum of a mixture of gadolinium oxide with calcium oxide is of special interest as it lies almost wholly in the ultraviolet. He found that from one to one and a half per cent of gadolinium oxide gave the strongest fluorescence. In order to introduce a visible as well as an ultraviolet fluorescence, he used calcium oxide containing traces of manganese. The orange fluorescence due to this enabled him to align his spectroscope. The optimum proportion of gadolinium oxide in calcium sulphate is 0.3 per cent, and admits of less variation. A further study of Lenard's preparations has been carried out by Pauli<sup>34</sup>, with a view to examining the effect of the solvent on the phosphores-He found that by modifying the dielectric constant cence. it was possible to alter the position of the luminescent band at will. His results support Lenard's view that the vibrations set up in a phosphorescent substance are analagous to those of an electric oscillator whose period depends upon inductance and capacity, and that the wave length of a band is consequently proportional to the square root of the dielectric constant of the medium. He suggests that the ultraviolet light emitted by a substance has a secondary effect in stimulating fluorescence in the visible region. With regard to the fluorescence of the alkaline earth metals. the number of ultraviolet bands is largest in phosphorescent

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calcium, while strontium has less and barium none at all. Pauli observed that a few preparations, on being subjected to intense cathode ray excitation, emit momentarily an ultraviolet light of such short wavelength that it extends into the region where the absorption of air affects it. A typical example of this is a CaCuK phosphorescent material. He also gives the following formula for a material which emits a purely ultraviolet fluorescence: 2 gms. CaS, 0.1 gm. K<sub>2</sub>SO<sub>4</sub>, 0.0002 gms. Ag, heated to redness for twenty minutes. The writer has been unable to find a published set of photographs of fluorescence spectra in the ultraviolet region. For work in which a photographic plate is used to record the light from a fluorescent screen, a knowledge of the quality of this light is desirable. Consequently it seemed worth while to make a photographic study of the spectral quality of substances that could be used for fluorescent screens. Owing to various experimental difficulties peculiar to ultraviolet fluorescence, not many spectra have been recorded so far, but further work which promises to be more fruitful is now in progress.

### EXPERIMENTAL WORK

## A. On Fluorescent Materials

The apparatus constructed for the examination of fluorescence under cathode rays is shown diagrammatically in the sketch and also in the accompanying photograph of the experimental set-up. The tube is built out of Pyrex glass  $l\frac{1}{2}$ " diameter. The anode and cathode are both made of aluminium. The samples to be examined are mounted on elliptically shaped discs of sheet aluminium and held in position at SS by means of an aluminium holder. The cathode beam excites the material on the disc so that its fluorescence may be examined spectroscopically through the quartz window WW. The ground glass joint GG enables the tube to be opened and



the sample disc changed with great facility. Pyrex glass was used to ensure mechanical strength and also in case of heating under the cathode ray bombardment. The sharp right angle bend in the lower section of the tube was made by cutting the tube and welding on a piece at right angles. This joint was made in the laboratory of the Northern Electric

Company. The tube is connected to the glass vacuum line by means of a horizontal wax joint. A drying tube containing phosphoric anhydride is connected in the vacuum line. By means of a quartz lens, an image of the sample disc is thrown on the slit of the spectroscope. This ensures that the fluorescent light entering the spectrograph is due entirely to the sample under observation and not in part to particles of previous samples which may be sticking to the walls of the tube. The spectra were photographed by a Hilger E31 Quartz Spectrograph. For obtaining comparison spectra the light from a mercury 'Lab-arc' was used. A small mirror of polished Woods metal was used for reflecting this light into the slit, so that it was unnecessary to move the spectrograph between exposures. All photographs were taken with the same slit width.

Two kinds of photographic plates were used, Wratten and Wainwright Panchromatic, and Eastman Speedway. The latter were used in all cases except when the red end of the visible spectrum was of interest. According to Harrison<sup>35</sup> who made a study of the characteristics of photographic materials in the ultraviolet, Speedway plates are very sensitive to weak light and are consequently easily fogged by stray light, but on the other hand they have very little tendency to acquire chemical fog. Their speed changes uniformly above 2500 A and their contrast is rather low. The Wratten and Wainwright plates have even greater uniformity but are very much slower. When it is desired to bring out the weakest light impressions, and contrast is of no importance, the choice of developer lies between metol and rodinal. The latter was chosen because it can be bought in a concentrated solution of standard strength and is not as irritating to the fingers as metol. Each plate was developed for five minutes in a freshly mixed solution of 3 ccs. of rodinal in 45 ccs. of water at  $18^{\circ}$ C. By standardizing the development in this way a rough estimate could be made of the intensity of the fluorescence.

A universally satisfactory binder for the fluorescent material has not yet been discovered. A solution of sodium silicate, known as waterglass, is ideal for those materials with which no chemical action takes place. It binds well to glass or quartz and is almost perfectly transparent to ultraviolet light. When salts of the various metals are added to a solution of sodium silicate, the insoluble silicates are precipitated. For example:

 $Na_2 SiO_3 + CaCl_2 = CaSiO_3 + 2NaCl$ 

Moreover waterglass cannot be used as a binder for the sulphides of calcium, strontium, barium or magnesium, because these compounds hydrolyze with water, forming the hydroxide and acid sulphide. The majority of inorganic substances which possess binding properties are unfortunately opaque to ultraviolet light. All the resins and gums and nitrocellulose materials tried have failed in this respect.

No attempt was made to maintain the discharge constant other than by using cells of constant voltage in the primary circuit. The current in the discharge, as indicated by a D.C. milliammeter, was of the order of 0.1 milliampere. The quartz lens was placed directly in front of the quartz window so that it was about 20 cms. from the fluorescent disc. The spectrograph slit was about 10 cms. from the quartz lens. The image of the fluorescent light formed in the plane of the slit by the quartz lens is shown in Fig.3. The central spot of light is the image of the disc, while the surrounding rings are reflections from the tube. The slit width for all pictures after Fig.3 was .75 of 1 division = 0.38 mm. approx. The comparison spectra were obtained from a mercury 'Lab-arc' In most pictures this was used directly, but the Woods metal reflector has since been adopted to avoid moving the spectrograph.

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Apparatus for study of Cathodo-Fluorescence



Experimental Oscillograph .



Fig.1

### WILLEMITE

Wratten Panchromatic (Plate 5) Hilger glass spectrograph Slit width: 0.12 mm. Hg Lab-arc: 45 seconds Iron arc: 60 seconds Fluorescence: 1 hour

# Fig.2 WILLEMITE

Wratten Panchromatic (Plate 4) Hilger E31 Quartz Spectrograph Slit width: 0.25 mm. Fluorescence: 45 minutes Hg Lab-arc: 30 seconds



440 49 40 40 40



# Fig.3 CALCIUM TUNGSTATE

Eastman Speedway plate exposed in the plane of the slit, showing luminescent flash caused by a single 'break' of the primary circuit. The central spot is the image of the sample disc; the remaining light is due to reflection. (Plate 9)



# Fig.4 COMPARISON SPECTRUM

Hg Lab-arc Eastman Speedway plate Slit width: 0.38 mm. Wavelengths in Angstroms x 10



# Fig.5 CALCIUM TUNGSTATE Deposited from ethyl alcohol Eastman Speedway (Plate 8)

(a)	20 r	ninutes
(b)	5 r	ninutes
(c)	1 r	ninute

Hg Lab-arc: about 10 seconds

ZINC SULPHIDE

(Muster Nr E23)

Eastman Speedway (Plate 10)

Binder: waterglass

20 minutes

5 minutes

1 minute





Fig.7

Fig.6

(a)

(b)

(c)

# (a) CALCIUM TUNGSTATE

Binder: waterglass Eastman Speedway (Plate 11) 5 minutes

# TRANSMISSION SPECTRA

- of Hg Lab-arc, 10 seconds, through
- (b) Quartz plate
- (c) Waterglass on quartz
- (d) Canada Balsam



.

# Fig.8 BARIUM SULPHIDE

Binder: waterglass Eastman Speedway (Plate 14)

(a) 5 minutes(b) 30 minutes

Fig.9 (same)

Eastman Speedway (Plate 15)



# (a) 1 minute(b) about 2 hours

Spectra in Figs. 8 and 9 may really be due to Barium Hydroxide formed by hydrolysis.



## Fig.10 BARIUM SULPHIDE

Binder: Canada Balsam dissolved in Ethyl Alcohol. Eastman Speedway (Plate 16)

(a) 1 minute
(b) 5 minutes
(c) 20 minutes



# Fig.11 GADOLINIUM IN CALCIUM

Gd<sub>2</sub>O<sub>3</sub> : 0.051 gms. CaCO<sub>3</sub> : 5.544 gms. Mixed and heated for 30 minutes in a blowtorch furnace. Ratio of atoms Gd:Ca = 1:197

Binder: waterglass Wratten Panchromatic (Plate 17)

(a) 5 minutes
(b) 20 minutes
(c) 1 hour

Comparison spectra: Hg Labarc reflected by sheet aluminium, 20 seconds



#### Fig.12 (same)

Eastman Speedway (Plate 18)

(a) 1 minute(b) 5 minutes

Comparison spectra: Hg Lab-arc reflected by tin, 45 seconds



# Fig.13 TRANSMISSION SPECTRA

Eastman Speedway (Plate 20) Hg Lab-arc, 10 seconds, through

(a) Air

- (b) Quartz plate
- (c) Celloidin on quartz
- (d) Gum Mastic on quartz
- (e) Paraffin wax on quartz

# Discussion

By comparing the bands obtained in Figs.5 and 6 for different lengths of exposure we can get an idea of the energy distribution in the spectrum. The band is sharply defined at the visible end and its intensity decreases slowly at the ultraviolet end. The Zinc Sulphide used in Fig.6 fluoresces brightly under light as well as cathode rays, and its phosphorescence is exceptionally bright and lasting. The colour however is a yellowish green and is not very efficient photographically. Fig. 7(b) shows that waterglass transmits perfectly as far into the ultraviolet as the Speedway plate is capable of recording. Canada Balsam, as may be seen from Fig.7(d), should not be used for any material which emits wavelengths less than 3000 A. In Figs. 8 and 9 waterglass was used as a binder for the Barium Sulphide. It is probable, though not certain, that Barium Hydroxide was formed when the sulphide was added to the solution of waterglass. Fig.9(b) shows a remarkable spectrum consisting of one main band and a series of evenly spaced bands which go as far down into the ultraviolet as the plate will record. A repetition of this experiment, using a plate sensitive to the far ultraviolet and possibly a vacuum spectrograph, should give very interesting results. Of the lines visible in the spectrum, most if not all are due to traces of mercury vapour. Fig.10 shows the spectra of Barium Sulphide with Canada Balsam as a binder. The spectral band obtained is similar to that obtained in

Figs. 8 and 9, but it is much stronger and is not followed by the series of weak bands. In any case these would be absorbed by the Canada Balsam. Fig.11 shows the ultraviolet spectrum of calcium oxide with gadolinium as the active agent. Some gadolinium oxide was obtained from the University of Illinois The calcium carthrough the kindness of Professor Hopkins. bonate used came from the Chemistry Department. It probably contained traces of manganese, as the spectrum shows the characteristic citron band of this element. The ultraviolet spectrum of gadolinium is very characteristic, and contains a number of lines superimposed on bands as well as several distinct lines. Here again the binder causes difficulty, for undoubtedly the calcium oxide combines with the water to form calcium hydroxide  $Ca(OH)_2$ . If the CaO remained as such the fluorescence would be much brighter. It is hoped that by using the optimum proportion of gadolinium and a purer calcium carbonate a photographically efficient fluorescent material will be developed. Fig.13 shows some more transmission spectra. Celloidin (a very pure nitrocellulose) transmits ultraviolet light well, but its behaviour under cathode ray bombardment is unsatisfactory. It forms a skin which seems to absorb the cathode rays, and it does not adhere as well as waterglass. A different method of applying it may lead to better results. A thin layer of paraffin wax does not transmit well in the visible region, but is surprisingly transparent for ultraviolet light. Its

behaviour under cathode rays has not been tested. The possibility of examining the spectral quality of any fluorescent material, which is to be used as a screen, is dependent on the use of a satisfactory binder. The discovery of a suitable binder is therefore of primary importance.

#### B. Experimental Oscillograph

The accompanying photograph shows an experimental oscillograph which was designed by the writer and built partly with the aid of Mr. H. T. Pye. The fluorescent screen is coated on the inside of a quartz window which forms the top end of the instrument. A greased conical joint renders this window accessible, so that the screen can easily be changed. Experiments are in progress with a view to obtaining an electron beam of high current density through the anode.

#### CONCLUSION

The development of the cathode ray oscillograph for commercial use requires the use of a fluorescent material with a spectral band of maximum intensity at about wavelength 3500 A. The search for such a material has already given unexpected results which may be of value from a theoretical point of view, so that the continuation of this investigation seems highly desirable both for its commerical applications and for its theoretical interest.

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