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ATOMIC WEAPONS RESEARCH ESTABLISHMENT

REPORT No. O-4/53

Studies of Organic Phosphors for Use as Scintillation Counters

Part I.

The Growth of Large Crystals of Stilbene

K. T. B. Scott
S. K. Hutchinson
Ruth Lapage

A.W.R.E.
Aldermaston, Berks.

September, 1953

RESTRICTED

Ministry of Supply

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CAPENHURST ASSEMBLY DIVISION

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(SCI Branch)

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1. Introduction

The application of photo-electric detection to the measurement of nuclear radiation by counting the light pulses emitted from fluorescent materials when irradiated was first reported by Kallman[1], followed by Deutsch[2] and then Marshall and Coltman[3]. Mono-crystals of naphthalene were used for this purpose by Kallmann. This material has the advantage over the inorganic phosphors in common usage in that it is transparent to its own fluorescent radiation. Naphthalene is among the poorer of the fluorescent organic compounds and anthracene was suggested as an alternative in both the papers by Kallmann and Deutsch. Bell[4] actually prepared crystals of purified anthracene and found the pulse height with gamma rays to be about three times that of naphthalene. Taschek and coworkers[5] investigated a number of organic crystal phosphors and their experimental evidence indicated that stilbene has an approximately threefold efficiency relative to anthracene. This, however, is contrary to general experience including our own which has involved extreme purification of stilbene in various ways: a possible explanation is that the sample of anthracene used by these workers behaved anomalously as the result of a trace impurity, since its performance was little better than naphthalene and, as is well-known, anthracene is notoriously difficult to purify. Soon a whole range of organic phosphors had been examined and reported (Hofstadter[6]).

Concurrently with the search for new materials efforts were being directed towards the growth of large single crystals since the counting of both high energy gamma and cosmic rays requires an adequate thickness of a fluorescent material which is transparent to its own radiation. There is considerable literature on the growth from the melt of various types of crystals, metallic, inorganic and organic. It is clear that, in general, single metal crystals can be produced much more readily and at a higher growth rate than the other two classes: for instance Goss and Weintroub[7] quote rates for tin of up to 20 mm/minute, whereas Menzies and Skinner[8] indicate as suitable speeds 2 to 4 mm/hour for the alkali halides and Stockbarger[9] 1 mm/hour for the higher melting fluorites. For satisfactory growth with organic crystals the rates should not exceed 1 to 2 mm/hour (10, 11 and 15). The question of the temperature gradient across the solid/melt interface appears to be less critical than the growth rate for the formation of single crystals.

An important feature in the growth of single crystals and one that has only received cursory attention in the published literature is the initiation of the growth of the melt by a single seed. The problem does not seem so difficult with inorganic crystals which Stockbarger[9] is able to grow successfully by preferentially cooling the tip of the cone of the container holding the melt. But it is very real in the case of organic materials. Here the accepted method is to seed from a long, fine capillary attached to the main container, a device which was

originated by Tammann at the end of the last century. This method almost invariably leads to the formation of several seed crystals at the capillary exit, having a common orientation parallel to the capillary axis, viz. that of greatest growth but otherwise randomly disposed. The resulting crystal mass thus consists of a number of parallel growths and in the case of a material such as stilbene with a high degree of anisotropy of thermal expansion the individual crystals separate on cooling. We have extended and developed this technique of seeding both for production of a single crystal and for controlling the orientation of growth. Preliminary experiments indicate that the method is of general application to organic phosphors and work is proceeding on the growth of large single crystals of anthracene and tolan.

2. Purification of Stilbene

Since high purity of the stilbene is very necessary for the growth of good crystals, methods of purification are detailed.

Trans-stilbene was prepared in 5-Kilogram batches by reduction of benzoin and recrystallisation twice from ethanol and once from trichlorethylene. At this stage it contained small amounts of benzoin as the main impurity. Stilbene of this quality was used as the starting material for the greater part of the crystal growth programme. Stilbene of improved quality became available when a method was developed for markedly reducing the benzoin impurity at the ethanol recrystallisation stage. This method involved the conversion of the benzoin to benzoin-oxime by treating the ethanolic solution of stilbene with a mixture of hydroxylamine hydrochloride and sodium acetate. The oxime remained in solution when the stilbene was crystallized out.

Further purification was effected by either a preliminary growth from the melt or by scrubbing with n-pentane.

(a) From the melt

During a preliminary growth from the melt the stilbene underwent a considerable degree of purification. Clear, colourless, but never single, crystals formed with a dark brownish-yellow liquid remaining on top of the crystalline mass and smelling strongly of benzaldehyde. If the benzoin was removed by conversion to the oxime, as outlined above, then the quantity of brownish-yellow liquid was greatly reduced. Surface contamination of the colourless crystals with this liquid was readily removed by immersion for a few seconds in trichlorethylene. If the stilbene was contaminated by substantial quantities of benzoin, the crystals became riddled with fine "worm-holes" during growth probably due to decomposition of the benzoin to benzaldehyde and volatilisation of the latter.

(b) By scrubbing with n-pentane

Purification by scrubbing with n-pentane was suggested by the work of Leininger[11] who, by refluxing n-pentane through a column containing 150 grams of finely powdered stilbene above a 20-inch column of alumina, obtained the purified stilbene in the boiler. It was found with our samples of stilbene that, after refluxing for a short period, (about $\frac{1}{2}$ hour) a broad yellow band appeared at the top of the alumina column and moved slowly down on continued refluxing of the pentane. This early appearance

of the band indicated that by simply washing the stilbene with n-pentane marked purification could be achieved. This view was confirmed by U.V. absorption measurements, using a Unicam S.P.500 Spectrophotometer, and by melting-point determinations as the following table illustrates:

Sample	Molecular Extinction Coefficient (E_{max}) at 2960 Å	MP, °C
Purified from melt	28,000	122
Pentane scrubbed	28,200	124.5
Ex-boiler of pentane scrubber	27,800	122
Starting material	27,700	120
Pure single crystal	28,000	124.5

(cf. E_{max} = 26,300 at 2950 Å (18); 27,000 at 2940 Å (19); 28,500 at 2940 Å (20))

The effect of removing the benzoin as its oxime before the n-pentane scrubbing was shown by a large reduction in the size of the yellow band on the alumina column.

This purification by pentane scrubbing suggests that the chief impurity is absorbed on the stilbene crystals during their final recrystallisation from trichlorethylene or else crystallises out as discrete crystals under the same conditions as the stilbene. Various other solvents were examined for the recrystallisation of stilbene but none made much difference to its purity.

(c) Distillation

To minimise nucleation of crystals by dust particles during crystal growth and also to effect a final purification the stilbene, purified by either of the above methods, was distilled at about 2 mm. pressure directly into the crystal-growing container using an apparatus of the same design as Leininger's[11]. The apparatus used is shown in Figure 1. About 400 grams of stilbene were placed in the distillation flask which was heated electrically to about 180°. During distillation the stilbene was prevented from solidifying in the tubes and crystal container A by gentle heating with a flame. Since stilbene expands by approximately 20 per cent on melting, it was found advantageous to maintain the stilbene molten in the container A until the container was sealed off. This avoided the danger of over-filling the container and consequent fracture of it on melting the stilbene prior to crystal growth. Stilbene prepared in such a way remained a water-white liquid however long it was maintained at the melting-point provided it was under vacuum.

3. Furnaces

In published work two types of furnace have in general been used for growing organic crystals.

(1) The static furnace in which a temperature gradient is maintained and the melt inside the furnace cooled at a controlled rate (about .1°C/hour) by appropriately reducing the furnace temperature. This type has been used by Alley[12] and Huber and coworkers[13].

(2) The travelling furnace in which the melt is made to traverse a temperature gradient. This is the classic method of Bridgman[14] and is the one that has found most favour. Hendricks and Jefferson[15] used this type of furnace for growing naphthalene crystals whilst more recently Feasel and Smith[16] have grown anthracene as well as naphthalene crystals in this manner. Baret and coworkers[17] have likewise successfully grown a number of organic scintillation compounds.

We have investigated both types of furnace using electric heating and concluded that the static furnace was much more difficult to control owing to fluctuations in the mains; furthermore larger crystals were always obtained and a much greater tendency towards mono-growth was observed with the travelling furnace. For these reasons we latterly confined our attention to the Bridgman method and the present report deals with its application to the growth of stilbene.

Two modifications of the travelling furnace, a screw-type and a hanging-type, were used. In the screw-type the crystal container was held in a brass cup which was slowly lowered from below using a screwed rod. In the hanging-type, the container was suspended in the furnace and lowered from above.

Since the growth of large single crystals of stilbene from the melt is a very slow process it was necessary to build a number of furnaces in order to investigate the various factors influencing the crystal growth.

Of the three types of furnace, the screw-type gave the most promising results and therefore a battery of eleven such furnaces (type A (see below)) was made. Experience gained with these furnaces was used for the design of a more permanent furnace (type B (see below)) giving finer control of temperature, growth and cooling rates.

3.1 Screw-Furnace (A)

The furnaces D (Figure 2) were made from 2-litre aluminium beakers (diameter 5 inches) covered with alundum cement and wound with a spiral of 24 S.W.G. Nichrome Wire, resistance 130 ohms. Further alundum cement covered the wires and an inch thick covering of asbestos wool for thermal insulation was placed between the beakers and an outer housing of stiff papier-mache board. The two furnaces were separated by a baffle plate (G) of asbestos board which had a central hole through which the container could just pass.

The stilbene container (A), made of Pyrex glass 2.5-3 inches diameter and approximately 8 inches long, rested in a brass cup (B) attached to a screwed rod of 1 mm. pitch which passed through the bottom of the furnace into a threaded sprocket (C). The brass cup was tapered at its base and the Pyrex container was supported and insulated by asbestos wool except at the tip which made thermal contact with the brass shaft to induce nucleation of the stilbene by local cooling. The sprocket (C), mounted in ball races, was chain-driven at about 1 rev/hour so that the container moved down at about 1 inch/day. To prevent the screw from turning, two keyways were cut in it and two keys (I) were fixed on to the bottom of the sprocket mounting.

The temperature of the furnaces was measured by copper-constantan thermocouples (F); one an inch above and the other an inch below the baffle plate (G). For stilbene a temperature gradient of 20°C/inch was maintained between the two furnaces. The temperature was controlled by a bimetallic thermostat (E) which operated a vacuum-switch relay. Since the furnaces only required about 100 watts to maintain them at 130°C, a Variac was inserted into the circuit to reduce the mains current when the relay was closed. The two furnaces were connected in parallel with a variable resistance in series with the lower furnace so that the temperature gradient could be readily controlled.

3.2 Screw-Furnace (B)

This furnace was designed to possess the following features; good temperature control, accurate and readily controllable speeds of growth and slow-cooling of the crystal. In addition the furnace could be evacuated when growing crystals which cannot be sealed in vacuo in a glass container.

The furnace, shown in Figures 3 and 4, was made from a length of chromium-plated steel pipe $8\frac{1}{4}$ inches internal diameter divided by a steel baffle plate. Each half was wound with nichrome wire embedded in alundum cement and thermally insulated with a $1\frac{1}{2}$ inch thick layer of refractory insulating powder. These circuits and thus the temperature of the two halves of the furnace were controlled by Variacs and bimetallic thermostats (one shown). Temperatures were recorded on mercury dial thermometers the bulbs of which were situated 1 inch above and below the baffle plate.

Constancy of temperature is of great importance for the growth of single crystals of good optical and mechanical properties. Small quick fluctuations in the air temperature of the furnace are of less importance owing to the relatively high thermal capacity of the sample than slow steady changes, especially decreases in temperature. A decrease in temperature is, in effect, a speeding up of the rate of growth of the crystal as the freezing level of the furnace is thereby raised. It is for this reason also, that the temperature gradient in the region of the baffle should be large, since given changes of temperature will then influence less the position of the freezing level.

The furnace was operated with air temperatures of 140° ± 2° C. in the upper half and 100° ± 2°C. in the lower half. Under these conditions temperature fluctuations at the freezing level even at the circumference of the growing crystals were found by thermocouple measurement, to be not greater than ± 0.3°C. (See Figure 7).

Two small windows of heat-resistant glass were let into the side of the furnace diametrically opposite each other and just below the baffle plate. A small electric bulb was set in a heat-resistant plug behind one of the windows so that the state of the crystal could be observed during growth. The other window was normally covered by a similar plug. There was also a removable window of heat-resistant glass, 5 inch diameter, in the top of the furnace.

The stilbene container was held in a brass cup mounted on a shaft which terminated in a screw of 3 mm. pitch. The screw entered a bevel gear connecting via a second bevel gear and a train of gears to a small induction motor. To maintain vacuum tightness in the furnace the screw and bevel gears were enclosed, (see Figure 8) the shaft of the second

bevel gear passing through a vacuum tight stuffing box to the train of gears. Several gear trains were made up in interchangeable units so that various speeds of descent of the container could be obtained. The available speeds were 5, 2.5, 1.6 and 1 mms. an hour together with their reciprocals 1/5, 1/2.5, and 1/1.6 mms. an hour. The reciprocals were obtained by reversing the gear units on the motor and bevel gear spindles. The 1:1.6 gear (A) can be seen in place on the right of Figure 8. A further gear unit permitted the slow and steady cooling down of the furnace. This unit linked the motor and the shaft of a Variac placed between the mains supply and the furnace. Two days were required for the Variac to be turned down from 270 volts to 0 volts. A further gear unit allowed for the manual winding up and down of the container.

The motor was automatically controlled by a series of microswitches. The first switch stopped the motor when the screw reached the end of its travel. A second switch started the motor again when the gear unit for controlling the Variac was placed in position. A third switch cut out the motor when the Variac reached 0 volts.

3.3 Hanging-Type Furnace

The furnace (Figure 5) was constructed of glass so that the growth of the crystal could be observed throughout the experiment and thus greater control exercised than with the operation of screw-type (A) furnace.

The external and internal walls of the furnace (D) and (C) were Pyrex pipes 12 inch and 6 inch diameter respectively and of wall thickness $\frac{3}{4}$ inch. Two coils of wire, separated by a baffle (G), were wound on a Sindanyo framework (F) between the two pipes. An asbestos baffle (G) was hung in the middle of the inner pipe. The temperature of the furnace was measured on a thermometer which could be moved up and down for determination of the temperature gradient. It was impossible to maintain as sharp a gradient as in the screw-type furnaces but a gradient of 7°C/inch could be obtained. The temperature was controlled by the thermostat (E), the circuit of the furnaces being identical with that of the screw-furnace.

The container (A) was slowly lowered down the furnace by a Meccano crane device operated by an electric motor. The motor was geared down so that a movement of 1 inch - $\frac{1}{2}$ inch a day was obtained.

In attempting to nucleate the stilbene by a single seed emerging from a capillary attached to the lower end of the container, the capillary was made about 3 inches long since, under the operating conditions of the furnace, the stilbene supercooled quite considerably. With a short capillary the rapid crystallisation which set in when seeding occurred led to a polycrystalline mass in the bottom of the container.

This supercooling of the stilbene was considered to be due, firstly, to the capillary tube being surrounded by air instead of a material of high thermal conductivity such as the brass cup in the screw-type furnace and, secondly, to a shallow temperature gradient at G. Figure 5 indicates that at the commencement of lowering of the container, G is not functioning as a true baffle (compare with the brass cup in Figure 2 when it first reaches the baffle G). Hence the position of the freezing level is not steady. Moreover the massive brass cup with attached rod tend to preserve a better thermal balance across the furnace during early growth and consequently to maintain the freezing level steady.

By suitably designing the furnace to overcome these defects it should be possible to reduce the length of the capillary, thus reducing the time taken to grow a crystal, and also to improve the seeding of the melt.

Using a straight capillary a single crystal was not produced. Working on the same principles of container design (see later) as with the screw-type furnace a single crystal was grown. However, whilst it was possible to produce a single crystal, good control of the furnace conditions was more difficult to achieve than with the screw-type furnace, hence the hanging-type furnace was not selected for the main crystal growth programme.

3.4 Stationary Furnace

This furnace (Figure 6) was made from an inverted aluminium beaker (B) coated with alundum cement. The beaker was wound with four separate spirals of Nichrome wire with the coils getting progressively closer towards the top. The coils were wired in parallel with a variable resistance in series with each coil. A gradient of about 40°C could be maintained from top to bottom of the furnace by suitable adjustment of the rheostats.

A heat shield (H) was placed over the sample inside the furnace. This shield consisted of a wide glass tube, rounded off at one end, which had been lined with silver foil and coated outside with asbestos paper. This shield reduced fluctuations in the sample temperature due to variations in the furnace temperature.

The whole furnace was heated until the sample had completely melted. The temperature was then adjusted so that the bottom was just on the melting point and the top about 40°C above it. The temperature of the whole furnace was then slowly reduced to just below the melting point. This took about 4 days. When the sample had crystallised it could then be cooled rather more rapidly to room temperature. This furnace was only tested with anthracene and gave a clear crystalline mass consisting of numbers of discrete crystals up to a maximum size of about 1 cm. × 1 cm. × .2 cm. although only a plain conical container was used. However, without a constant voltage transformer, temperature control of the furnace during cooling was difficult and the method was abandoned in favour of the other two methods.

4. Initiation and Orientation of Growth of a Single Crystal

Various designs of container have been studied for seeding the melt with a single crystal. Stockbarger[21], for growing single crystals of LiF, used a container of simple design (a) (Figure 9). Its application to the growth of stilbene crystals proved unsatisfactory in the screw-type furnace, a dozen or more crystals being produced in the container. Bridgman[14] describes a container of the type (b) (Figure 9) for the growth of single metal crystals. Leininger[11] used this design for stilbene crystals but he obtained only multiple crystal growth. Our experience with this type of container in both the screw and hanging-type furnaces confirms this multiple growth. However, it is an improvement over type (a), the number of crystals grown being reduced to about six.

Another device aimed at producing nucleation at one point only in the tip of the cone of the container, was the use of a short length of tungsten wire sealed into the glass (c) (Figure 9). The tungsten wire was set in Wood's metal in the brass cup, thus allowing greater cooling at the tip. No improvement over type (b) was obtained by this procedure.

Again, it was observed that, whilst the tip of the container of type (a) contained a polycrystalline mass, after about $\frac{1}{2}$ inch of growth only about 12 major crystals would be growing up the tube. In order to isolate a single seed the container was fitted with a baffle consisting of a funnel-shaped piece of glass with a hole 1 mm. in diameter in the centre, see (d) (Figure 9). Originally the baffle was sealed to the wall of the container but cracking invariably occurred at the junction, probably due to the volume changes of the stilbene. Therefore a container fitted with a free but close-fitting baffle was used. This method whilst reducing the number of crystals to 2 or 3 did not produce a single crystal.

Since neither type (b) nor (d) produced single crystals it was apparent that two or more baffles would be required. Accordingly, a container with two baffles with their holes not in the same vertical line (e) (Figure 9) was tried and this arrangement was successful in producing a single crystal. An arrangement on similar lines (h) (Figure 9) when used in the hanging-furnace was not so successful probably due to the lower degree of control of the operating conditions of the furnace.

It should be noted that the seed emerging from the capillary in container (b) is subject to wider temperature fluctuations than that passing through the lower baffle in container (e) since in the latter the seed is surrounded by material of a much greater thermal capacity.

A second successful method for initiating and growing a single crystal was by using a baffle carrying an open zig-zag shaped capillary (f) (Figure 9). Even if two or three crystals entered the capillary tube the corners successfully eliminated all but one. It was found advantageous not to extend the zig-zag capillary right to the bottom of the container where a polycrystalline mass occurs since this increased the number of crystals entering the tube.

The use of a zig-zag capillary attached to the container (i) (Figure 9) proved successful for initiating a single crystal in the hanging-type furnace.

To ensure nucleation of a single crystal by a capillary-tube it is essential to have a zig-zag shaped tube. Experiments with a container possessing a baffle carrying a straight capillary or even one of design (g) (Figure 9) were not entirely successful since there was no reduction in the number of crystals leaving the capillary over those entering.

Whilst using zig-zag capillaries it was observed that if the limb of the capillary adjacent to the tip of the conical baffle was nearly horizontal then the resultant crystal readily cracked, either during cooling or by handling, across the diameter of the container. However, if this same section of the capillary was almost vertical, it was found that cleavage was vertical also and that the crystals were much more resistant to thermal shock.

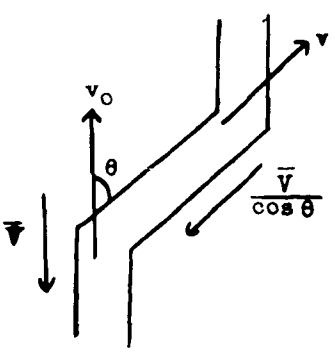
The difference in growth orientation was confirmed by cutting small cubes from the crystals and determining the three linear thermal expansions interferometrically. Stilbene crystals are monoclinic and have a marked thermal anisotropy. The expansion at right angles to the cleavage plane (001) is approximately double that along any direction in the (001) plane. (A detailed account of the thermal anisotropy of stilbene crystals is being reported separately). Thus the orientation of growth of the crystals can be readily determined.

A further difficulty is that nucleation may occur on the baffle plate and give rise to a secondary crystal which may occasionally equal in size the crystal coming through the capillary. This secondary growth seldom occurs with horizontally grown crystals but is more common in the case of crystals growing with the cleavage plane vertical. When this happens the individual crystals separate on cooling and can be parted by cleaving into large single components.

5. Theory of Crystal Growth

The dependence of growth orientation on the shape of the capillary attached to the baffle may be explained by considering the rates of growth of a stilbene crystal along its axes. The greatest rate of growth is in the (001) plane parallel to the diad axis. Hence in a cylindrical container of type (a) (Figure 9) the crystals which emerge from the polycrystalline mass at the tip of the cone will be orientated with their diad axis approximately vertical since the crystals with this preferred orientation will outstrip and thus exclude those with different orientations. The crystals will therefore enter a capillary with their diad axis and thus the (001) plane vertically orientated. This orientation will be maintained through a zig-zag capillary provided that the movement of the freezing level along the capillary does not exceed the growth velocity of the crystal operating in each section of the zig-zag. It will be clear that as each limb of the capillary departs more and more from the vertical the rate of movement of the freezing level along it increases and may ultimately exceed the rate of crystal growth. Figure 10 illustrates this point.

Figure 10



If $\bar{V}$ = rate of movement of the freezing level,

v_o = maximum rate of crystal growth, i.e. along the diad axis,

v = maximum velocity of growth along the inclined capillary limb with the diad axis vertical,

and θ = inclination of capillary limb to the vertical,

then if $v > \frac{\bar{V}}{\cos\theta}$ there will be no change of orientation of crystal growth. If $v < \frac{\bar{V}}{\cos\theta} < v_o$ then conditions are favourable for a change of orientation but if $\frac{\bar{V}}{\cos\theta} > v_o$ multicrystalline growth in the inclined limb will occur.

An extension of the above analysis will show that in order to avoid a reversal of the change in orientation by going from the inclined to the vertical part of the tube, $\overline{V}$ must be less than the vertical rate of growth in the new direction of orientation. On the basis of these theoretical considerations it should be possible to grow single crystals of any desired orientation by a suitable choice of $\overline{V}$, the speed of descent of the container, and of θ, the inclination of the final capillary limb. Whilst we have not yet been able to explore fully these possibilities we have succeeded in growing crystals having orientations of the diad axis up to 25° from the vertical.

The actual mechanism of the change of orientation is not clear. Examination of a capillary by polarised light shows discontinuities in the crystal growth at or near the bends of the capillary with no obvious indication of formation of small crystals. One explanation of the change in orientation could be the formation of a polycrystalline layer on going from the vertical to the inclined limb as $\overline{V}/\cos\theta$ exceeds v, followed by selection of one or perhaps more crystals orientated such that the speed of growth along the axis of the inclined limb of the capillary exceeds $\overline{V}/\cos\theta$. A second possible explanation is that as $\overline{V}/\cos\theta$ increases with respect to v during the bend in the capillary, a gradual distortion of the crystal lattice takes place until a position is reached when the lattice will grow along the new direction at a rate just exceeding $\overline{V}/\cos\theta$. A third possibility is that a sudden change may occur in the lattice front due to reorientation of a molecular layer which may be easier than fresh nucleation if the speed of the former process is more rapid than that of the latter.

According to Gross and Möller[22], who studied crystal growth of phenylsalicylate (orthorhombic) from a supercooled melt in stationary curved tubes, crystal seeds tend to be produced in the angle between the advancing front of a single crystal and the wall of the capillary tube. A seed formed in this manner may be orientated such that, as growth proceeds in the curved tube, it becomes the main crystal. This process may then be repeated throughout the bend of a curved tube resulting in a series of single crystals divided by sharp boundaries. The direction of maximum growth of the crystal hence follows the axis of the tube.

This change of orientation in a curved tube is determined, according to Gross and Möller, by such factors as the degree of supercooling of the melt (which, in our studies, is equivalent to the speed of descent of the crystal container), by the radius of curvature of the bend and by the diameter of the capillary tube. Whilst the crystal-growing systems of Gross and Möller and of the authors are rather different, thus preventing direct analogy, the theory of Gross and Möller presents a further possibility of explaining the change of orientation at the bends in a zig-zag capillary tube.

The earlier work of Palibin and Froiman[23] on obtaining a predetermined orientation of a zinc crystal from the melt is in some respects comparable to this work. They used a tube ending in a capillary which was sealed into a thin-walled sphere. The crystals grew radially in the sphere and one particular orientation was selected by the capillary, the orientation depending on the inclination of the capillary to the main tube. In our case however, a vertically orientated crystal enters the capillary and change of orientation is effected in the capillary itself. Moreover with organic crystals their method would not yield single crystals. (cf. container type (g) (Figure 9)).

6. Rate of Descent of Crystal Container

The influence of the rate of movement of the freezing level on the direction of orientation of the crystal when seeded from a zig-zag shaped capillary tube is discussed above. For crystals grown with the (001) plane parallel to the axis of the cylindrical container, it was possible to lower the container at about 1 inch per day but stronger and clearer crystals were obtained at lower speeds of the order $\frac{1}{2}$ inch - $\frac{3}{4}$ inch per day. Crystals orientated with the (001) plane horizontal, grown at these speeds, were not as strong and frequently contained small laminar striations giving the appearance of white flecks. It may be possible to improve the qualities of crystals with this orientation by reducing the speed of growth even further.

7. Crystal Quality

It has been observed above that crystals grown with different orientations possess different qualities. Figure 11 (a) (taken approximately normal to the (001) plane) illustrates a crystal grown with the cleavage plane horizontal. Examination of this crystal under polarised light (Figure 11 (b)) showed it to be composed of layers of a large number of small crystals, all with their (001) planes horizontal but each separate crystal at a slightly different orientation from its neighbours. The variation in orientation was about 25°. As can be seen the crystal is completely transparent (Figure 11 (a)) the discontinuities were only observable by reflected light from a polished face. Since the thermal expansions in all directions in the (001) plane are not markedly different, the mosaic crystal after being grown does not separate into the component pieces on cooling. This mosaic character accounts for the lack of stability to thermal shock of the crystal; the instability may in part be due to reduced mechanical strength. However, the scintillation properties are not affected. In this connection it may be added that it is possible to build up a composite phosphor of stilbene crystals of complex shape using butyl methacrylate cement without much loss of efficiency.

Figure 11 (c) and (d) show photographs (again taken normal to the (001) plane) of a crystal grown with the (001) plane vertical, (d) being taken using polarised light. The singleness of the crystal is apparent.

Due to the ease with which newly grown crystals crack during cooling and subsequent shaping and polishing it was not possible to prepare a flawless crystal conforming to the shape of the container but many full sized crystals were grown. Indeed the main obstacles to the production of a complete single crystal from the container are firstly the after-growth cracking and secondly the secondary growth in the case of vertically grown crystals. It is to the elimination of these defects that our attention is now directed. Figure 12 shows a group of some typical pieces of stilbene grown by the techniques described in this report.

8. Scintillation Efficiency

The scintillation response of these pure stilbene crystals to gamma radiation (Co_{60} source) has been tested. The average pulse height was found to be approximately 60 per cent that of the best sample of anthracene available.

For comparison of the efficiencies of phosphors, anthracene, because of its greater light response to radiation, is generally taken as the standard. In view of the extreme difficulty in obtaining pure anthracene and also of the tendency of purified samples to deteriorate on storage, we consider anthracene to be unsuitable as a standard. Since stilbene crystals of high chemical purity and stability can be prepared by the methods detailed in this report, it is our view that stilbene should in future be taken as the primary standard for comparing the scintillation efficiencies of phosphors.

9. Shaping the Crystals

The crystals can readily be shaped by scraping with a sharp knife, but extreme care is necessary to avoid cracking by localized heating. To this end chamois leather gloves should be worn during all finishing operations. After scraping, the surfaces may be polished by use of emery powder graduating down to jewellers' rouge on chamois leather. For a final finish, chamois leather damped with metal polish (a solution of oleic acid in white spirit) has proved the most effective. The use of volatile solvents for polishing should be avoided as the surface of the crystal will crack as the solvent evaporates. If parallel faces are required a microtome can be used but great care has to be taken to avoid chipping the edges of the crystals. A beautifully smooth and optically clear surface can be produced in this manner along the (001) plane, but faces normal to this assume a semi-matt appearance on cutting and are easily fractured at their edges during the process. The semi-matt surfaces may be polished however to the same degree of optical clarity as the (001) faces.

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23. Palibin and Froiman. Z.Krist A85, 322, 1933.

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MEA.

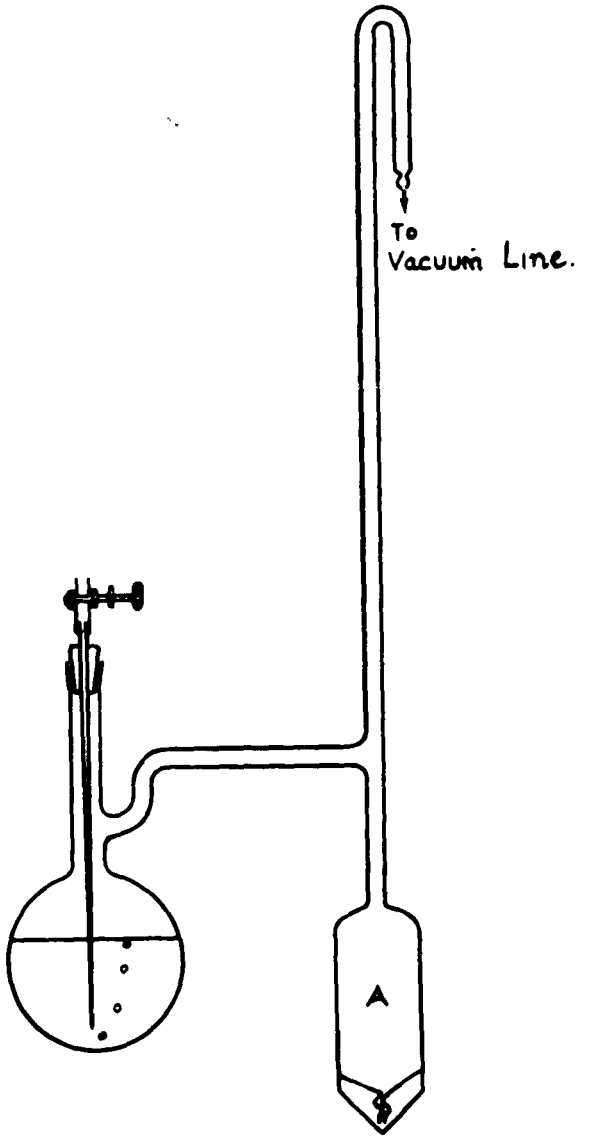


FIG. 1.

DISTILLATION APPARATUS.

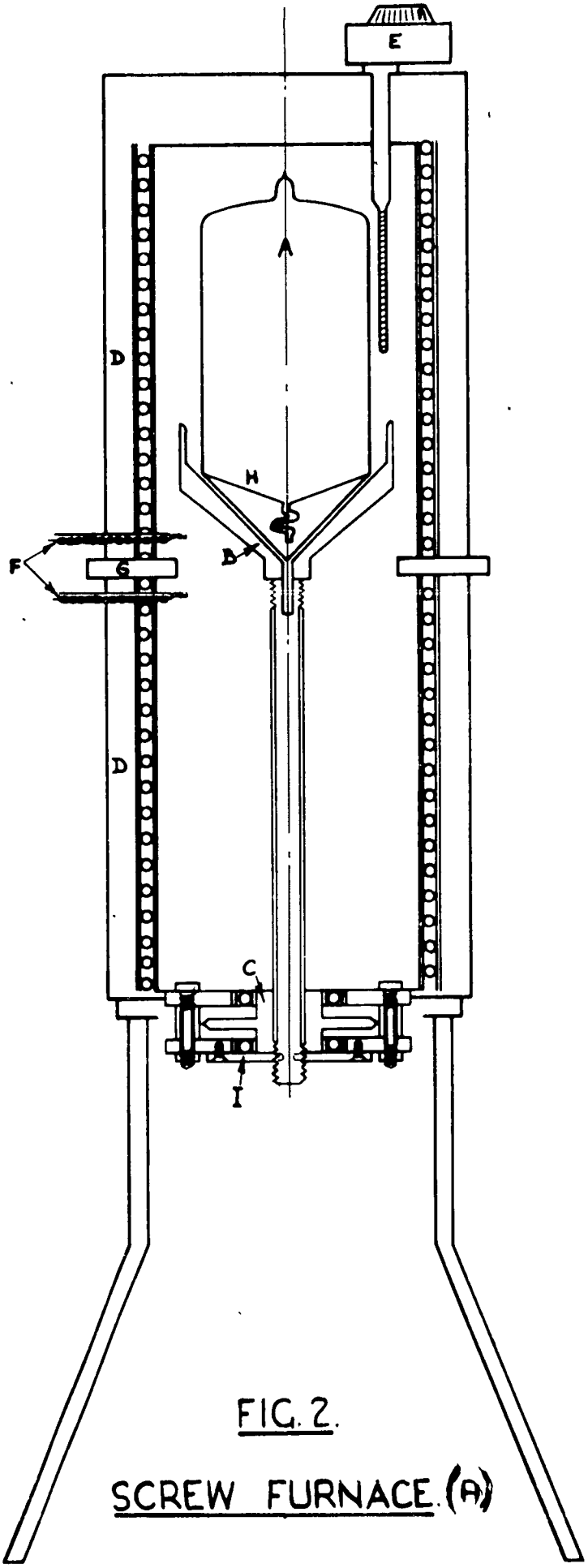


FIG. 2.

SCREW FURNACE (A)

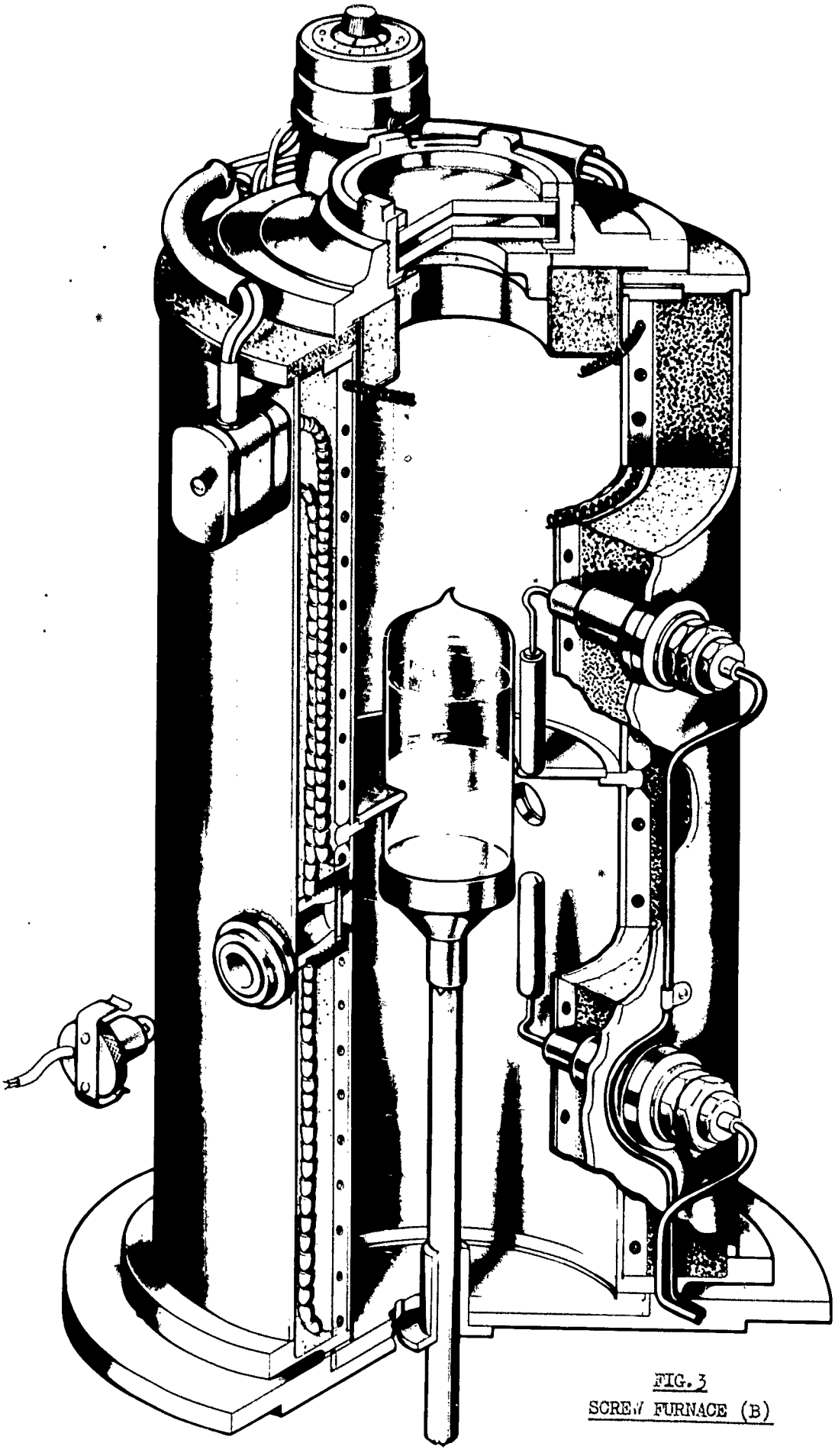


FIG. 3
SCREW FURNACE (B)

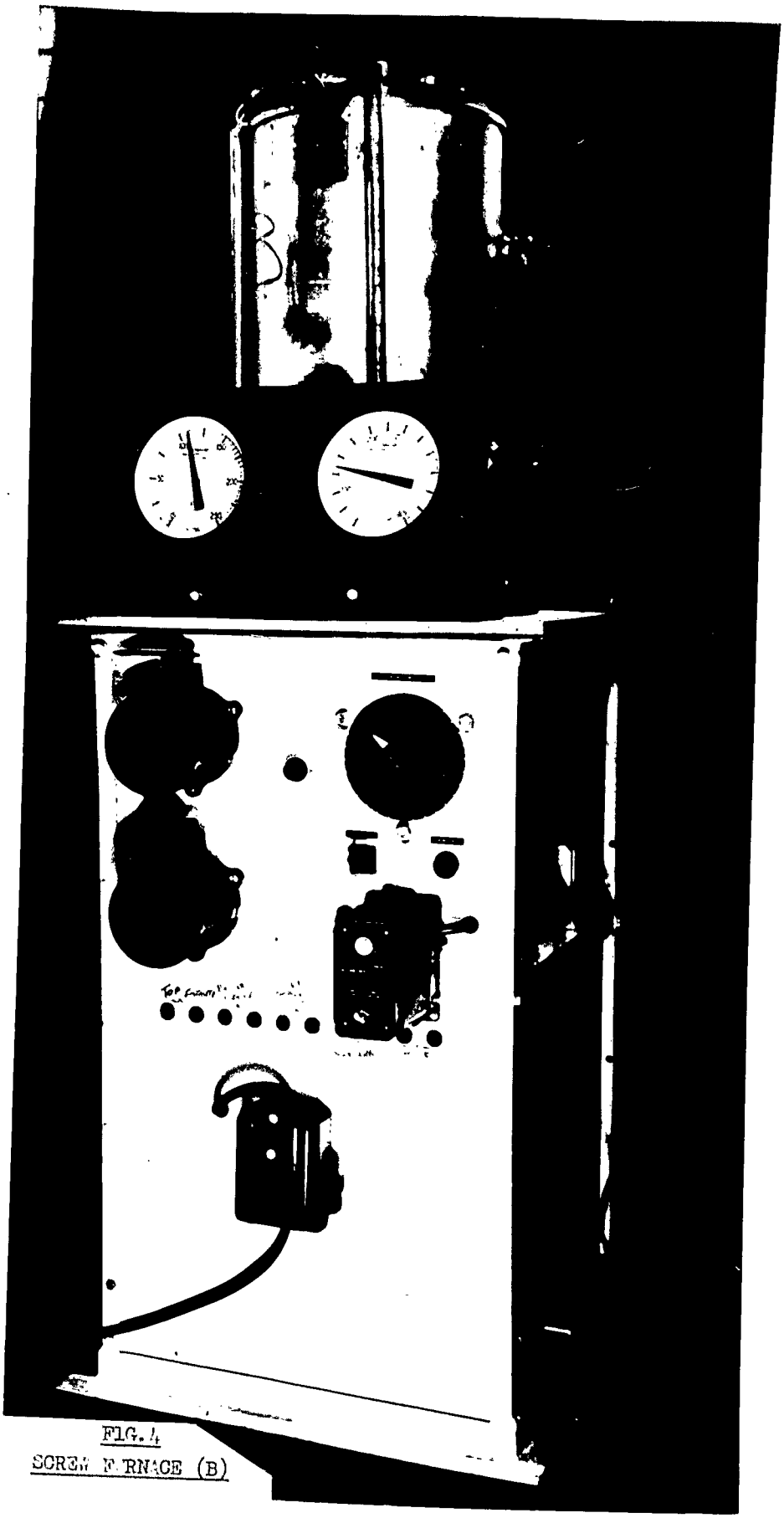


FIG. 4

SCREW FURNACE (B)

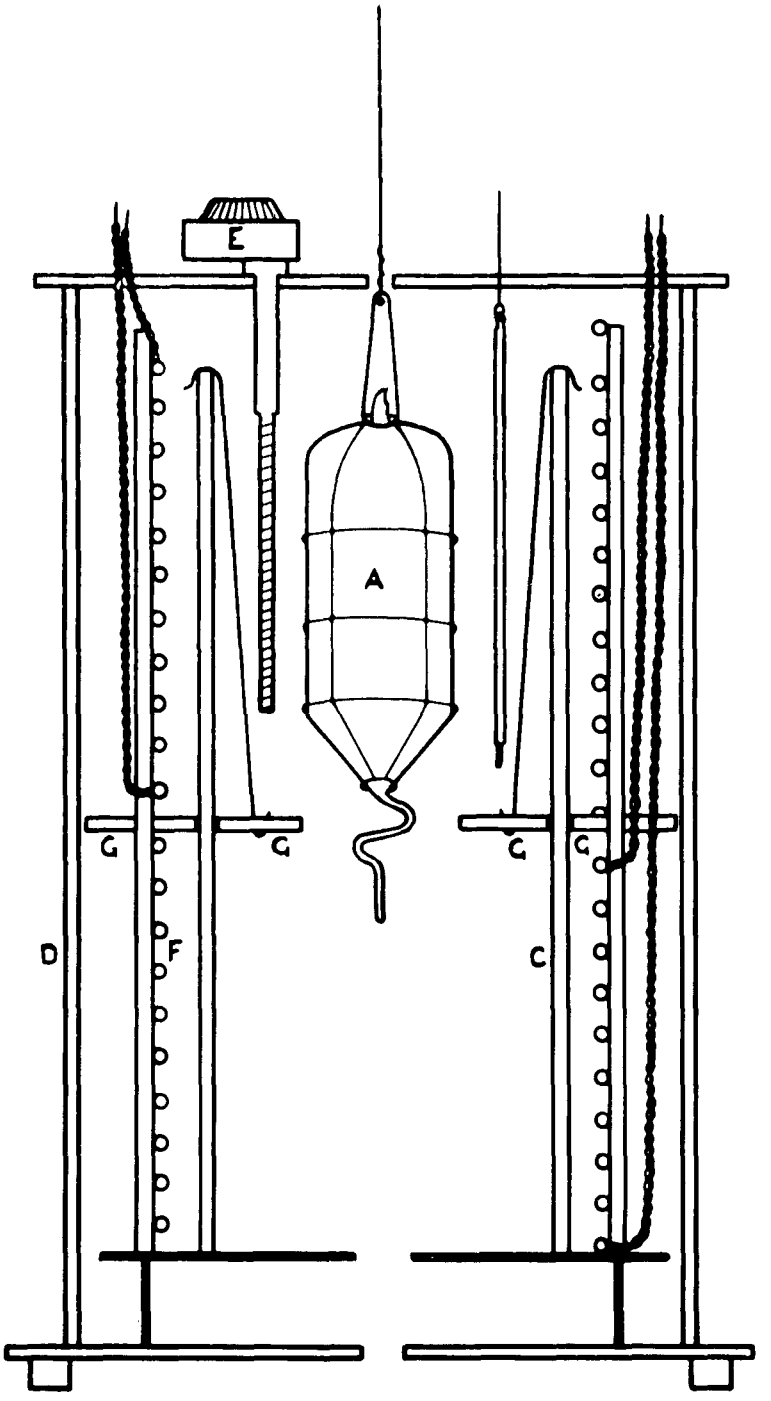


FIG. 5.

HANGING FURNACE.

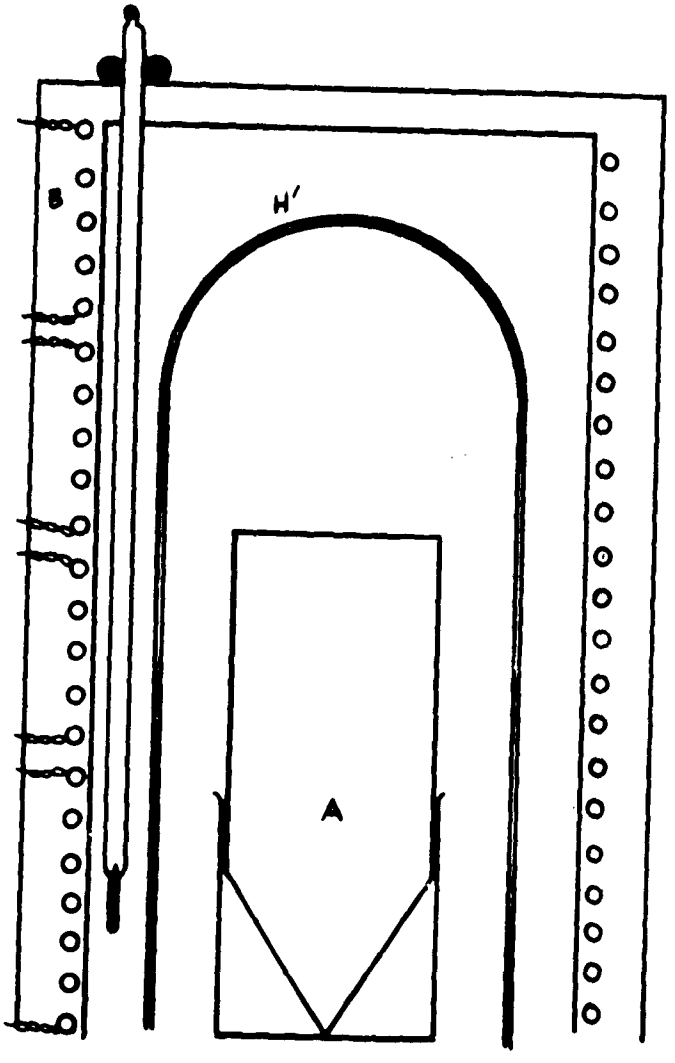
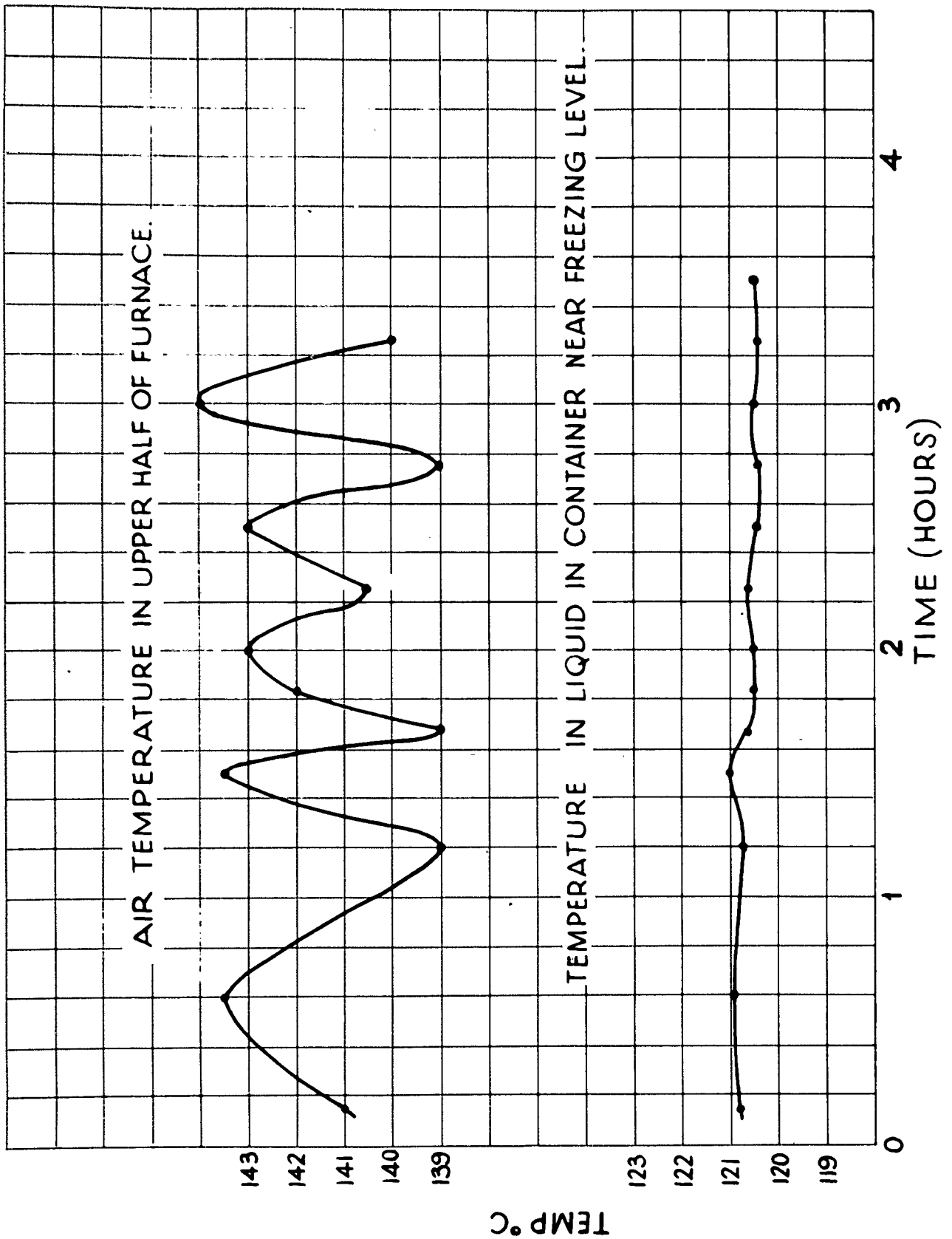


FIG. 6.

STATIONARY FURNACE.

FIG. 7. TEMPERATURE CONTROL IN SCREW FURNACE (B)



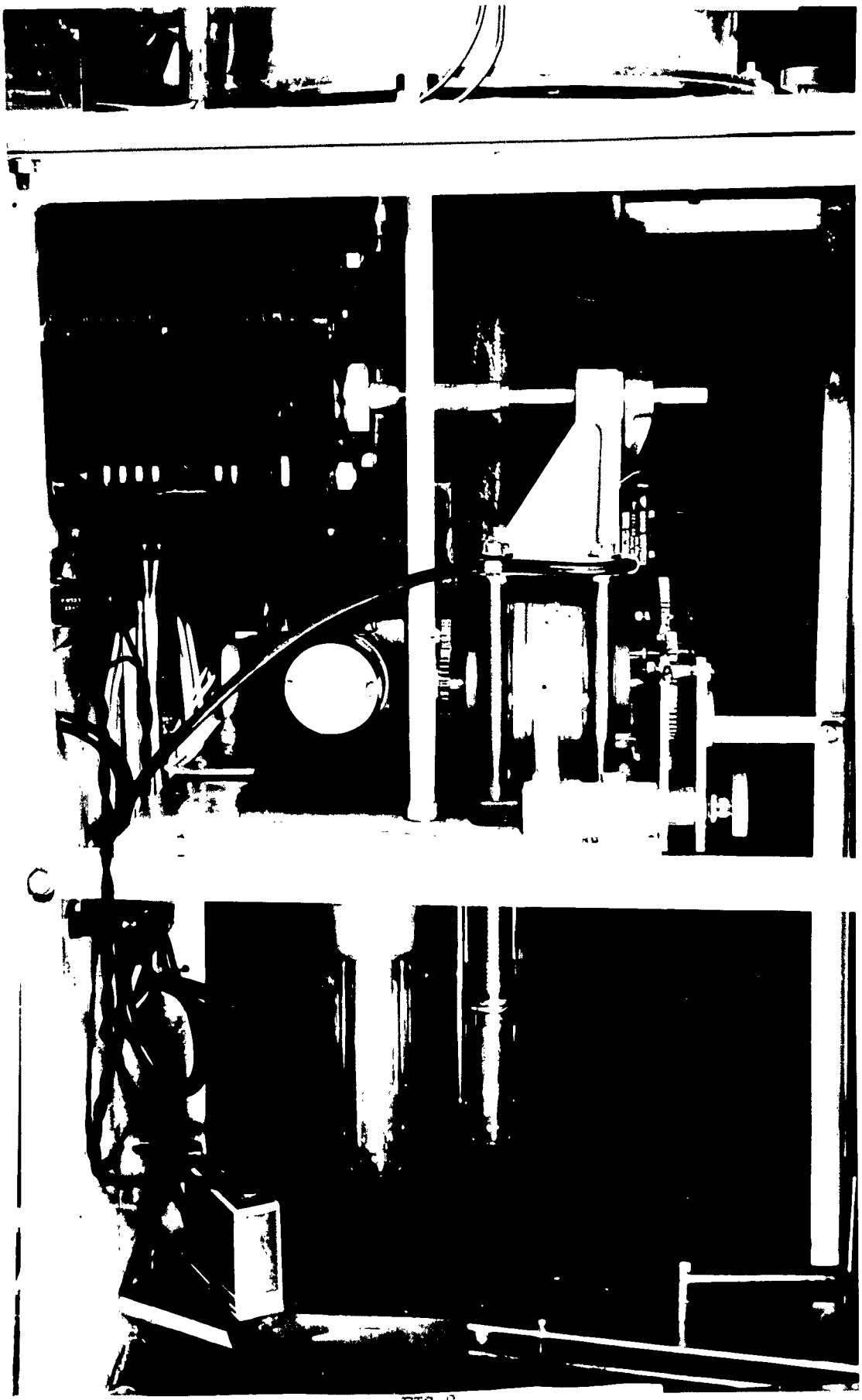
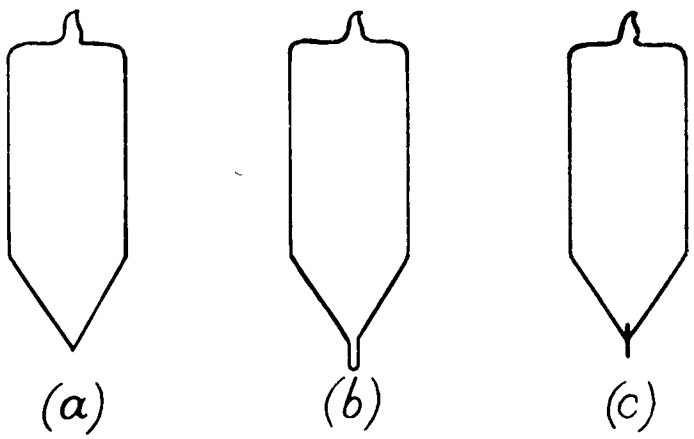
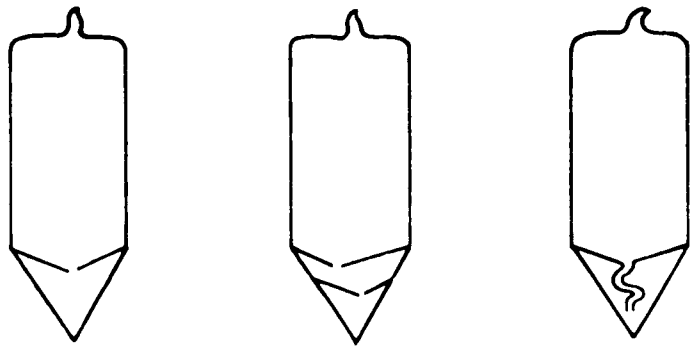


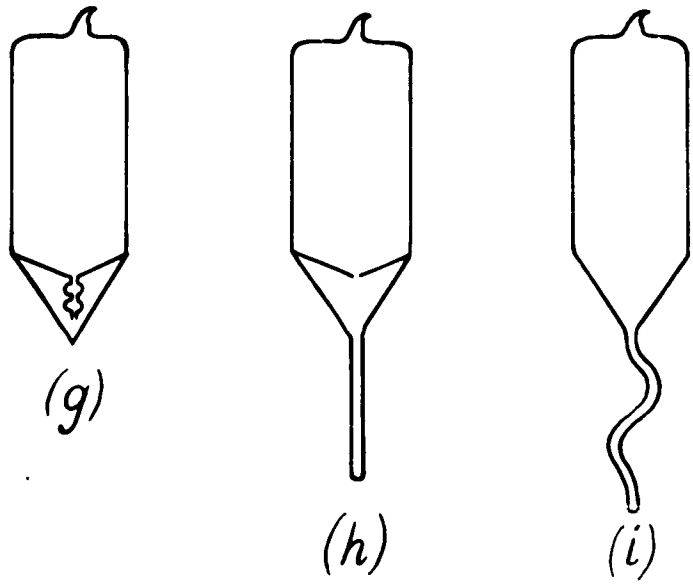
FIG. C

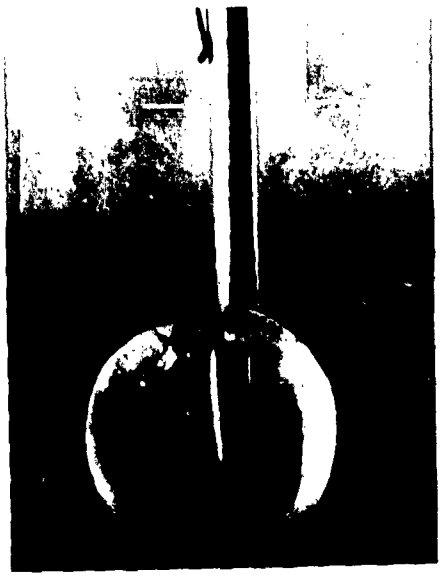
GEARING MECHANISM FOR JOB [illegible]

STILBENE CONTAINERS FIG.9.


(a) (b) (c)

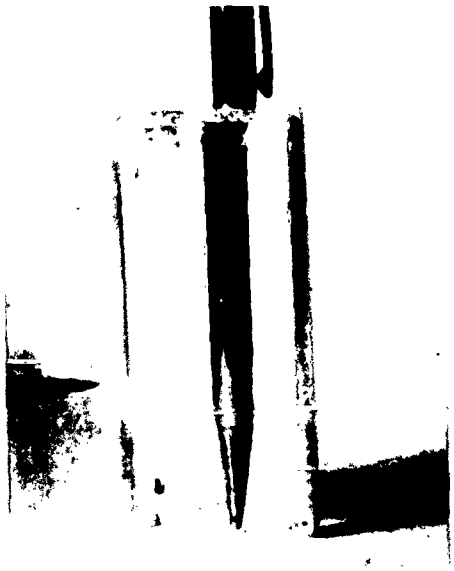

(d) (e) (f)


(g) (h) (i)



(a)
Ordinary Light
Perpendicular to (001)

(b)
Crossed Nicols
Perpendicular to (001)



(c)
Ordinary Light
Perpendicular to (001)

(d)
Crossed Nicols
Perpendicular to (001)

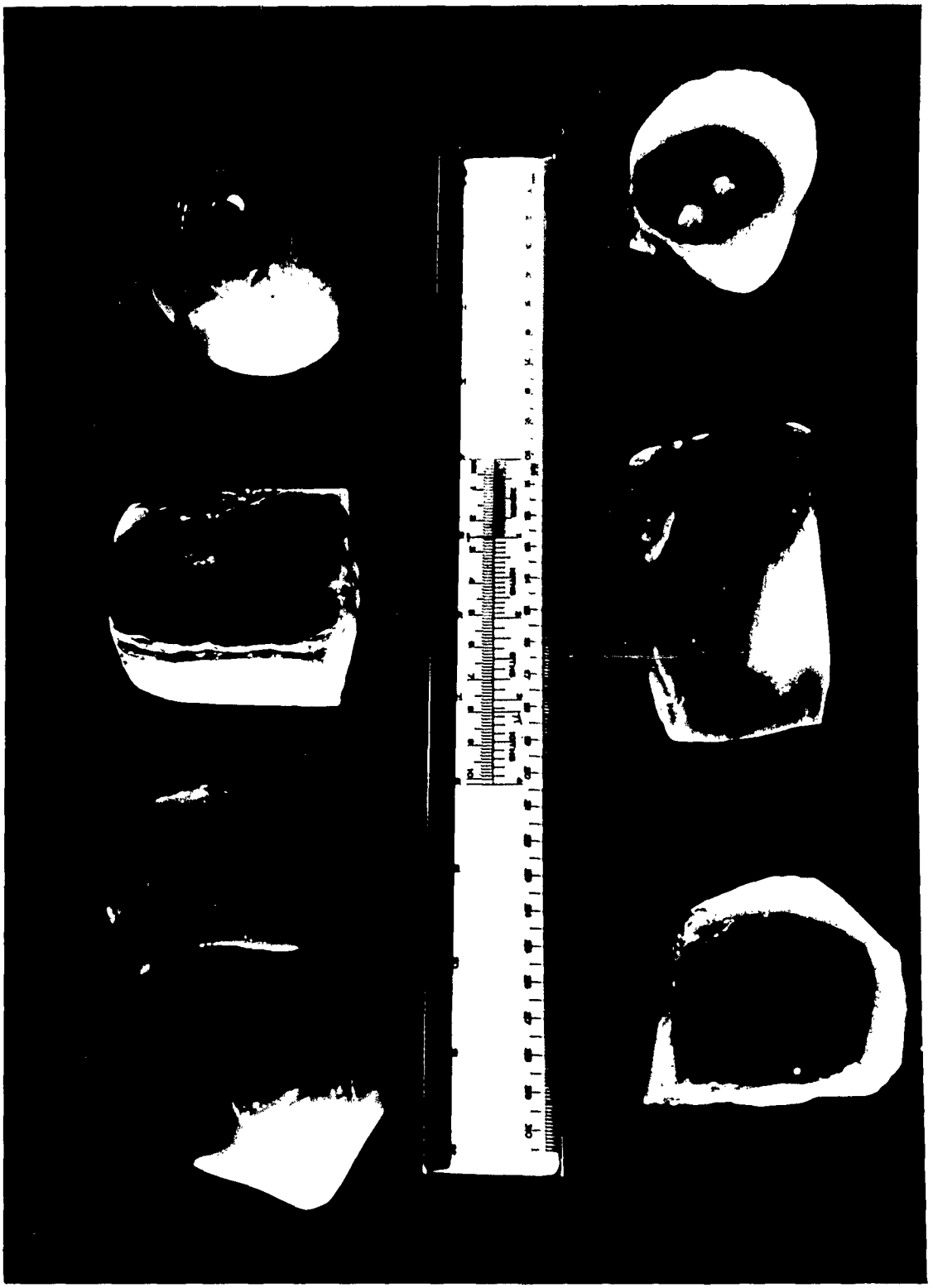


FIG. 12
TYPICAL STILBENE CRYSTALS

[dstl]

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Fax 01980-613970

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