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RESEARCH AND INVESTIGATION ON PHOSPHOR SCREENS
FOR HIGH RESOLUTION DISPLAY DEVICES

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-1097

MARCH 1963

Electronic Technology Laboratory
Aeronautical System Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

Project No. 4156, Task No. 415605

Prepared under Contract No. AF 33(616)8509

by CBS Laboratories, A Division of
Columbia Broadcasting System, Inc.
Stamford, Connecticut

Authors: R. Rutherford, Jr.
and K. Spiegel

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FOREWORD

This report covering research performed from June 1961 to July 1962 was prepared by CBS Laboratories, Division of Columbia Broadcasting System, Inc., Stamford, Connecticut, on Air Force contract AF33(616)8509, under Task No. 41653-7 of Project No. 1670-4156, entitled Research and Investigation on Phosphor Screens For High Resolution Display Devices. The work was administered by the Electronic Technology Laboratory (ASRNE), Aeronautical Systems Division. Mr. William Nelson acted as project engineer for the laboratory.

The work reported herein is the result of several persons efforts and ideas, the chief contributors have been R. Heck (metal film electrodes), K. Speigel (phosphor deposition), and J. Schechtel (partical analysis).

The work was performed in the Electron Tube Department under the direction of Dr. B. Linden with R. Rutherford, Jr. as project engineer.

The report is the final report under the above contract and it concludes the work on that contract.

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Abstract

The final report on a development program to improve phosphor screens for high resolution display devices describes an investigation and experimental study of a method of cataphoretically depositing phosphors. An analytical study to predict optimum screen structure, a method of cataphoretically depositing phosphor on glass using a removable metal film, and an evaluation of the performance of the screens produced including the modulation transfer characteristic are described.

PUBLICATION REVIEW

Publication of this technical documentary report does not constitute Air Force Approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

WILLIAM H. NELSON
Chief, Sensor and Display Section
Electronic Technology Laboratory

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Introduction

This report¹ describes a one-year investigation conducted for the purpose of improving high resolution phosphor screens. The scope of the program was limited to the development of material processing techniques using available materials. The objective of the program in terms of screen performance was the capability of transferring information at a rate equivalent to a bandwidth of 15 megacycles per second with a signal-to-noise ratio of 30 db and with a peak radiant intensity sufficient to expose high resolution film through a high quality optical system of f:4.

Preliminary Analysis of the Problem

A review of various approaches to the problem suggested that the greatest improvement in phosphor screens could be realized in a program of limited duration by working with the electrophoretic process. Electrophoretic screens are known to have a fine, dense grain structure as compared with settled screens. Although the brightness of some electrophoretic screens is less than that of settled screens, it is considerably higher than that of evaporated or vapor-reacted screens.

¹Revised Manuscript released by the authors March 1963 for publication as an ASD Technical Documentary Report.

Because of the above advantages, electrophoretic screens are used at present in some high resolution display devices. In present electrophoretic screens, however, the advantages are counteracted by some major disadvantages. According to the standard process, the phosphor is deposited on glass that has previously been coated with a transparent, conductive layer of tin oxide (hereafter referred to as ECG, electrically conductive glass). The function of the ECG is to serve as an electrode which attracts the phosphor particles during electrophoresis and produces the screen. In practice it is found that ECG coatings do not have a uniform conductivity throughout and do not cover all points on the glass surface. Consequently, areas of higher conductivity attract a heavier layer of phosphor than areas of lower conductivity. The small points on the glass surface that are not coated with ECG attract no phosphor and produce voids in the screen. Furthermore, in the completed screen under operating conditions in a tube, there is a loss of light output amounting to 10 percent or more in transmission through the ECG coating.

The analysis of the problem indicated that significant improvement could be made in electrophoretic screens if an improved conductive coating could be produced on glass.

The ideal conductive coating would be a smooth, uniform layer with light transmission of 100 percent. A literature search was conducted to seek such a coating.

Transparent Metal Conductive Coatings

No coating was found in the literature that met both requirements of the ideal coating. Previous experience indicated that smooth coatings of uniform conductivity could best be obtained by evaporating metals on glass surfaces. The most transparent of the highly conductive metal coatings, according to the literature¹, was a thin film of gold on bismuth oxide. Light transmission up to 75 percent has been reported for these coatings with a resistivity of 10 ohms per square.

Experiments were conducted to evaluate gold-bismuth oxide as a transparent conductive coating. Gold-bismuth oxide coatings were prepared on glass plates and electrophoretic P16 screens were deposited on the gold films.

Visual inspection of the screens indicated that gold-bismuth oxide could meet the first requirement of the ideal

¹Holland, L., Vacuum Deposition of Thin Films, John Wiley and Sons (New York, 1960).

conductive coating, but not the second. The uniformity of these screens was better than that produced by electrophoresis on ECG glass. The light transmission of 75 percent was considered inadequate.

From these tests it was concluded that the continued use of metal films was justified for improved uniformity but that the transmission of light must be increased. (Note: During this series of tests efforts were also made to deposit P15 and P24 phosphors on gold-bismuth oxide coatings. Using the electrophoretic process effective for P16, there was little or no deposit of P15 or P24).

Convertible Metal Conductive Coatings

Experience prior to this investigation had demonstrated that opaque zinc coatings on glass could be made transparent by oxidizing the zinc to zinc oxide. It was decided to utilize this phenomenon in this investigation.

Zinc metal was evaporated to form an opaque, conductive film on glass plates. Using the zinc film as an electrode, electrophoretic P16 screens were deposited on the plates.

The screens were heated in an oven at 415°C for thirty minutes in order to convert the zinc film to the more transparent zinc oxide. (As a control test, zinc coated glass with no phosphor screen was also heated at 415°C).

The results again demonstrated the advantage of using a metal film rather than ECG coating on the glass. The phosphor deposit was uniform over-all. However, the zinc oxide film on the glass had a cloudy appearance and was observed to be not completely transparent. (In this test series, similar efforts to convert tin and aluminum into transparent oxides were unsuccessful).

Intermediate Analysis of the Problem

At this point in the investigation attempts to produce an ideal conductive coating were only partly successful. The use of metal coatings instead of ECG improved the uniformity of the electrophoretic Pl6 screens. However, in all cases, the light transmission through the metal or metal oxide coatings was far short of the 100 percent considered ideal. Considering all known possibilities, it was concluded that the only way to achieve 100 percent light transmission would be to remove the metal coating after the screen was deposited on it.

Soluble Metal Conductive Coatings

One method of removing a metal coating from glass is by dissolving the metal. Laboratory bench experiments demonstrated that tin coatings on glass plates could be dissolved completely by immersion in dilute nitric acid.

Experimental glass plates were coated with an evaporated layer of tin, and electrophoretic Pl6 screens were deposited on the plates. One of the plates was placed in a Petri dish with the screen facing upward and was wetted carefully with 1.0 normal nitric acid. After ten minutes all the tin was dissolved. The screen was then rinsed with distilled water. The wet screen was intact on the glass plate and the conductive coating was successfully removed. After drying, however, the screen did not adhere to the glass.

Evaporable Metal Conductive Coatings

A second method was proposed whereby the metal coatings would be removed from the glass plates by evaporation in a vacuum. The metal chosen to test this method was zinc, since zinc can be evaporated in a vacuum at relatively low temperatures (under 400°C).

An experimental glass plate was coated with an evaporated film of zinc and an electrophoretic P16 screen was deposited on the plate. The screen was placed in a bell jar and heated to 400°C at a pressure of 2.5×10^{-5} mm Hg. After fifteen minutes all the zinc was evaporated off the glass. The result of this experiment was an electrophoretic P16 screen bonded directly to glass with no conductive coating remaining between the phosphor and the glass. Obviously, the light transmission between the phosphor and the glass would now be 100 percent.

The new screen was inspected by visual observation. There was no deterioration at all in the screen quality as a result of the evaporation process. The phosphor deposit was uniform over-all due to the uniform conductivity of evaporated zinc coatings. The strength and adherence were tested by wetting the screen as a step in the lacquering process. The wetting caused no voids or lifting of the screen from the glass. The screen was mounted in a cathode ray tube for evaluation under CRT operating conditions. There was no shift in the spectrum of the P16 phosphor, indicating that there was no contamination of the phosphor by the zinc previously present. There was

also no evidence of zinc or zinc oxide remaining on the screen or on the glass.

This screen is believed to be the first electrophoretic screen ever formed directly on glass with no conductive coating present between the phosphor and the glass. The removable zinc coating met both requirements of the ideal coating described in the section entitled "Preliminary Analysis of the Problem". The new process was believed to be a significant new screening method which could result in a significant advance in the state-of-the-art of high resolution phosphor screens. The remainder of the investigation was devoted mainly to the further development of this process.

Improved Metal Conductive Coatings

The experiments leading up to the new process were performed on small, rectangular glass plates approximately 1" x 2" or 2" x 3". After the first experiments demonstrating the feasibility of the process, the emphasis was changed to larger glass plates up to five inches in diameter.

The first zinc coatings evaporated on five-inch glass plates were observed to have as many as 150 pinholes in the zinc. In addition, the zinc coatings had a matt

appearance, characteristic of porous or partially oxidized coatings, rather than a "mirror" finish characteristic of dense unoxidized, metal coatings.

Efforts were made to improve the zinc coatings by introducing the following variables into the evaporation procedure:

- a. Depositing the zinc on a heated substrate.
- b. Nucleating the glass substrate with tin prior to zinc deposition.
- c. Evaporating a second coating of zinc over the first coating.
- d. Cleaning the glass substrate with NH_4HF solution, distilled water, and acetone.
- e. Evaporating the zinc from a covered tantalum boat with an orifice at the center of the cover.
- f. Nucleating the glass substrate with silver prior to the zinc deposition.

These experiments are summarized in Table I. Procedures (e) and (f) above were the most successful and are discussed in paragraphs immediately following.

The elimination of pinholes was successfully accomplished by Procedure (c), the evaporation of a second coating of zinc over the first coating. One of the double coatings had a single void; a second double coating had none. Electrophoretic screens deposited on the double coatings were acceptable with respect to grain structure and uniformity. The screens were fine, dense, and uniform and had no area defects or blemishes. Photographs of a Pl6 screen made by the procedure may be found in Figures 6 and 9 in the section entitled "Evaluation and Photography of Three Screen Types" of the technical discussion.

Although the double zinc coating produced uniform screens that were free of pinholes, the process was considered to be not completely satisfactory for two reasons:

- (1) As a general rule, it is better practice to produce a perfect coating in a single evaporation than to apply a corrective coating to an imperfect first one.
- (2) The coatings had a matt appearance (rather than a shiny, mirror-type appearance) and left a very slight residue, of zinc oxide, visible only in reflected light, between the screen and the glass after the final evaporation.

TABLE I
PREPARATION OF EVAPORATED ZINC COATINGS ON 5-INCH GLASS PLATES

Date	Variation in Experimental Procedure	Results	Comments
2-28-62	Initial experimental conditions, ¹ except: zinc deposited on heated substrate.	Zinc coating opaque and irregular.	Unsatisfactory procedure.
3-1-62	Initial experimental conditions. No variations.	Coating slightly opaque.	Unsatisfactory procedure.
3-7-62	Glass nucleated with tin.	Slight opaque. Approx. 100 pinholes.	Possibly insufficient tin.
3-7-62	Second zinc coating evaporated over first coating.	Slight opaque. One pin-hole, edge. ¹	Effective procedure.
4-17-62	Glass cleaned with 3% NH_4HF , distilled water, acetone.	Opaque. One void.	Procedure nearly effective.
4-18-62	Glass cleaned with NH_4HF , distilled water, acetone. Zinc evaporated from covered tantalum boat with orifice at center of cover. Two coatings of zinc.	Slightly opaque. No voids.	Effective procedure.
5-23-62	Same as preceding procedure, except: glass nucleated with silver, one zinc coating.	Uniform, shiny mirror finish. 8-10 tiny pinholes.	Effective procedure.

¹Initial experimental procedure: Glass cleaned with methanol, wiped with lens paper. Zinc evaporated from open tantalum boat.

For these reasons, efforts were continued to develop a uniform, shiny zinc coating that could be produced with one evaporation of zinc.

A zinc coating that met these requirements was produced according to Procedure (f). The five-inch glass plate was first nucleated by evaporating an invisible coating (very small quantity) of silver on the glass surface. The zinc was then deposited in a single evaporation on the nucleated surface. An electrophoretic Pl6 screen was deposited on the zinc-coated glass and the zinc was subsequently removed by heating in a vacuum.

The zinc coating produced by this method was uniform over-all and had a shiny finish. Pinholes were very nearly eliminated (8-10 pinholes were detected, but were too small to cause voids in the screen). In the completed screen, however, there was one significant defect that could have been caused by the nucleation. This was the presence of pockets, 2-3 mils in diameter, between the screen and the glass substrate. A photograph of these pockets may be seen in Figure 1. This photograph should be compared with Figure 6 (in the section entitled "Evaluation and Photography of Three Screen Types" of this report), a photograph of an electrophoretic Pl6 screen prepared on a non-nucleated glass surface.

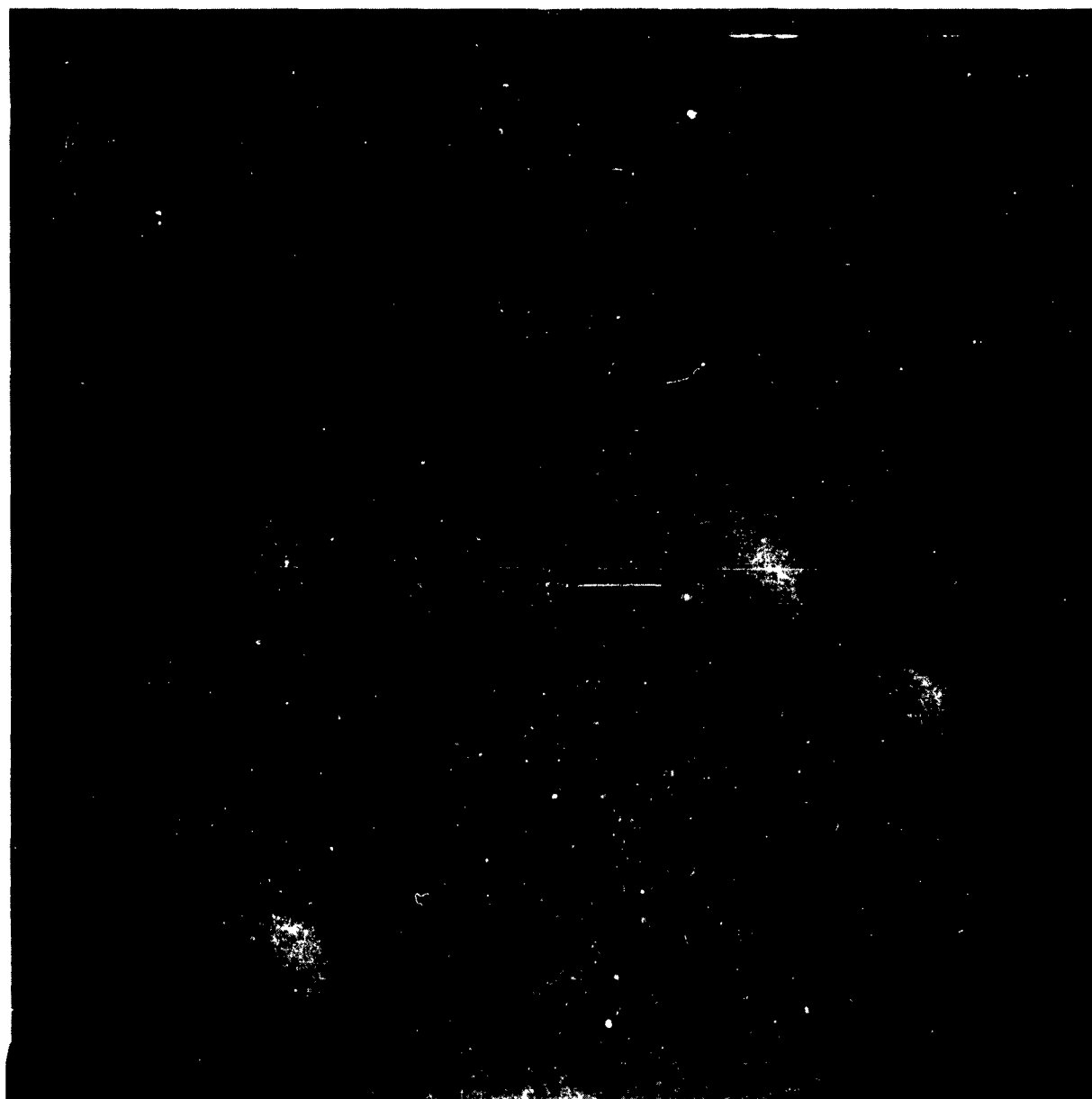


Figure 1

Grain Structure of an Electrophoretic Pl6 Screen on Clear Glass
Magnification - 250X

Process: Removable zinc electrode process

Note: Glass was nucleated with silver prior to the zinc deposition

Surface Photographed: Plane of contact between phosphor and glass
substrate

In spite of the undesirable side-effect, the nucleation procedure is considered to be a promising method. By experimenting with varying quantities of silver or other nucleating materials, it is believed possible to produce uniform, shiny zinc coatings that would not cause pockets in the screen. Time did not permit the further development of the nucleation procedure.

Improved Screen Surface Structure

The first five-inch screens produced, with the use of removable zinc electrodes, were evaluated (a) by inspection of the screen surface under a 100 power microscope, and (b) by scanning the screen in a flying spot scanner and observing the screen image on a monitor tube. Both tests revealed a rough surface structure on the side of the screen facing the electron gun. Under the microscope, it could be seen that the roughness was caused by small ridges in the screen surface; without a microscope, the ridges were too small to be seen. The surface structure of the electrophoretic screen is shown in Figure 2. Comparison can be made with the surface of a fine, settled screen by turning to Figure 3.

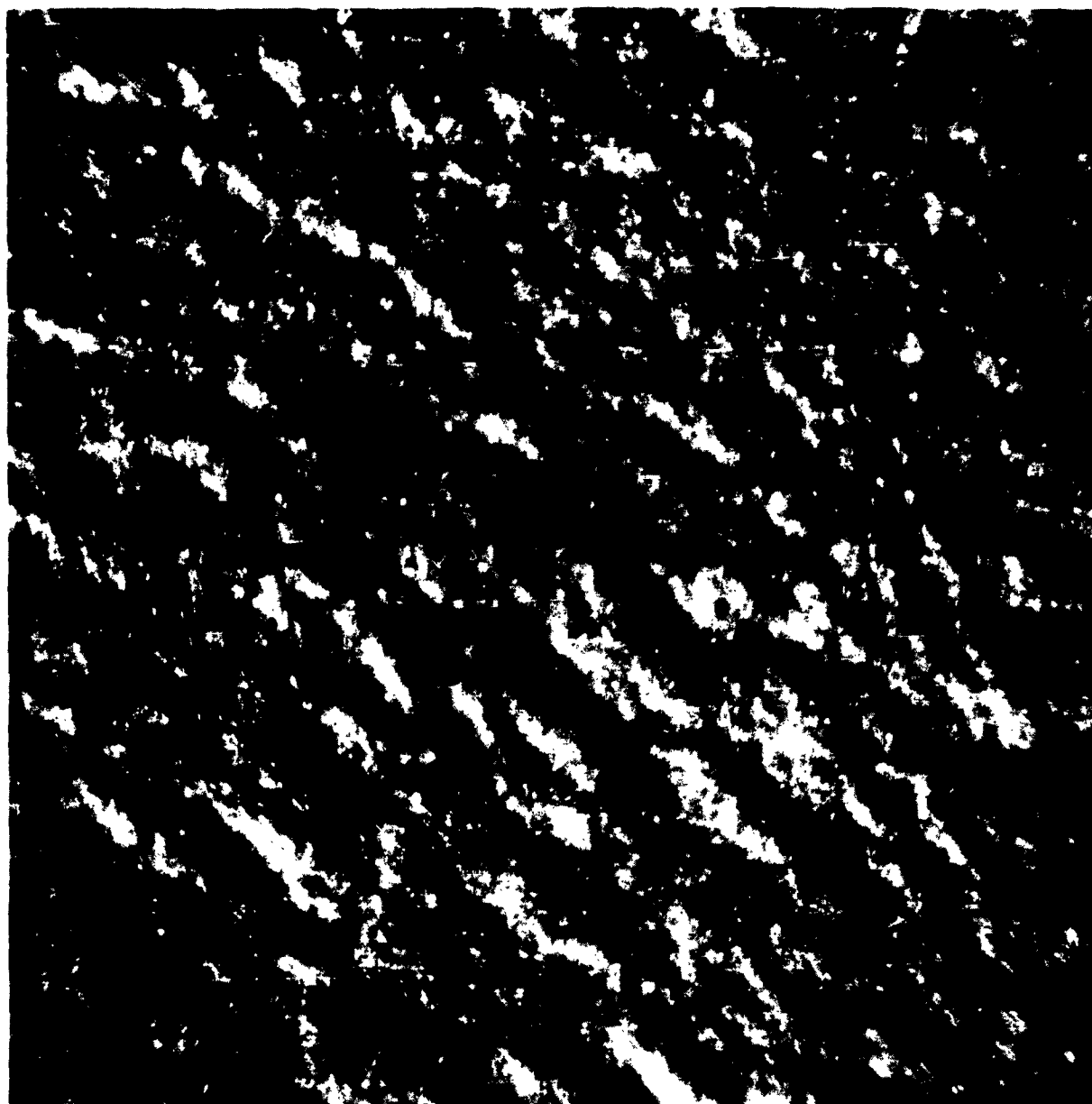


Figure 2

Surface Structure of an Electrophoretic P16 Screen on Clear Glass

Magnification - 250X

Process: Removable zinc electrode process

Note: Glass was nucleated with silver prior to the zinc deposition

Surface Photographed: Outer screen surface, side facing the electron gun

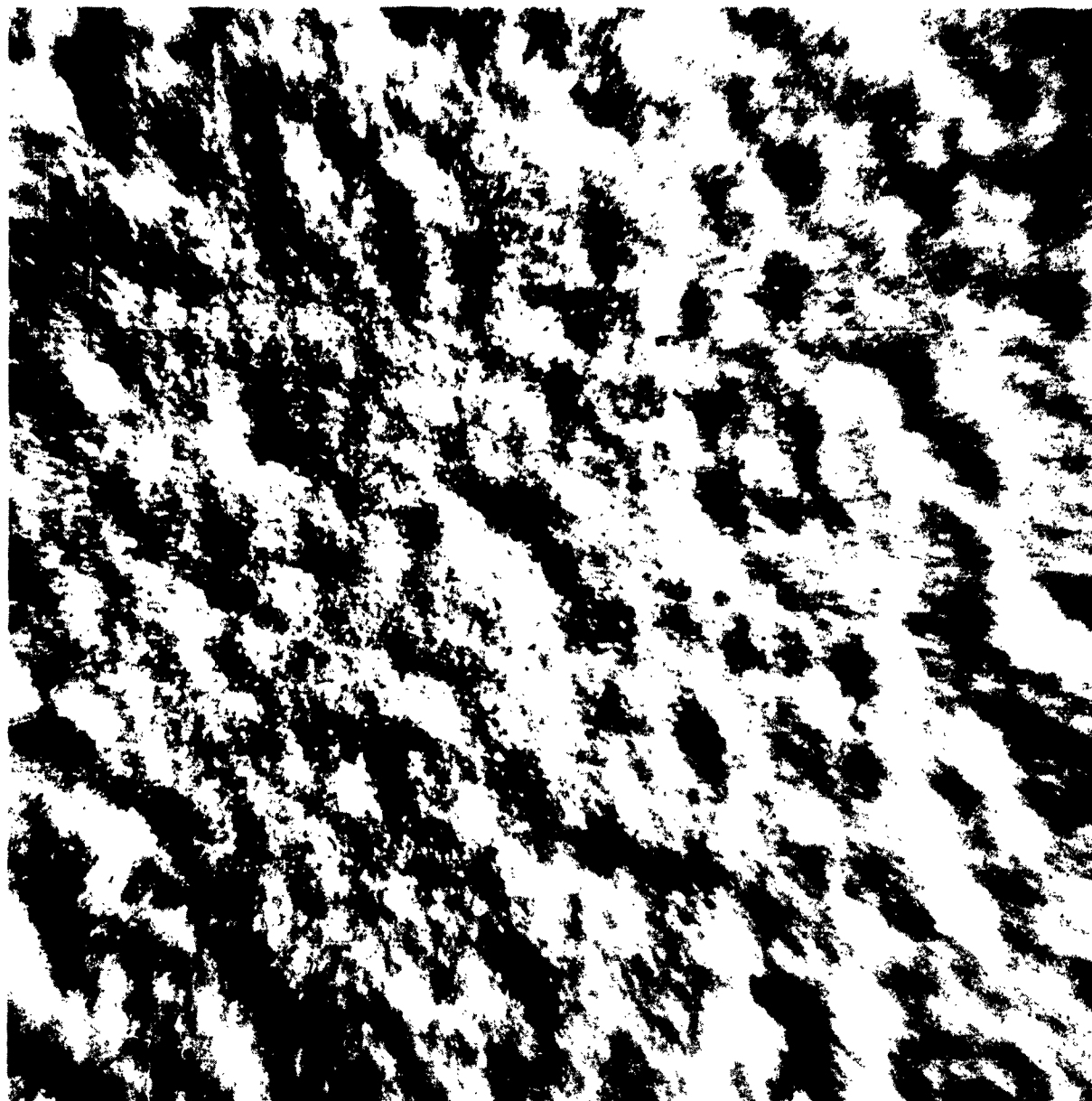


Figure 3

Surface Structure of a Fine, Settled P16 Screen on Glass

Magnification - 250X

Processing Details: Fine phosphors selected by elutriation.

Particle size range, 0-5 microns.

Surface Photographed: Outer screen surface, side facing the electron gun.

Attempts were made to produce a smooth, flat screen surface by reducing the electrophoretic coating time from 45 minutes to 10 minutes. In one such test on a stainless steel plate, it was observed that the screen surface was smooth and flat in a small area near the clip lead. The test proved that flat screen surfaces can be achieved by the electrophoretic process and indicates that the flatness is a function of voltage and time variations. Further work would be required to achieve the same flatness of surface over an entire five-inch screen.

Preparation of Five-Inch Screen Specimens

The contract calls for the delivery of five-inch screen specimens representative of the state-of-the-art achieved through the use of different deposition techniques. Three screens were prepared and delivered to ASD. The screens are identified and described as follows:

No. 114-1 - Settled Pl6 screen prepared from fine phosphors (0-5 microns in diameter) selected by elutriation.

No. 114-2 - Electrophoretic Pl6 screen deposited on ECG coated glass.

No. 114-3 - Electrophoretic Pl6 screen prepared-
directly on nucleated glass with the
use of removable zinc electrodes.

The screening processes of No. 114-1 and No. 114-2 were selected for two of the specimens because these are the methods most commonly used in high resolution devices available at present from commercial sources. The ECG coated glass for Screen No. 114-2 was purchased from Pittsburgh Plate Glass Company and was the most uniform ECG coating that could be produced at the time of purchase. The third specimen screen, No. 114-3, demonstrates the new process developed under this contract.

Evaluation and Photography of Three Screen Types

The three processes used for preparing the specimens were evaluated by inspecting typical screens under a microscope. Photographs were taken to compare the grain structure and over-all uniformity of the three types. The results of these evaluations are described in the paragraphs immediately following.

a. Grain Structure - Each screen to be inspected was supported on a microscope stage with the phosphor on the under side of the glass. In this position, it was possible to observe and photograph the grain structure of the screen at a magnification of 100 times or more by focusing the microscope on the screen at the plane of contact with the glass.

Figure 4 shows the grain structure of a settled screen as photographed through a microscope. The screen was observed to have a rough, granular appearance caused by the loose-packed structure characteristic of settled screens and by the tendency of the largest phosphor particles to settle out first on the glass substrate.

Figure 5 shows the grain structure of an electrophoretic screen on ECG coated glass. This screen was observed to have a fine, dense structure. However, there was a scattering of small dark spots (voids) less than 0.1 mil in diameter, caused by points of low conductivity in the ECG coating. In the area photographed, a single void, 1-1/2 mils in diameter, can be seen at a point where the ECG coating did not cover the glass surface.

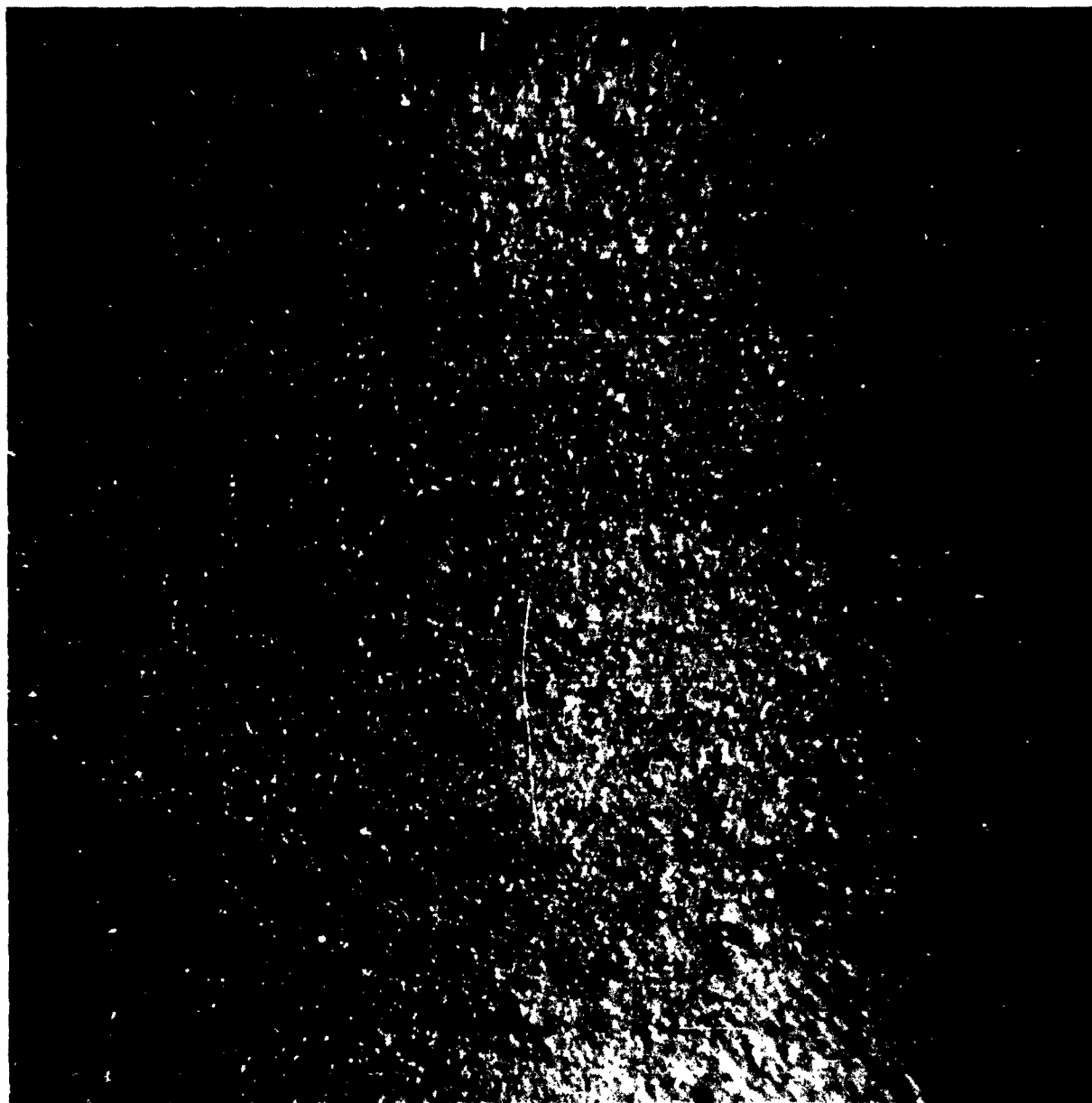


Figure 4

Grain Structure of a Fine, Settled P16 Screen on Glass

Magnification - 250X

Processing Details: Fine phosphors selected by elutriation.

Particle size range, 0-5 microns.

Surface Photographed: Plane of contact between phosphor and glass substrate



Figure 5

Grain Structure of an Electrophoretic P16 Screen on ECG-coated Glass

Magnification - 250X

Surface Photographed: Plane of contact between phosphor and glass substrate

Figure 6 shows the grain structure of an electrophoretic screen deposited on clear glass with the use of a removable zinc coating. This screen was the best of the three and was observed to have a fine, dense structure. It was completely free of observable defects or irregularities. Due to the fine grain structure and the good uniformity, it was found to be quite difficult to focus the camera on the phosphor screen. It was finally necessary to make a scratch on the phosphor screen in order to focus the camera on a definite image. The improvement in grain structure, shown in Figure 6, is one of the accomplishments of this development program. It should be noted that the glass substrate of the screen in Figure 6 was not nucleated prior to the zinc deposition.

b. Over-all Uniformity - The screens were inspected visually to detect irregularities in the phosphor deposit and spot defects of any kind. Photographs of the three screens were taken and enlarged to four times the actual size of the screens.

Figure 7 is a photograph of a settled screen. The screen was observed to have good over-all uniformity. Any selected area of the screen looks approximately the same as any other area. There are no irregular shapes or patterns in the screen.

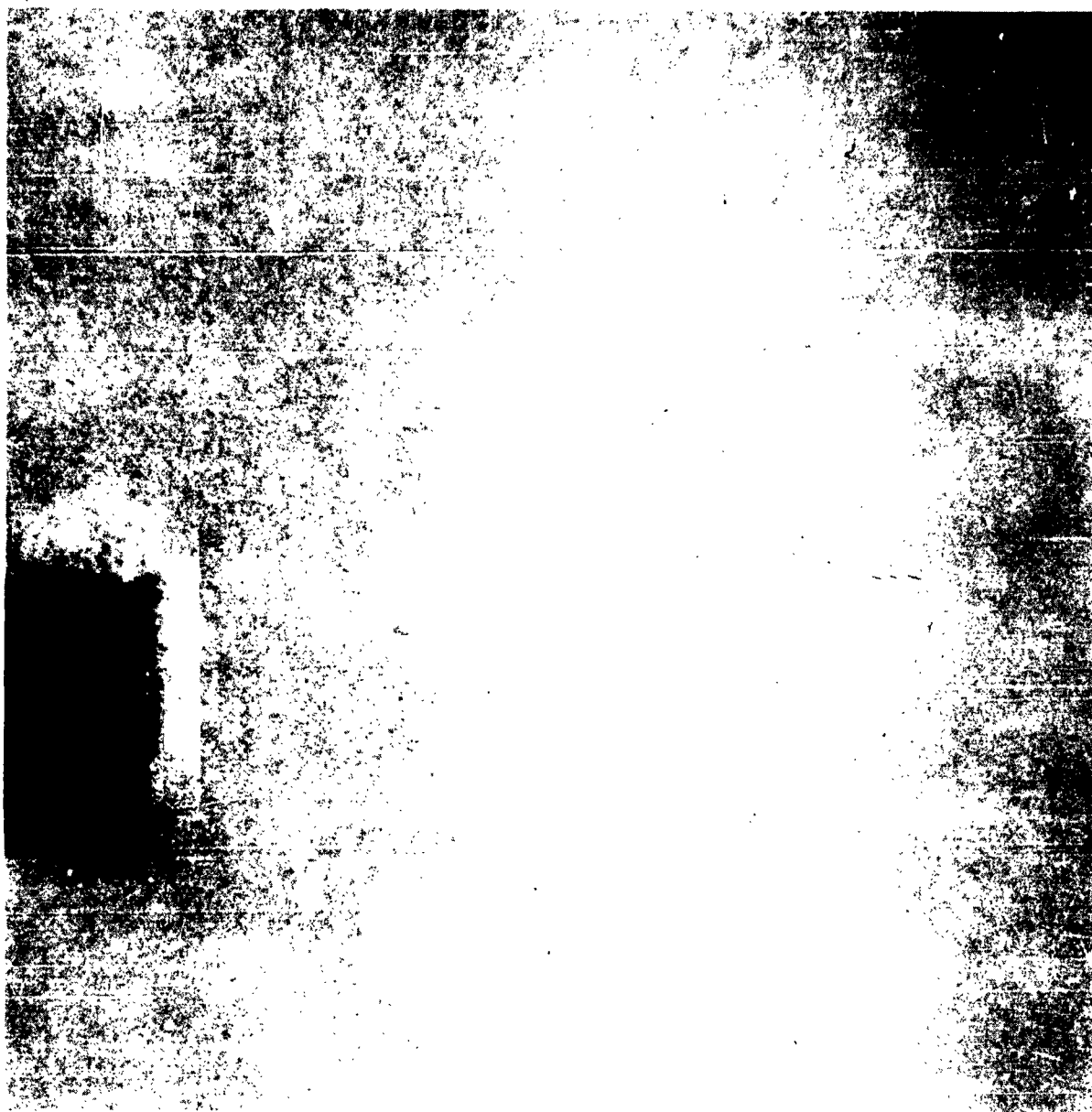


Figure 6

Grain Structure of an Electrophoretic P16 Screen on Clear Glass

Magnification - 250X

Process: Removable zinc electrode process

Note: Zinc was deposited directly on the glass without prior nucleation

Surface Photographed: Plane of contact between phosphor and glass substrate

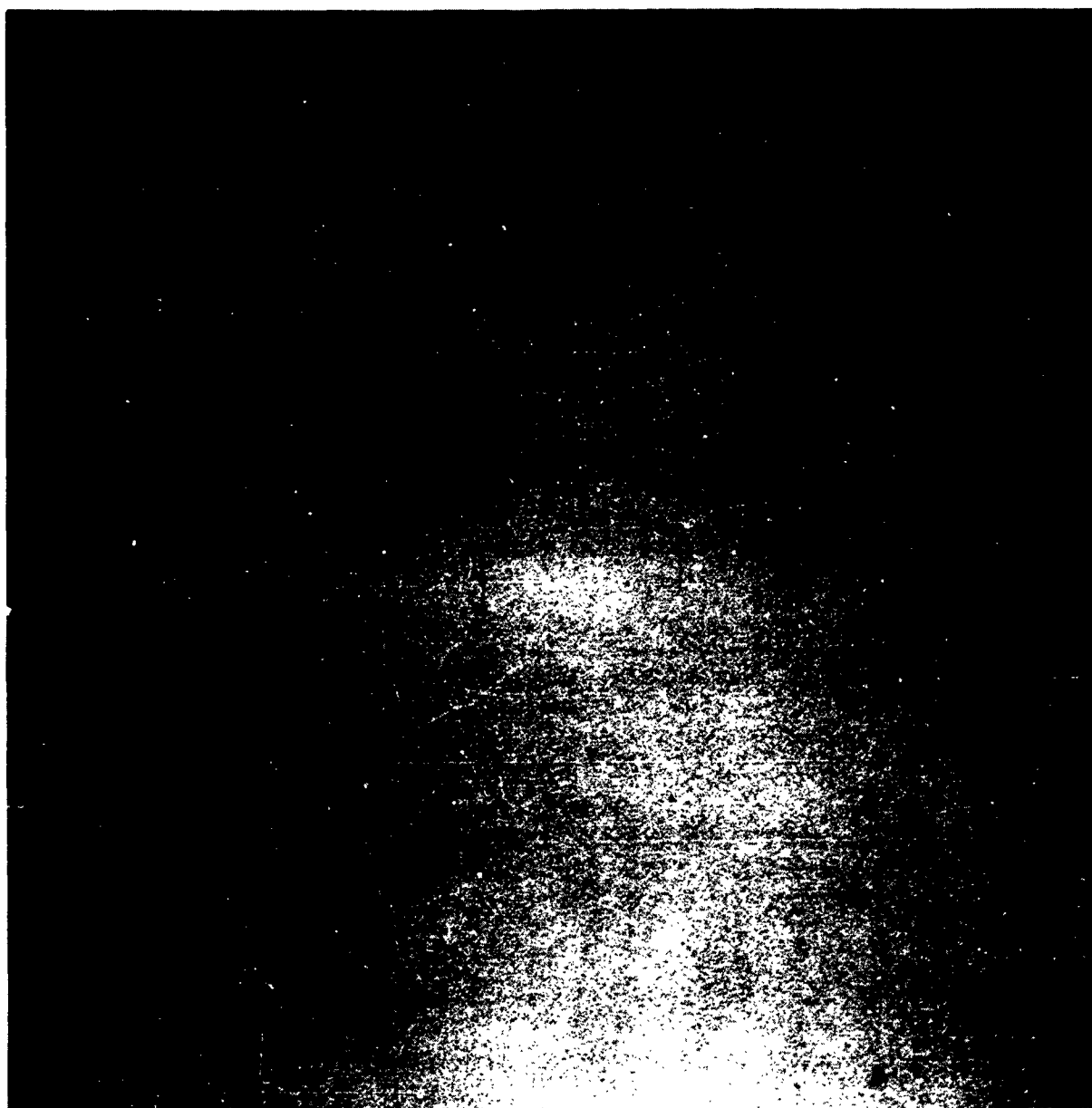


Figure 7

Over-all Uniformity of a Fine, settled P16 Screen on Glass
 Magnification - 4X
 Processing Details: Fine phosphors selected by elutriation.
 Particle size range, 0-5 microns
 Surface Photographed: Outer screen surface, side facing
 the electron gun.

Figure 8 is a photograph of an electrophoretic screen on ECG coated glass. The uniformity of this screen was judged to be poor. A random pattern of small white shapes (1-2 mils in size) was observed over the entire surface of the screen. Close inspection of the white spots revealed that they were accumulations of heavy phosphor deposit caused by local areas of high conductivity in the ECG coating. These non-uniformities are a characteristic of ECG coatings in general, and make the ECG coatings unsuitable for use as an electrode for high resolution screens. The parallel striations in Figure 8 were caused by the pour-off of the particular screen photographed and are not to be attributed to the ECG coating.

Figure 9 is a photograph of an electrophoretic screen prepared with the use of a removable zinc coating. This screen was judged to have excellent uniformity. There were no area irregularities or spot defects that could be attributed to the zinc coating used as the electrode for electrophoresis. This photograph demonstrates a second achievement of this development program, the improved uniformity of electrophoretic screens deposited on removable zinc electrodes as compared with electrophoretic screens deposited on ECG coated glass.

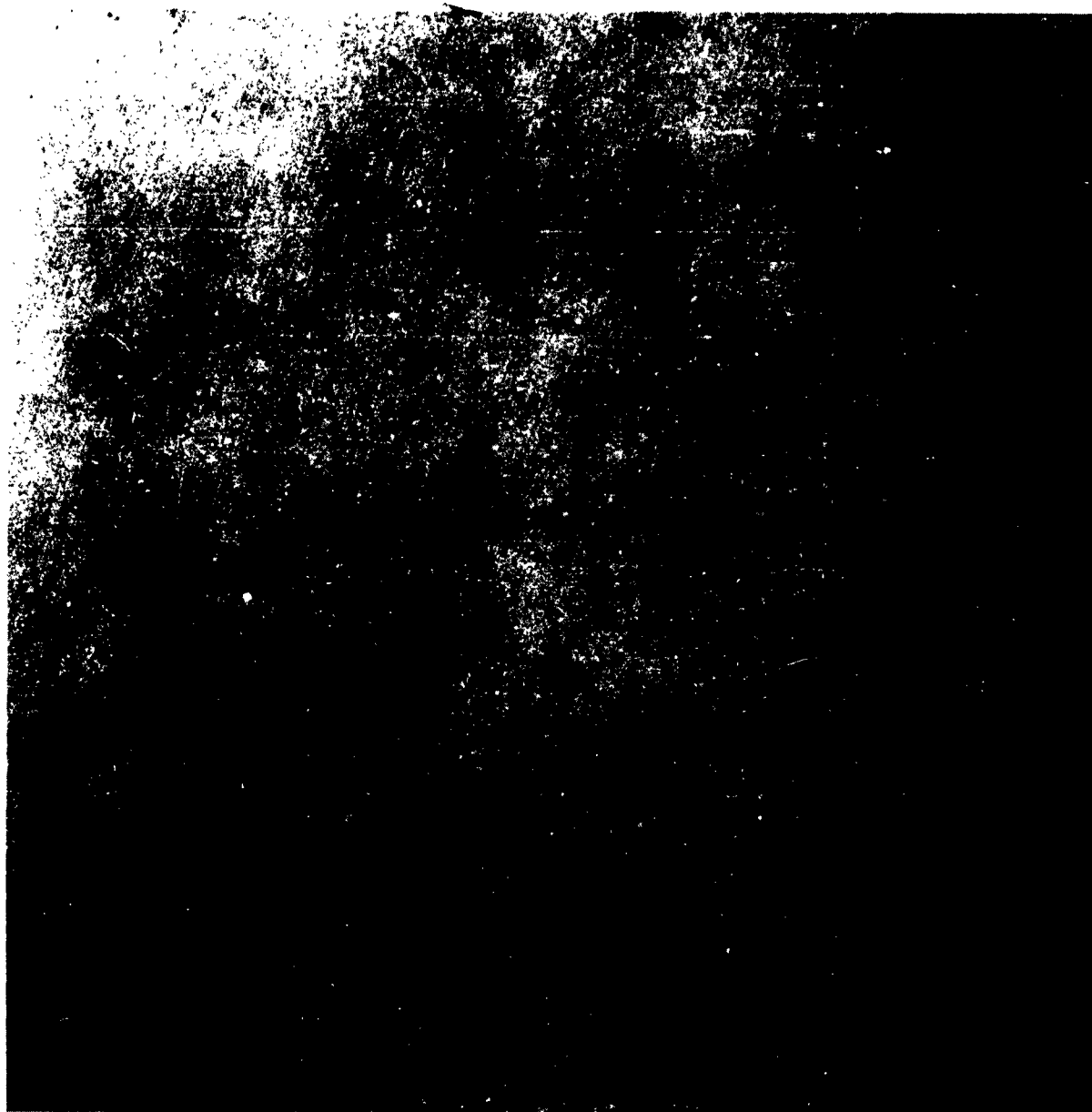


Figure 8

Over-all Uniformity of an Electrophoretic P16 Screen on ECG-coated Glass
 Magnification - 4X
 Surface Photographed: Outer screen surface, side facing the electron gun

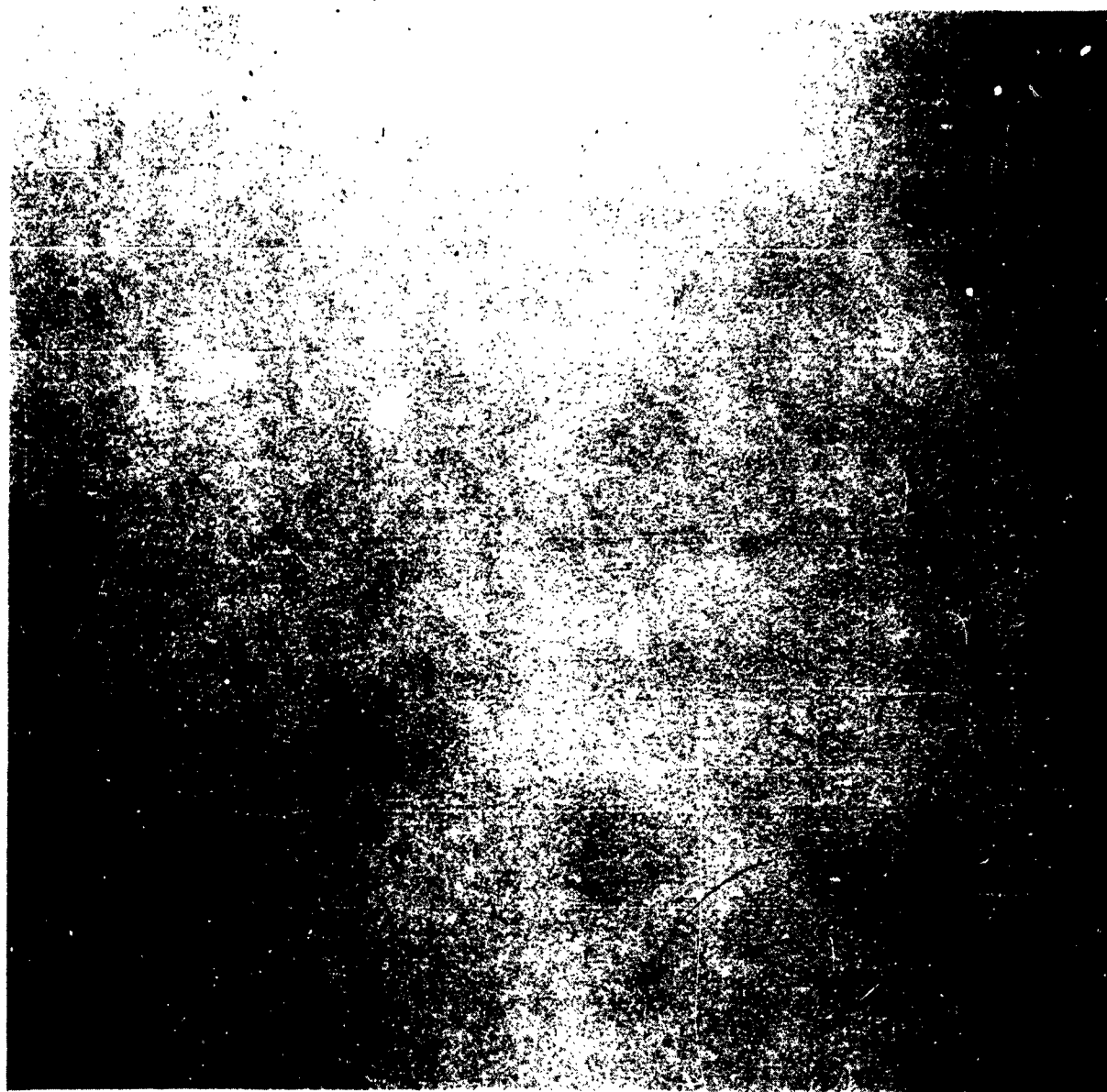


Figure 9

Over-all Uniformity of an Electrophoretic P16 Screen on Clear Glass
Magnification - 4X

Process: Removable zinc electrode process. Glass was nucleated
with silver prior to zinc deposition

Surface Photographed: Outer screen surface, side facing the electron gun.

Performance Data for Settled and Electrophoretic Screens

The information capability of an optical component of a data transmission system can be described in a manner similar to that used to describe electrical components of such systems.¹ The modulation transfer characteristic, as the spacial frequency response has come to be known, is essentially a curve of the modulation or contrast obtained in the image of a black (or white) repetitive object on a converse field produced by the component under test as a function of the spacial frequency (elements per linear dimensions). The characteristic obtained is analogous to the amplitude-frequency response characteristic of electrical components.

The primary object used in the transfer characteristic measurement of the phosphor screens was a variable size electron beam having a gaussian intensity distribution. The beam was scanned across the screen and the light output produced imaged upon a test reticular consisting of high contrast bar patterns of various spacial frequencies. The modulation produced by the image of the light spot scanning across the pattern was observed

¹O. H. Schade, Optical Image Evaluation, N.B.S. Circular 526, 231-258 (1954).

on a cathode ray oscilloscope and the response characteristic calculated.

The response characteristic of the electron beam was obtained by observing the characteristic of the light spot produced when the electron beam scanned a very thin phosphor coating ($\sim 5\mu$) on a metal electrode and was viewed from the same side as the beam was bombarding.

The response characteristic of the phosphor screen was obtained by scanning the phosphor with the above electron beam and viewing the light spot through the screen. The characteristic of the phosphor screen is computed from the observed response characteristic and the beam response characteristic: the combined response characteristic being the product of the beam and phosphor characteristics.

The apparatus set up is shown in Figure 10 and the results shown in Figure 11.

The phosphor screen tested was a settled P16 phosphor screen of oscillograph application quality. The limiting visual resolution of such a screen would be between the 2 and 5 percent response spatial frequencies which in this case is better than 20 lines per mm. Note that information is being lost at spacial frequencies of 5 lines per mm.

A measurement of radiant intensity was made by exposing Ansco Hyscan film to the light output of the settled and electrophoretic P16 screens which were mounted in cathode-ray tubes and operated in flying-spot scanner equipment.

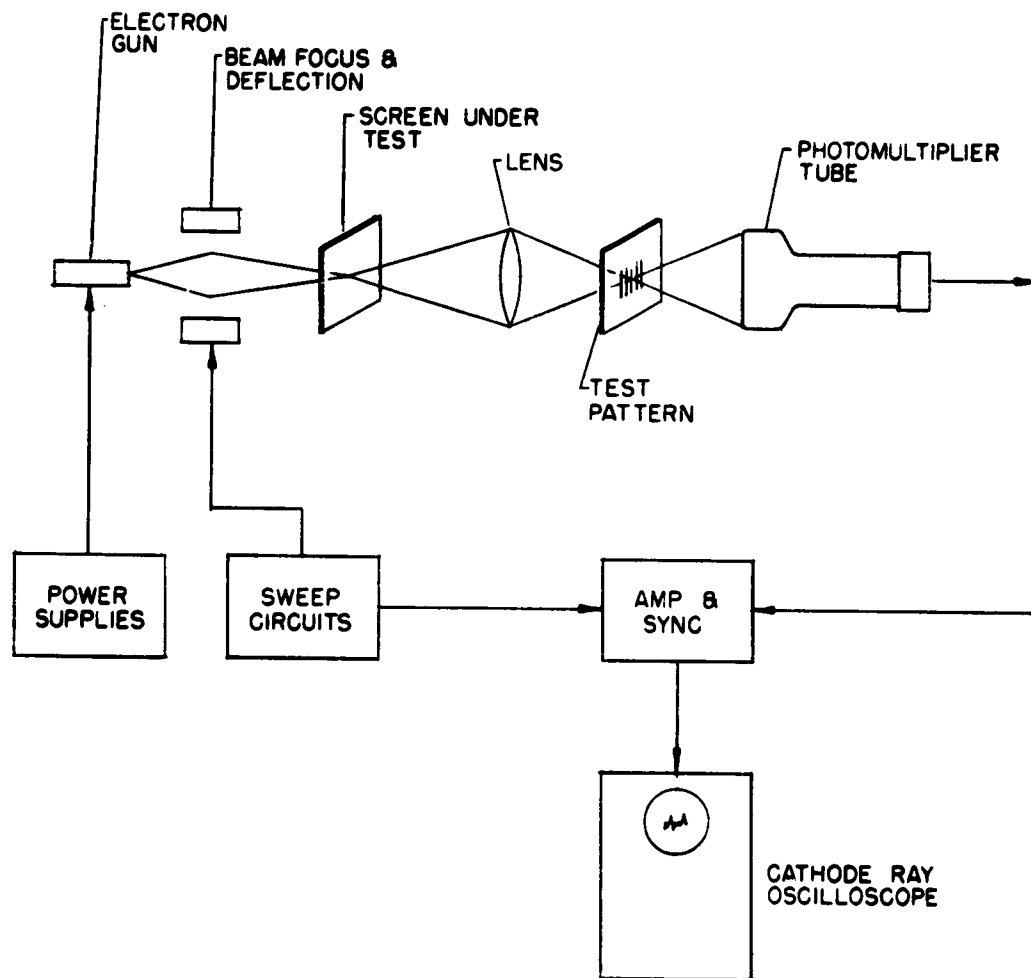


FIGURE 10
MODULATION TRANSFER CHARACTERISTIC APPARATUS

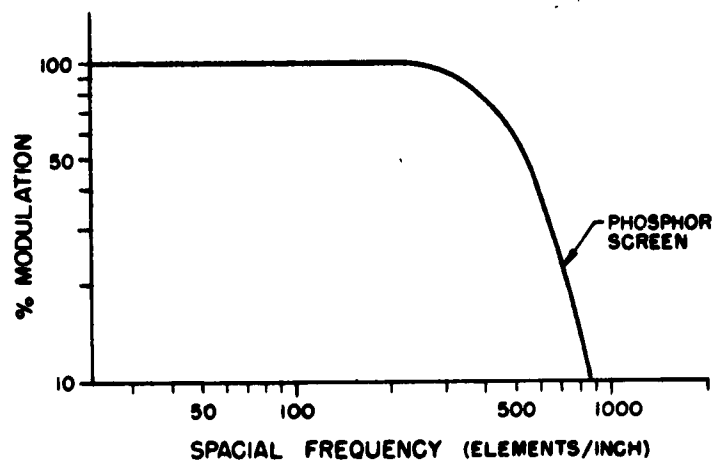
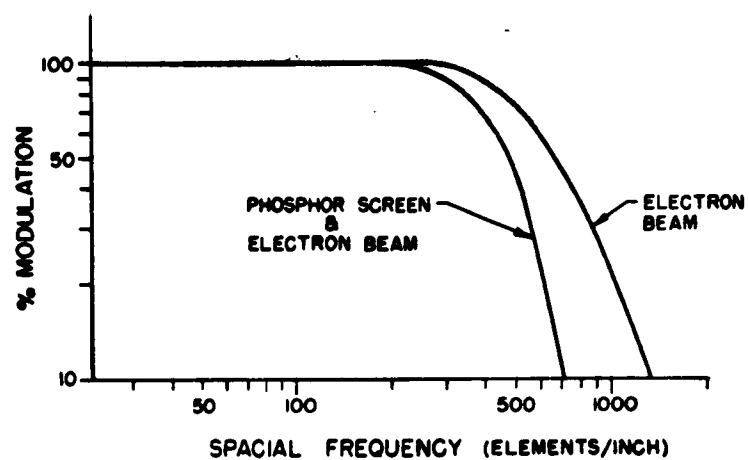


FIGURE II
SCREEN MODULATION TRANSFER CHARACTERISTICS

The settled screen at a beam current of 10 uA and a spot writing rate of 5000 inches per second achieved a density of 3. The electrophoretic screen under the same conditions achieved a density of 2.

A signal-to-noise ratio measurement was made using a photomultiplier and a video channel bandwidth of 12 megacycles (3 db down point). The best electrophoretic screen achieved a ratio of 34 db.

Comparison of Phosphor Particle Size - Settled and Electrophoretic Screens

Studies were conducted to compare the particle size of the phosphors in fine, settled screens and in electrophoretic screens (and in raw phosphor powder as purchased). For the settled screens and the raw powder the phosphor samples were prepared on glass slides and the particles were measured and counted with the use of a 210 power microscope. The same procedure could not be used for electrophoretic screens because the particles were too small to be measured under the microscope. These phosphors were measured and counted with the use of an electron microscope. Particle size data for the three phosphor samples are given in Table II.

As the results indicate, the median particle diameter for fine, settled screen phosphors was approximately seven times the median diameter of electrophoretic phosphors. The particle size data are in general agreement with the screen evaluations of sections entitled "Evaluation and Photography of Three Screen Types" and "Performance Data for Settled and

TABLE II

PARTICLE SIZE DISTRIBUTION
OF
THREE PHOSPHOR SAMPLES

<u>Phosphor Sample</u>	<u>No. of Particles</u>	<u>Modal Diameter (Microns)</u>	<u>Median Diameter (Microns)</u>	<u>Micron Range</u>
Phosphor Powder ¹	1224	7.5	9.0	
Fine Settled Screen	392	0.6	1.2	99.995% 5.6u
Cataphoretic Screen	404	0.09	0.175	95% 0.8u ²

¹ Starting material for all three samples was RCA Pl6 phosphor, lot 131.

² This figure is based upon electron microscope analysis. A slight error is introduced by the fact that the electron microscope could not detect particles larger than 2.0 microns.

Electrophoretic Screens" of this report. The improved grain structure, resolution, and noise characteristics of electrophoretic screens are due, in part, to the small size of the phosphor particles. The reduced brightness might also be due, in part, to the fine particle phosphors. On balance, the fine particle size of the phosphors is one major advantage of the electrophoretic process for high resolution screens.

Analytical Study to Predict Optimum Screen Structure

An analytical study was made to determine the range of particle sizes that would produce a screen approximating a maximum phosphor density. The largest particle size was limited by resolution considerations and was experimentally selected, based upon known milling characteristics of P16 phosphor. The study indicated that the maximum realizable density would be achieved using the following distribution of phosphor particles.

<u>Particle Diameter Range</u> (microns)	<u>Weight Percent</u>
1.75 - 2.25	64.10
0.175 - 0.225	25.64
0.0175 - 0.0225	10.26

a. Basic Concept

Assume a packing of large phosphor particles contain a fixed amount of voids, V1. If smaller phosphor particles (small compared to the pores of the large particles) are

introduced into the packing, the volume of the packing will not substantially change. We may obtain, however, a mixture such that all of the original voids (V_1) among the large particles are filled with the smaller component. But the smaller components also have voids, equivalent to V_2 , no matter how small the particle; when all the large voids are thus filled, we have $W_1 = (1-V_1) P_1$ for a unit-cell where W_1 is the weight of the large constituent, and P_1 its true specific gravity. Similarly, for the smaller component, $W_2 = V_1 (1-V_2) P_2$ where W_2 and P_2 correspond, respectively, to the weight and true specific gravity of the small constituent. The degree to which the large particles are saturated by the small ones is then,

$$S_1 = \frac{W_1}{W_1 + W_2} = \frac{(1-V_1)P_1}{(1-V_1)P_1 + V_1(1-V_2)P_2}$$

Solving for a condition of maximum density, whereby $P_1 = P_2$ and $V_1 = V_2 = V$, we resolve,

$$S = \frac{1}{1 + V}$$

This equation holds as long as the particles have the same shape (not necessarily spherical), and the voids generated are relatively constant for each additional component particle.

b. Formulation

Under the conditions established, let d_1 be the diameter of the large particles. The amount of material having a diameter d_2 which will fill all of the interstices of d_1 is $1-S$; similarly, a third component, d_3 , of the still finer phosphor particles can be introduced into the interstices of the second component. The basic process may be repeated indefinitely, until we obtain the total absolute volume of the solids, V_s as a geometric series with a constant inter-term ratio equal to $(1-S)/S$;

$$V_s = S + (1-S) + (1-S) \frac{(1-S)}{S} + \dots (1-S)^n \frac{(1-S)}{S}$$

since $(1-S)/S = V$, this equation becomes,

$$V_s = \frac{1}{1+V} + \frac{V}{1+V} + \frac{V^2}{1+V} + \dots \frac{V^n}{1+V}$$

where each term of the series applies to a single, discrete component particle diameter and there are n -terms for n -components.

If each term of the series is divided by V_s and multiplied by 100, we obtain the percentage of each component by volume in a mixture to produce the minimum voids when the voids in each component are V .

For example, assume V was initially equal to a 40% void, and 4 component particles d1, d2, d3 and d4 were considered for packing all with the same specific gravity P;

$$V_s = .7143 + .2857 + .1143 + .0444 = 1.1587$$

$$V_s\% = 61.65\% + 24.66\% + 9.86\% + 3.83\% = 100\%$$

NOTE: Distribution approximates the Rosin-Rammler equation

$$n = 100 \exp \left(-\frac{d}{c} \right)^b \text{ where } (c=d) \text{ (n) is a number percent, and (b) is a shape parameter.}$$

Therefore, for an initial (V) void in packing of 40%, with 4 component particles, the percent volume to be occupied by each particle, % Vf (d) as a function of its diameter is:

$$f(d1) = 61.65\% \quad f(d2) = 24.66\% \quad f(d3) = 9.86\% \quad f(d4) = 3.83\%$$

c. Limitations and Restrictions

In order to satisfy both resolution and intensity parameters, limitations are enforced on the largest possible particles diameter d1, applicable to this model's maximum random packing density. This constituent diameter restricts the range of smaller component sizes, and gives rise to the consequences of light conversion efficiency and scattering inherent with very fine phosphor particles.

d. Experimental Model

(1) The primary diameter (dl) of 2 microns (u) was considered as the constituent component.

(2) An initial weighted void of 40% was resolved by:

Volume Rhombus <u>Pore</u>	Volume Square <u>Pore</u>	Volume Triangle <u>Pore</u>
$V_{p1} = \frac{3}{2} dl^3 - \frac{II dl^3}{6}$	$V_{p1} = dl^3 - \frac{II dl^3}{6}$	$V_{p1} = \frac{3}{4} dl^3 - \frac{II dl^3}{12}$
$= 2.77 u^3$	$= 3.82 u^3$	$= 1.38 u^3$

Since Triangular Pores are generated in pairs the percent initial unit volume (V_p/VT) x 100 =

34.6%	47.8%	34.6%
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Weighted percent initial void -

$$= 3(V_{p1}\%) + 3(V_{p2}\%) + 2(V_{p3}\%) = \frac{316.4}{8}$$

$$= 39.6 \quad 40\%$$

NOTE: Weightings of voids are based empirically on their relative frequency of occurrence for Rhombohedral packing of particles. See footnote¹ for substantiation of experimentally verified information.

(3) Consider the total unit volume (V_1) as $176 \times 10^9 u^3$ which approximates a 5 inch CRT with a phosphor deposition of about 14 microns in depth, including allowances for wall waste.

¹Dalla Valle, J. M. Micromeritics, The Technology of Fine Particles, Pitman Publishing Corp. (N. Y. '43) 35 Chapter 6, Pg. 103

(4) The distributed volume as a function of particle diameter $V_{Tf}(d)$ would be, from Page 37.

$$V1f(d1) = .6165 \times 176 \times 10^9 = 109 \times 10^9 \text{ u}^3 = .109 \text{ cm}^3$$

$$V2f(d2) = .2466 \times 176 \times 10^9 = 43 \times 10^9 \text{ u}^3 = .043 \text{ cm}^3$$

$$V3f(d3) = .0986 \times 176 \times 10^9 = 17 \times 10^9 \text{ u}^3 = .017 \text{ cm}^3$$

$$V4f(d4) = .0383 \times 176 \times 10^9 = 7 \times 10^9 \text{ u}^3 = .007 \text{ cm}^3$$

(5) The distribution weight as a function of particle diameter $W_{Tf}(d)$ would be, for an assumed specific gravity (p) equal to 2.95 gram/cm³;

$$W1f(d1) = .109 \times 2.95 = .321\text{g} = 321 \text{ mil g}$$

$$W2f(d2) = .043 \times 2.95 = .127\text{g} = 127 \text{ mil g}$$

$$W3f(d3) = .017 \times 2.95 = .050\text{g} = 50 \text{ mil g}$$

$$W4f(d4) = .007 \times 2.95 = .021\text{g} = 21 \text{ mil g}$$

$$W_{Tf}(dn) = W_n = 519 \text{ mil gram}$$

(6) Percent saturation $Sf(d)$ as a function of particle diameter equals

$$S1f(d1) = \frac{W1 \times 100}{W1 \times W2} = \frac{32.1}{.448} = 71.65\%$$

$$S2f(d2) = \frac{W2 \times 100}{W2 \times W3} = \frac{12.7}{.177} = 71.75\%$$

$$S3f(d3) = \frac{W3 \times 100}{W3 \times W4} = \frac{5.0}{.071} = 70.42\%$$

NOTE THAT THE PERCENTAGE REMAINS RELATIVELY CONSTANT FOR ALL COMPONENT PARTICLE SIZES, THUS AN EQUAL PROBABILITY OF SATURATION.

(7) Since $W_T f(dn)$ equals 519 milligrams and the area of a 5 inch CRT is about 126.7 sq. cm, the ratio results in a surface density of;

$$\frac{W_T f(dn)}{\frac{11 d^2(CRT)}{4}} = \frac{519}{126.7} = 4.097 \text{ mg/cm}^2$$

This is with the assumed thickness of 14 microns. Theoretically, the thickness required to be 99.5% confident of coverage is closer to 9.2 microns or 65.71% or 4.097 mg/cm². This is equivalent to 2.69 milligrams/square centimeter.

$(v)^L = 1-C$, where L is the number of average layers, V percent initial void, and C is the statistical confidence.

(8) Through a series of geometric proofs it was found the second, (d2); third (d3); and fourth (d4); generation of particle sizes must approach, respectively, .2, .02, and .002 microns in diameter in order to facilitate the saturation of pores created. As a matter of interest, therefore, the number (N) of each component particle can be resolved as follows:

$$N1f(d1) = \frac{6V1}{11 d_1^3} = 26.03 \times 10^9 \text{ parts. } @ d_1 = 2u$$

$$N2f(d2) = \frac{6V2}{11 d_2^3} = 10.29 \times 10^{12} \text{ parts. } @ d_2 = .2u$$

$$N3f(d3) = \frac{6V3}{11 d_3^3} = 4.06 \times 10^{15} \text{ parts. } @ d_3 = .02u$$

$$N4f(d4) = \frac{6V4}{11 d_4^3} = 1.67 \times 10^{18} \text{ parts. } @ d_4 = .002u$$

NOTE: THE d_4 (.002u) PARTICLE IS NOT FEASIBLE, AND THEREFORE REJECTS A 4 COMPONENT COMPOSITION AND MAKES A 10% VOID HIGHLY IMPRACTICAL TO OBTAIN.

(9) A redistribution using 3 component particles with a realizable void of about 19% is shown below.

	<u>% Vf(d)</u>	<u>Vf(d)</u>	<u>Wf(d)</u>	<u>Sf(d)</u>	<u>Nf(d)</u>
d1 (2u)	64.10%	.1128 cm ³	333 mg.	71.46%	26.93x10 ⁹ parts
d2 (.2u)	25.64%	.0451 cm ³	133 mg.	71.12%	10.77x10 ¹² parts
d3 (.02)	10.26%	.0181 cm ³	54 mg.	-	4.32x10 ¹⁵ parts
		Vf(d) = .1760 cm ³	Wf(d) = 520 mg.	Sf(d) = 142.58%	Nf(d) = 4330.8x10 ⁻² parts

$$\text{Surface density } (Df_s) = \frac{Wf(d)}{As} = \frac{520}{126.7} = 4.1 \text{ mg/cm}^2.$$

e. Permissible Particle Diameter Range

$d_1 \pm .126d_1$	1.75u - 2.25u
$d_2 \pm .126d_2$	.175u - .225u
$d_3 \pm .126d_3$	.0175u - .0225u

f. Comments

(1) It is noted from this model that the decrease in porosity is not very significant with the addition of a fourth constituent particle.

(2) It would be very difficult to prepare a screen of the maximum packaging density due to two considerations: the first is the necessity of separating the discrete sizes out of a batch of milled phosphor; the second is the necessity of depositing particles out of solution in a specified order to achieve the maximum packaging.

Procedure for Preparing an Electrophoretic Pl6 Screen on Glass

a. Deposition of zinc coating on glass - For the most part, standard laboratory equipment is sufficient to produce an electrophoretic Pl6 screen on glass. The first step in the process, the evaporation of the zinc coating on glass, is performed inside a fourteen-inch bell jar mounted on a vacuum coating unit capable of producing a vacuum of 1×10^{-5} mm Hg. (Consolidated Vacuum Corporation, Vacuum Coating Unit Type LCI-14B). The zinc is evaporated from a tantalum boat (Rembar Company, Inc., Dobbs Ferry, New York, Type 02.8638-C) and the voltage applied to the boat is controlled by a Variac on the coating unit. The arrangement of equipment for the coating of a five-inch glass plate is shown in Figure 1.

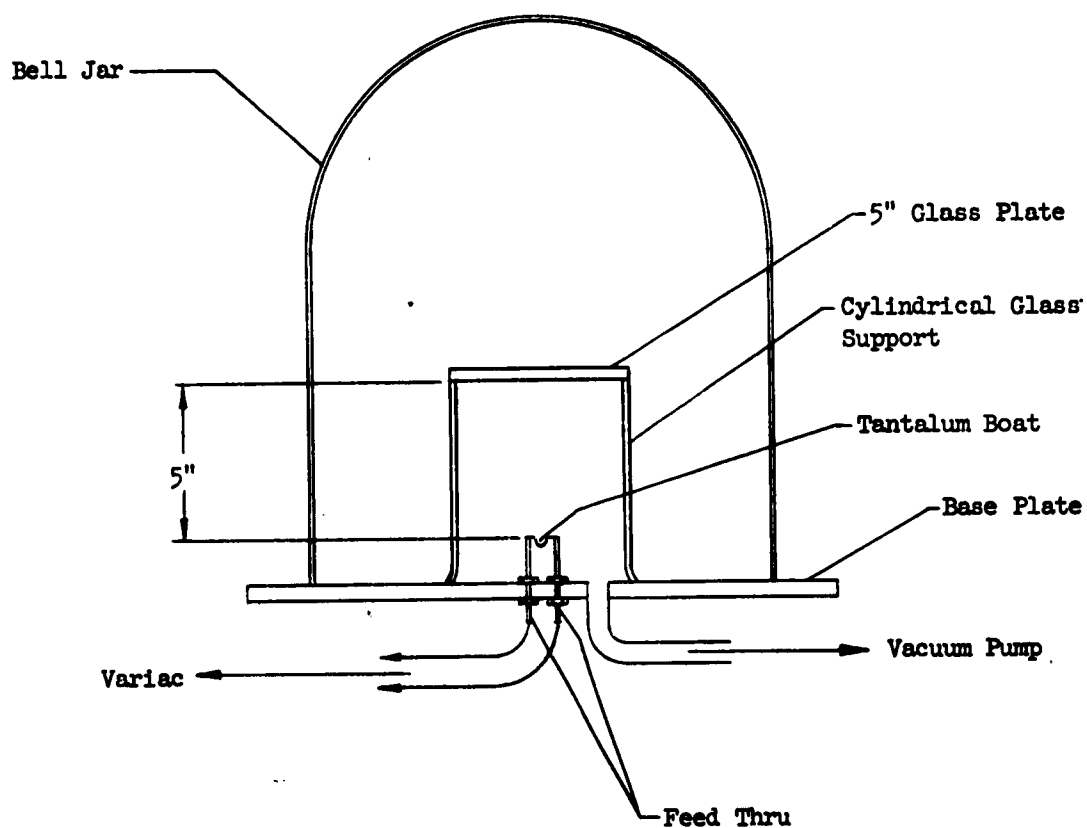
In order to deposit a zinc coating on the glass plate, 0.1 gram of zinc is placed in the tantalum boat. A clean, five-inch glass plate is mounted in the bell jar as in Figure 10. The bell jar is pumped down to a pressure of 2.5×10^{-5} mm Hg. The voltage on the tantalum boat is then raised slowly until the zinc begins to coat the lower walls of the cylindrical glass support. The zinc evaporation is continued until the tantalum boat

is no longer visible as viewed through a point one-inch from the top of the cylindrical glass support.

b. Deposition of Electrophoretic Phosphor Screen - Electrophoretic deposition of the P16 phosphor on a five-inch glass plate is done in a 4000 ml beaker. The zinc-coated glass which serves as the cathode is suspended in the beaker two centimeters distant from a row of seven 1/4" x 6" carbon rods which serve as the anode. Voltage is supplied by a Regulated Power Supply (Model 50, Lambda Electronics Corporation, Corona, New York).

For the phosphor deposition, 3000 ml of phosphor slurry (0.89 grams of P16 phosphor per liter of alcohol solution) is added to the 4000 ml beaker. The voltage is raised to 280 volts and is maintained for 40 minutes. The solution is then drained and the screen is allowed to dry.

c. Removal of Zinc Coating - The removal of the zinc coating from the deposited screen is performed in the same bell jar that is used for the original deposition of the zinc film. The five-inch plate is mounted on the cylindrical glass support shown in Figure 12. Heat is supplied by a row of five quartz infra-red heaters (General Electric



Equipment for Coating Zinc

on

Five Inch Glass Plated

Figure 12

44

Company, 500 watts) placed at a distance 3/4 inches above the screen.

A thermocouple is used to measure the screen temperature.

For removal of the zinc coating, the bell jar is pumped down to a pressure of 2.5×10^{-5} mm Hg. The screen temperature is raised slowly to 400°C. and is maintained at that temperature for thirty minutes. The screen is then allowed to cool to room temperature and is removed from the bell jar. The completed product is an electrophoretic Pl6 screen bonded directly to the glass plate, with no conductive coating between the phosphor and the glass.

Summary, Conclusions and Recommendations

It is believed that the purposes of this contract have been successfully accomplished. Under the contract, a new and original method has been developed for preparing electrophoretic screens directly on glass surfaces. The new process has important advantages over fine, settled screens and over electrophoretic screens deposited on ECG coated glass. Since the two latter types are used on most high resolution devices at present, they are considered to represent the present state-of-the-art. The new developments made under this program are, therefore, advances in state-of-the-art of high resolution phosphor screens.

The new process is summarized as follows:

- (1) A clean glass plate is mounted in a bell jar above a zinc source.
- (2) The zinc is evaporated under vacuum to form a thin, uniform coating on the glass.
- (3) Using the zinc coating as an electrode, a P16 electrophoretic screen is deposited on the coated glass plate.

(4) The plate is again mounted inside the bell jar.

(5) Under vacuum, the plate is heated to 400°C. and is maintained at that temperature until all the zinc has been removed, by evaporation, from the plate. The product of the new process is an electrophoretic screen on clear glass.

Screens prepared with the use of removable zinc electrodes have the following demonstrated advantages over present high resolution screens:

(a) A fine, dense screen structure, as compared with the loose-packed, somewhat grainy structure of the best settled screens.

(b) Uniform deposits of phosphor over the entire glass surface compared with the non-uniform deposit of phosphor on NESA coated glass.

(c) No loss of light output between the phosphor and the glass as occurs in screens deposited on NESA coated glass.

Further work remains to be done before the new process can be utilized in high resolution devices. Conditions must be established for depositing uniform zinc films on

glass in a simple, reproducible operation. Investigation of the electrophoretic process must be continued in order to produce a smooth, flat outer surface on the phosphor screens. The milling procedure, now a part of the electrophoretic process, must be eliminated in order to increase the light output of the screens. In addition, it would be desirable to extend the process to phosphors other than P16.

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ON PHOSPHOR SCREENS FOR HIGH RESOLUTION DISPLAY
DEVICES. Final Report, March 63, 48p.incl.
illus., tables, 2 refs.

Unclassified Report

The final report on a development program to
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display devices describes an investigation and
experimental study of a method of cata-
phoretically depositing phosphors. An
analytical study to predict optimum screen
structure, a method of cataphoretically
depositing phosphor on glass using a removable
metal film, and an evaluation of
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