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CONTINUOUS-TONE ELECTROSTATIC ELECTROGRAPHY

BATTELLE MEMORIAL INSTITUTE

2nd QUARTERLY REPORT
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January 6, 1949 RESTRICTED

Dr. John Dessauer
The Haloid Company
Rochester 3, New York

Dear Dr. Dessauer:

Enclosed are 54 copies of Quarterly Progress Report No. 2 on Continuous-Tone Electrostatic Electrophotography. This report covers work through the three-month period from September 15, 1948, to December 15, 1948.

Very truly yours,

C. D. Oughton

C. D. Oughton
Assistant Supervisor
Graphic Arts Research Division

CDO:swr
Enc.

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QUARTERLY PROGRESS REPORT NO. 2
(September 15, 1948, to December 15, 1948)

on

CONTINUOUS-TONE ELECTROSTATIC ELECTROGRAPHY

to

THE HALOID COMPANY

(Subcontract Under Signal Corps Prime Contract
No. W36-039 sc-36851)

(Department of the Army Project: 3-99-04-052)

(Signal Corps Project: 195 B)

by

R. M. Schaffert, L. R. Jackson, A. E. Middleton, L. E. Walkup, D. T. Williams, J. J. Rheinfrank, O. A. Ullrich, J. Stockdale, J. P. Wronski, P. G. Andrus, D. L. Fauser, J. P. Ebert, K. E. Cochran, K. E. Jackson, O. J. Mengali, N. B. Crane, and C. D. Oughton.

OBJECTIVE OF RESEARCH: To evolve an electrostatic electrophotographic system capable of reproducing continuous-tone photographs.

BATTELLE MEMORIAL INSTITUTE

December 15, 1948

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TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

exponential time variation which leads to the postulate that the primary mechanism for dark decay is one of thermal activation. A slight increase in slope (30% to 50%) was observed for positive dark decay curves immediately after a brief exposure of the plate to light. No consistent change was observed for the negative dark decay curve under similar conditions. Soaking a selenium-coated plate in ethyl alcohol for 36 hours had no apparent effect on the positive decay curves, but lowered the initial negative potential and increased the slope of the negative decay curves. An attempt to duplicate the results was unsuccessful and the effects may, therefore, be due to other causes. Selenium was evaporated onto stainless steel, nickel, cold-rolled steel, and copper plates in the same evaporation run. The plates showed inferior properties for positive charge and superior properties for negative charge in the above order, which is also the order of decreasing thermal conductivity.

Three methods other than vacuum evaporation were used for applying selenium films: (1) spraying molten selenium, (2) platen pressing as in rectifier production, and (3) spraying selenium pigmented paints. The selenium structure and purity when used for (1) and (2) are important. Tests were therefore made on various types of available selenium. ARQ selenium was satisfactory from batch to batch; DDQ selenium appears to be satisfactory, but further tests are required; and OOR selenium is not satisfactory without a thermal treatment apparently because of the presence of grey hexagonal crystals.

Indications are that the properties of electrophotographic plates will, in general, depend in part on the type of impurity content which results in a considerable variation in the quantity of charge accepted by the plates. Using ARQ selenium, the effect of binder material was studied. Apparently the binder has no effect on the electrophotographic properties or the structure of the film. It does affect the color of the film. Parlon-Rezyl and silicone are the best binders that have been found. Post heat treatment was used to improve the electrophotographic qualities of selenium-in-binder films. Polishing was used to eliminate background on prints from molten sprayed selenium films, but it did not reduce the overall background. Lacquer film on pressed selenium plates smoothed out the surface, but failed to eliminate background. A study of film structure versus photoactivity has indicated (1) that a film with an appreciable amount of grey hexagonal selenium or chemically precipitated red selenium will not be photoactive for electrophotographic purposes, and (2) that crystalline, alpha-monoclinic and amorphous selenium structures support photoactivity.

A preliminary theory relating electrophotographic sensitivity with the molecular structure of sensitive films is explained.

Selenium-pigmented paint films were prepared which varied in thickness from 0.0004 to 0.015 inch. Films less than 0.002 inch thick took less charge and showed greater light and dark decay rates. Electrophotographic plates were prepared by hot pressing selenium with 1 per cent to 10 per cent sulphur additions. The sensitivity of the plates appeared to decrease with the increase of sulphur.

Tests for photoactivity were made on Sb_2S_3, SeS, diamond, napthalene long-chain paraffin (Multiwax W-445). These materials, which were selected on the basis of their fundamental chemical structure, all showed photoactivity. Tests were initiated to determine the effects of temperature treatments (50 to 70°C.) on the photoactivity of the selenium film. No effect was noted on a selenium-pigmented parlon-rezyl film. A slight change in decay rates was observed on a sulphur-contaminated film and a hot-sprayed selenium film.

Forty-four additional materials, known or suspected to be photoactive were tested for photoconductivity by the powder method.

Cleaning the base plates by vapor degreasing with isopropyl alcohol before vacuum evaporation of selenium eliminated spots on the plate resulting from poor hand cleaning. Several plates were prepared under controlled temperature conditions. The plates held at the lowest temperatures took on a thicker selenium film for given conditions of firing distance and weight of charge. Plates maintained at or near room temperature had a bluish cast. Only small changes in electrical characteristics were observed.

Plates prepared and stored in total darkness before testing took on a low positive charge and had a low value of positive residual charge.

Selenium plates prepared on aluminum-coated glass and on polished brass showed a more homogeneous and uniform background than that obtained on polished aluminum plates. An optical flat was used to measure the thickness of the selenium films.

The use of a grounded auxiliary electrode near the surface of an electrophotographic plate (1/16 to 7/16 inch) during development of the image, resulted in improved continuous tone and better development of large dark areas. Improved results were also obtained on continuous-tone pictures by flashing the plate to a 120-line half-tone transparency of uniform dot area (75% opaque) before or after exposure to the image.

The vibrating probe electrometer was used to measure the resistivity of ethyl cellulose. Details of the construction and operation of the vibrating probe electrometer are included in the Appendix.

Also discussed in the Appendix are the methods used in the preparation, application, and testing of selenium and photoactive films, equipment revisions in the vacuum unit, a power supply for sensitizing electrophotographic plates, and light sources for use with the vibrating probe electrometer.

FUTURE WORK

Experimental work for the next three months will concentrate on the following problems:

1. Standardization of plate testing procedures.

2. Preparation of electrophotographic plates using antimony trisulfide, zinc titanate, and benzidine.

3. Study of the initial potential, the speed, and the spectral sensitivity of selenium, anthracene, sulfur, sulfur-selenium, antimony trisulfide, zinc titanate, and benzidine electrophotographic plates.

4. Detailed study of the preparation of selenium-coated electrophotographic plates--both vacuum-evaporated and painted plates. The effect of (a) backing-plate material, (b) impurities, (c) temperature, (d) pressure, (e) film thickness, and (f) crystal structure, will

be investigated. New binders (photoactive ones, for example) will be sought for use in preparing painted plates to help reduce the background in prints from the plates.

5. Effect of plate history on the electrical characteristics of electrophotographic plates.

6. Investigation of temperature treatment of various photoconductive films (preferred structures may result).

7. Investigation of the asymmetry in positive and negative polarity data, in the light of (a) the theory presented in this report, (b) rectification theory, and (c) data on selenium rectifiers.

8. Theoretical analyses of (a) the effect of plate temperature on the decay of electrical charge from electrophotographic plates in darkness, (b) the effect of film thickness on the electrical characteristics of photoconductive layers, and (c) the difference in the photoactivity of selenium, sulfur, and organic compounds.

9. Investigation of possible photoconductors. This will include (a) the extension of the list of possible photoconductors and (b) the procurement and analysis of these materials.

10. Investigation of electrophotographic developers and developing techniques. Smaller powders, one-component developers, and the effect of a constant potential electrode near the electrophotographic plate during the developing operation, will be studied.

PUBLICATIONS, TALKS, AND/OR DEMONSTRATIONS

During the period of September 15, 1948 to December 15, 1948, the following publications were released on electrophotography:

1. Life Magazine. A series of photographs showing the basic elements and operations involved in the process. Details were withheld on exact formulations and specifications. These photographs have not been used to date.

2. News Release Packet. A packet of information with photographs and a general description of the process was prepared and released jointly by Battelle Memorial Institute and The Haloid Company to the general press and magazine representatives.

3. Journal of the Optical Society of America. An article entitled "Xerography, A New Process of Photography and Graphic Reproduction," by R. M. Schaffert and C. D. Oughton, was released for publication in December, 1948. This article describes all of the essential details of electrophotography.

A number of demonstrations of the process of electrophotography have been given. These demonstrations have shown all of the essential details of the process for contact-copy and camera-copy application. A motion picture was prepared and shown at these demonstrations which revealed the vacuum evaporation of material to form plates and a description of all other major details of the process except for the exact nature of the photoconductive coating on the plate and exact composition of the developer materials.

This demonstration has been presented by Battelle Memorial Institute personnel before the following groups:

1. Approximately 200 representatives of newspaper and magazine editorial staffs at the Waldorf-Astoria Hotel, New York, New York, on October 19, 1948.

2. Approximately 1000 members and visitors of a meeting of The Optical Society of America at Detroit, Michigan, on October 22, 1948.

3. Approximately 20 Army and Navy representatives at Washington, D. C., on October 29, 1948.

4. Television audience over WABD network, New York City, on November 3, 1948.

5. Approximately 500 members and visitors of the National Editorial Association at Chicago, Illinois, on November 19, 1948.

6. Approximately 200 members and visitors of the Glass Conference, sponsored by the Ohio State University and the University of Illinois at Columbus, Ohio, on December 2, 1948.

7. Approximately 250 members and visitors of the Printing Industries of America during a visit to the Battelle Memorial Institute on December 6, 1948.

8. Approximately 150 representatives of the Department of the Army and other government offices at the Pentagon Building, Washington, D. C., on December 8, 1948.

9. Approximately 100 representatives of the Department of the Navy and other government offices at the Navy Building, Washington, D. C., on December 9, 1948.

BACKGROUND INFORMATION AND RELATED EXPERIMENTAL DATA

An electrophotographic plate develops a latent electrostatic image by a two-step process which can be of the following nature:

1. Exposing such a plate in the dark to a passing wire (a short distance above the plate) or a series of points or other sources of somewhat similar geometry held at high voltage in respect to the base of the plate, providing a corona discharge is present around the wire, or by charging the surface by a contact with a triboelectrically charged rod such as amber.

2. Subsequently exposing the charged plate to light from a source for which an image is desired.

Previous work on this project has given some information on (a) the structural and electrical nature of electrophotographic selenium films, (b) types of materials which can be photoconductive in the manner of electrophotographic needs, (c) methods of making satisfactory films, and (d) the range of electrostatic and light intensity conditions for which present electrophotographic plates can be used. Also, some very preliminary theories on (a) the mechanism of developing a latent electrostatic image, and (b) a hypothetical model of the film structure were presented. In addition, some analyses of light decay rates were made.

Among the results of these studies were the following:

1. In addition to applying a selenium film by evaporation, an electrophotographic film can be made by pigmenting a binder such as parlonrozyl with vitreous selenium powder, followed by spraying a thin film of this paint on a base plate.

2. Small particles of grey hexagonal selenium dispersed in a similar binder and sprayed did not produce film which would hold a surface charge in the dark.

3. Selenium, anthracene, acenaphthene, benzidine, fluoranthene, chrysene, and zinc titanate exhibited photoactivity.

4. Selenium-coated plates showing detectable crystallinity exhibited electrophotographic properties.

Through these results, considerations of various properties of electrophotographic film materials, and the nature of the electrophotographic process, it has been realized that an important first step in further developing electrophotography should consist of obtaining data on the structure of electrophotographic films and effects of various factors (known to affect structure of materials) on electrophotographic action.

Experimental and theoretical work designed to augment the information, summarized briefly above, has been carried out along a number of different lines and is described in this report.

The report is divided into several main sections. The first two sections which follow are concerned primarily with experiments of a more or less fundamental nature designed to explore the effect of a variety of variables on the type of photoactivity of interest to this investigation. For the third section, a theory is developed relating the electrophotoactive processes observed to the fundamental structure of the substances which have proved to be sensitive. While the development of the theory is not complete it appears to account qualitatively, at least, for the various effects observed so far, and furthermore appears to be capable of being used to direct research along the most fruitful channels.

INVESTIGATIONS OF THE ELECTROPHOTOGRAPHIC PROPERTIES OF EVAPORATED-SELENIUM FILMS

The experiments described in the section were intended to be as precise as possible in order to bring out some of the fine details that are always missed in more exploratory work. Evaporated films were chosen for this purpose because up to the present they are the most sensitive of the films explored, and because the manner of this preparation probably allows more complete control over variables entering into the formation of the films than do other methods that have been used.

Duplicability of Decay Data

In a proper rationalization of experimental work, it is of prime importance to know the reproducibility of data in order to be able to distinguish between true and spurious observations. Accordingly, a series of light decay curves were run on an evaporated selenium plate (11-7-47-A)* in order to see whether successive curves showed differences in shape. The procedure was to charge the plate with a given potential on the charging wire, and then to observe the potential as a function of time. This was repeated four times with charging wire positive. A similar series of four decay events were observed with charging wire negative. Finally, a series of eight decays were observed in which the initial charge was made with wire alternating positive and negative. The results of these three series of tests are shown in Figures 12, 13, and 14. The scatter of the

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* Xerographic plate 11-7-47-A was prepared by vacuum evaporation of selenium onto an aluminum plate under "normal" vacuum evaporation conditions. The electrical (photoconductive) properties of the plate when negatively charged may be classed as average. However, when charged positively, the initial charge is above average, the light decay rate faster than average, and the final potential negligible.

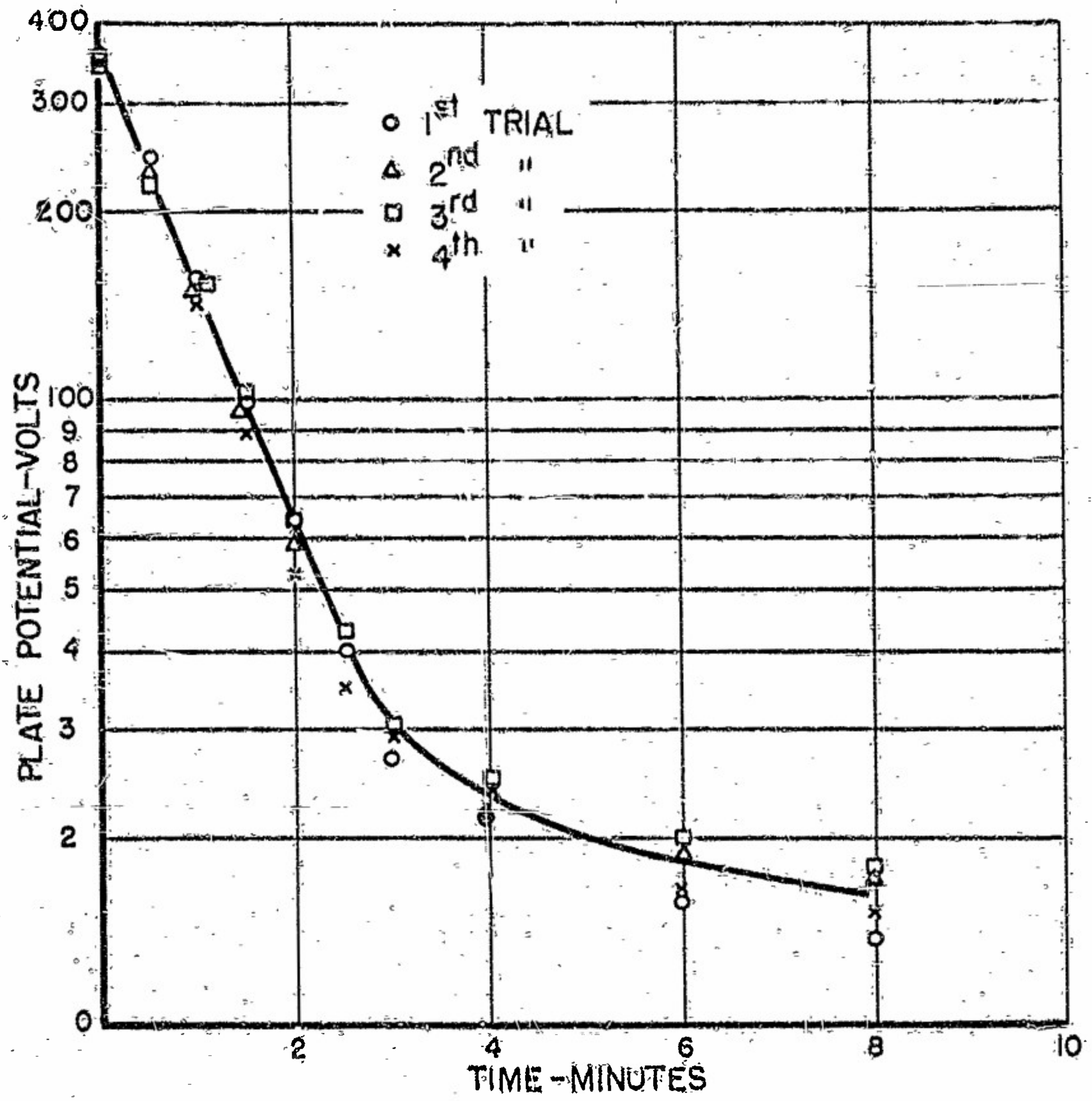

FIGURE 12. LIGHT DECAY CURVES FOR PLATE NO. 11-7-47A, 4000V (+) CHARGE POTENTIAL

0-10048

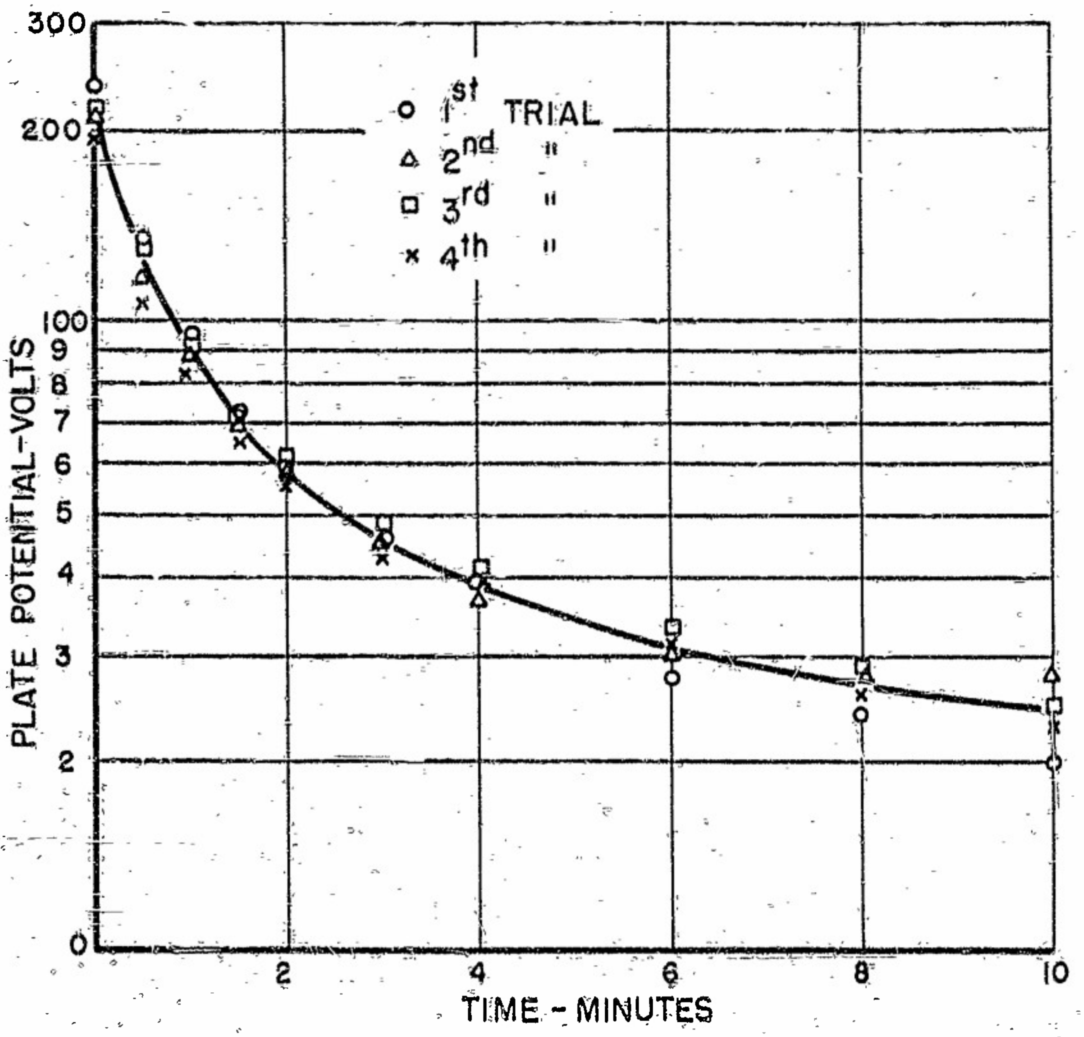

FIGURE 13. LIGHT DECAY CURVES FOR PLATE NO. 11-7-47A, 4000 V(−) CHARGE POTENTIAL

0-10049

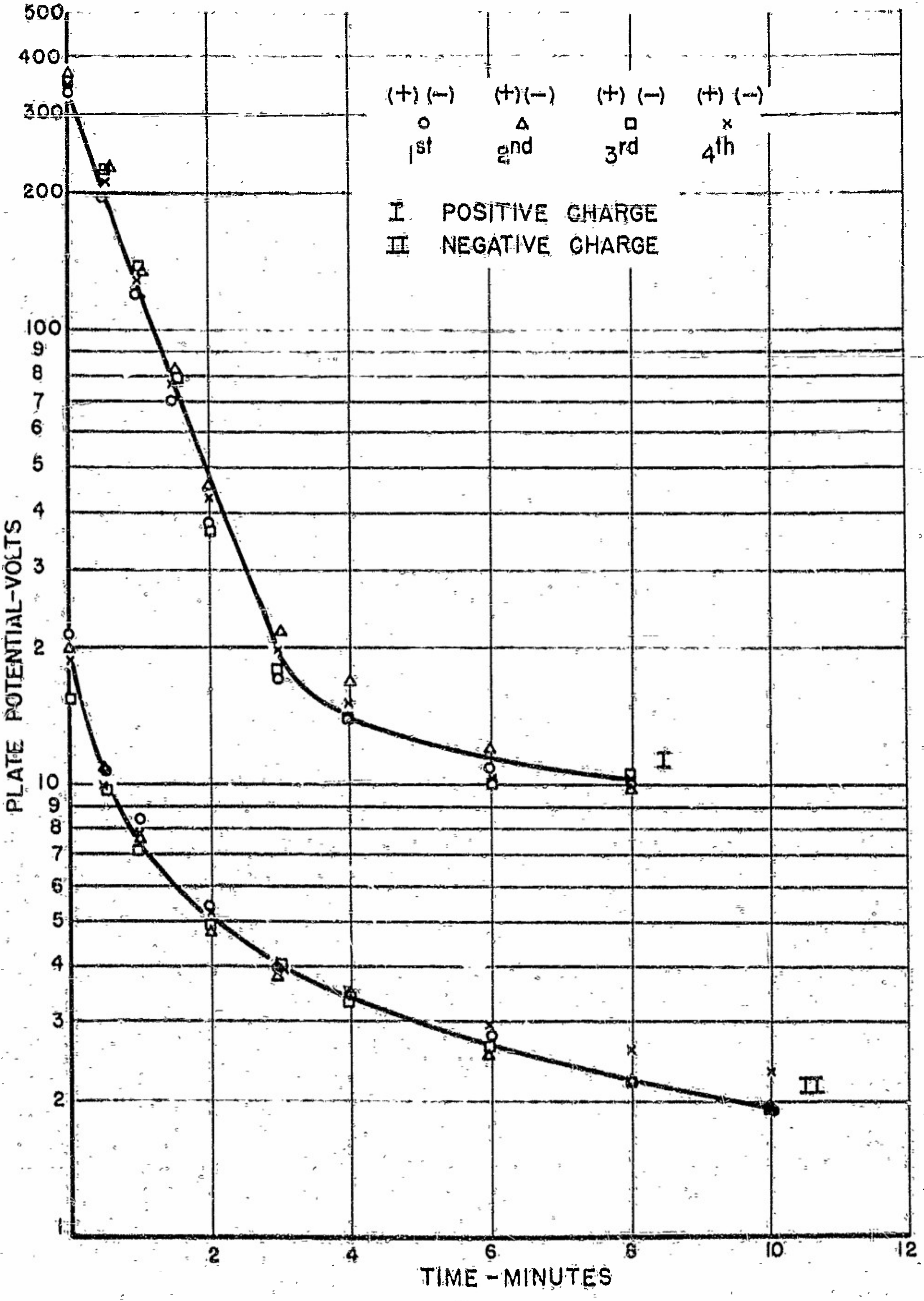

FIGURE 14. LIGHT DECAY CURVES FOR PLATE NO. II-7-47A, 4000-V CHARGE POTENTIAL

0-10050

experimental points in these curves are roughly the same in the three tests. As an estimate, it may be concluded that the data reproduced here to about ±5 per cent or better. The time for half decay shows no more than that same variability. No trend with successive chargings is here recognized.

Nature of Dark Decay

As will be noted later, the primary mechanism for dark decay is postulated to be one of thermal activation of a type approaching an exponential rate with time. To test this, Plate 11-7-47-A was charged and allowed to decay in the dark for 25 minutes. The curves are shown in Figure 15. Both positive and negative decay curves appear to be approaching an exponential time variation, as shown by a straight line in the semi-log plot of the figure. This indicates a thermal origin of the dark decay current, if the slope of the curve varies linearly with the reciprocal of the absolute temperature of the plate. If the dark decay is not of thermal origin, an exponential type of decay would still be anticipated. In such case, the origin of the dark-decay charge carriers would be an important thing to investigate.

Aftereffects in the Electrophotographic Sensitivity of Selenium Coatings

As a part of the information required for most effective utilization of electrophotosensitive coatings, it is important to know whether effects resulting from exposure to light cease immediately when the light is removed or whether the process continues. Such an effect might be made evident by studying the dark-decay rate immediately after the removal of illumination.

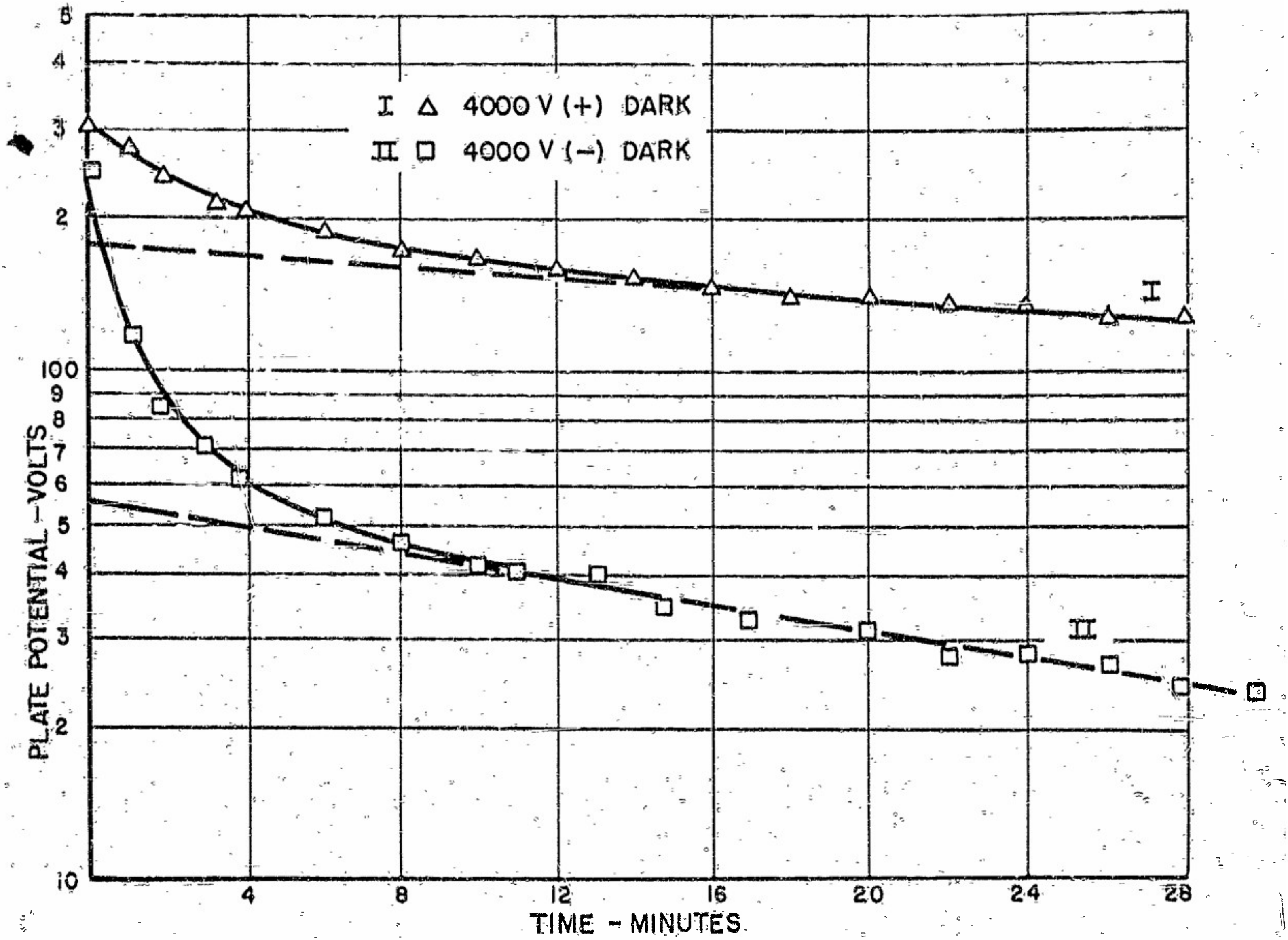

FIGURE 15. DECAY CHARACTERISTICS OF PLATE NO. 11-7-47 A

0-10051

To explore this, an evaporated Se plate 8-15-47-D-1* was charged, allowed to decay in the dark for a while, illuminated for a few minutes and then allowed to decay further in the dark. Results were then compared with dark and light decay curves produced under steady conditions. Results are shown in Figure 16, 17, and 18. Tests were conducted using both positive and negative charging.

A perusal of Figures 17 and 18 indicates that the dark decay curves with positive plate charge have the slope increased in the minute after illumination as compared to the dark decay curve of Figure 16. The increase in slope is between 30 per cent and 50 per cent during the first minute after illumination. On the other hand, there is no consistent change in slope observed due to illumination of the negatively charged plate. The slope of the appropriate dark decay curve of Figure 16 is dotted in on the curves of Figures 17 and 18 for comparison.

As will be discussed in a later section below, these results are not inconsistent with the theory.

Effect of Alcohol on the Electrophotographic Sensitivity of Evaporated-Selenium Films

The statement appears in the literature that soaking in alcohol will tend to cause vitreous selenium to change to the red monoclinic variety**. Accordingly, evaporated selenium plate 10-31-47-A was tested as to light and dark decay for positive and negative charge both before

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[*] Xerographic plate 8-15-47-D-1 was produced by evaporating two successive coatings of selenium onto the same aluminum base plate. Air was allowed to enter the bell jar between the deposition of the first and second coatings. Both "positive" light decay rates are a little above average. Other properties of this plate can be considered as average.

[**] Trans. Elect. Chem. Soc. 79, 11, (1941).

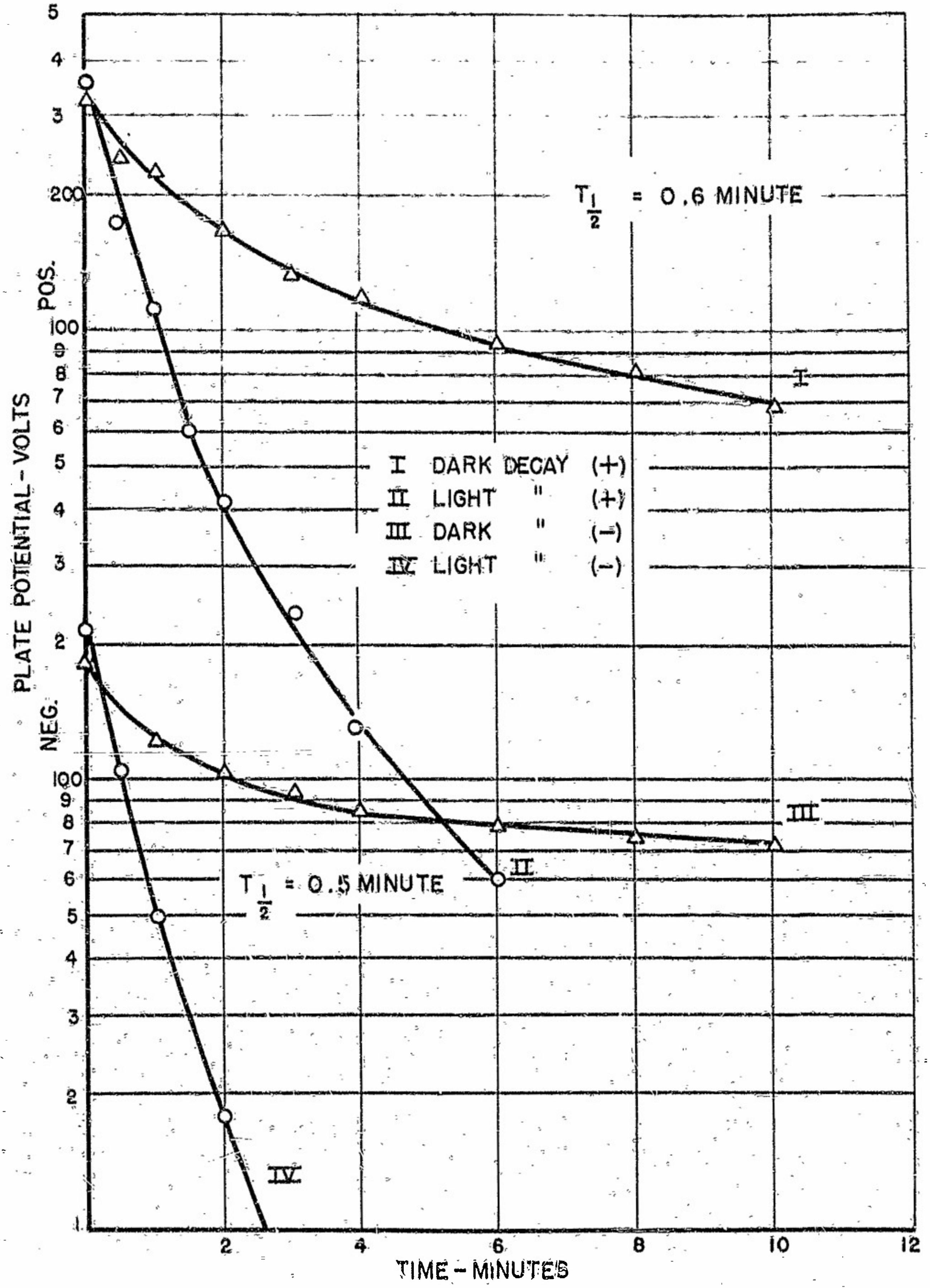

FIGURE 16. PLATE NO. 8-15-47 D-1, 4000 V.

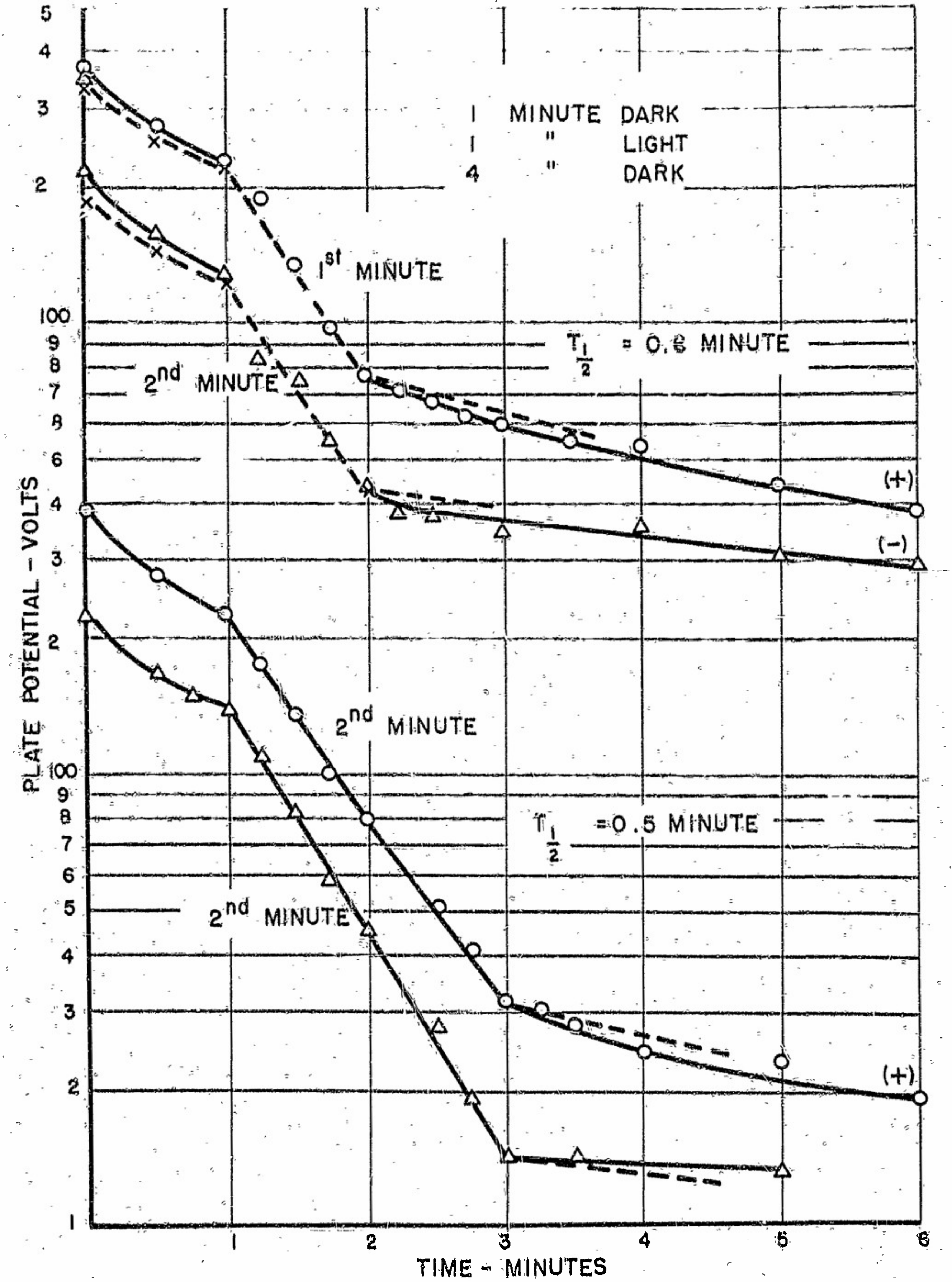

FIGURE 17. PLATE NO. 8-15-47-D-1, 4000 V.

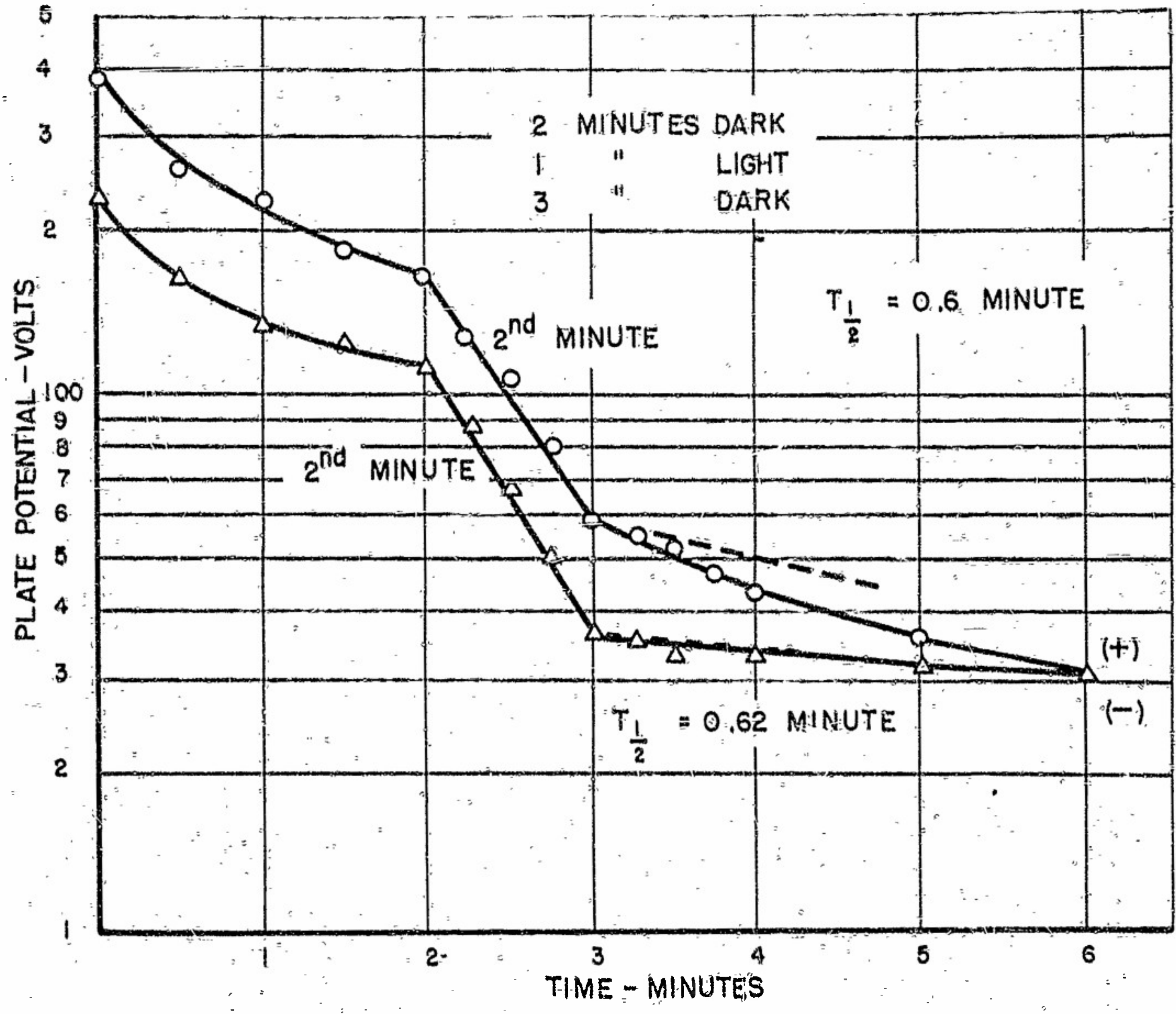

FIGURE 18. PLATE NO. 8-15-47 - D-1, 4000 V.

C-10054

and after soaking for 36 hours in ethyl alcohol in a closed drawer. Figures 19 and 20 show the results. It will be seen that the positive decay curves are not changed significantly by the soak. On the other hand, the negative decay curves start from a lower initial potential. The light decay curve is steeper, the half decay time being reduced from 1.35 to 0.65 minute. Furthermore, the exponential portion of the curve is longer, and the "residual" potential is lower after soaking.

The effects are apparently not due to cleaning the surface alone because of the different effects on the different curves. A portion of the effects might have resulted from exposure of the plate to light just before the test following the alcohol soak. An attempt to duplicate these results on two other plates was unsuccessful.

Effect of Different Backing Materials

There is some reason to feel that lower residual potentials are desirable in electrophotographic plates. It was surmised that such potentials might be due to a barrier at the selenium-backing plate interface. Accordingly, a set of four plates (stainless steel, nickel, cold rolled steel, and copper) were mounted on the same cooling platen; and a selenium layer was evaporated on the four simultaneously. The decay curves of the plates are shown in Figures 21, 22, 23, and 24.

The results of this test were quite unexpected. The stainless steel plate is what is called a "good positive plate," meaning one with positive light and dark decay curves widely separated. The other plates show inferior properties as positive, and superior properties as negative

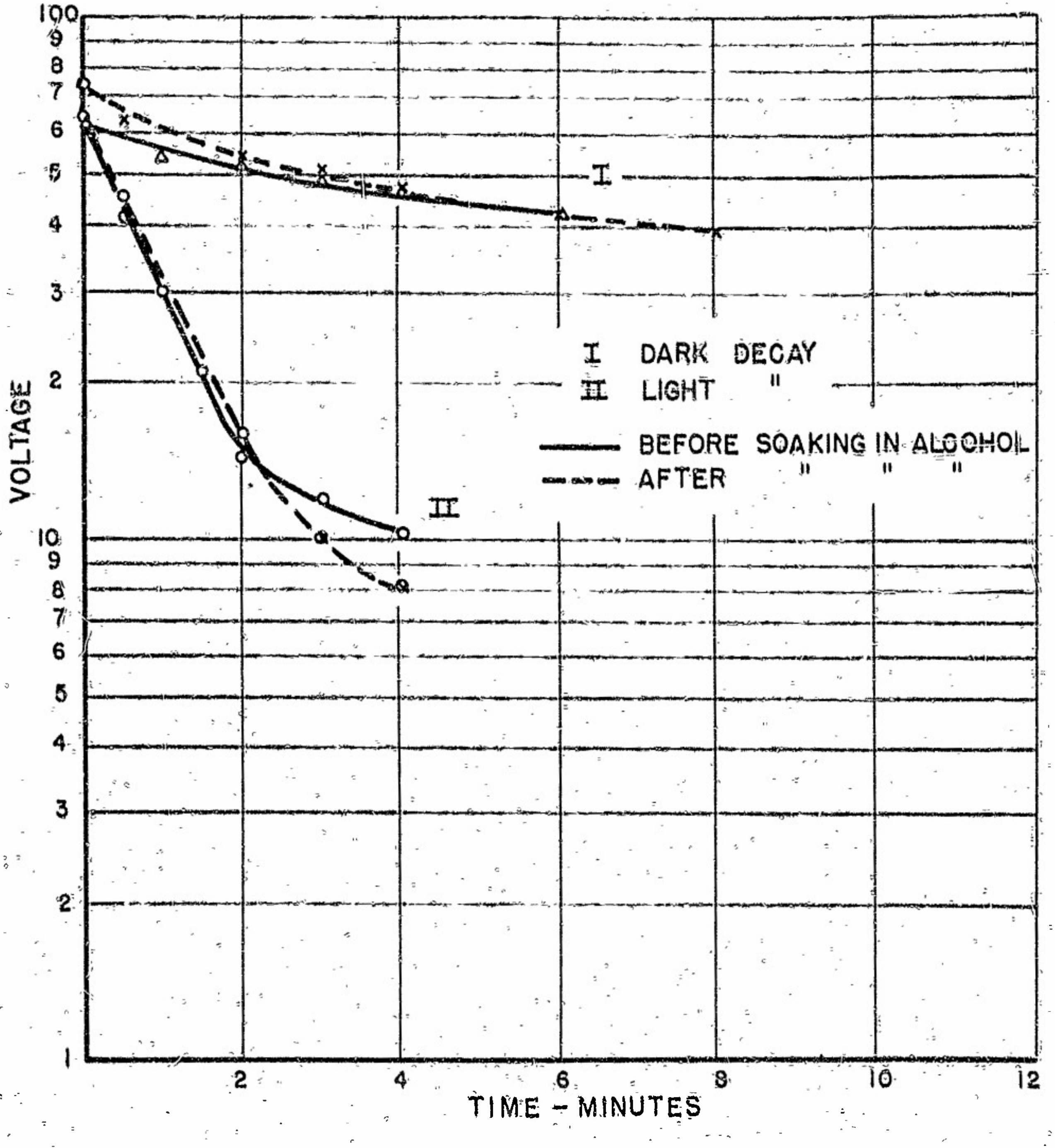

FIGURE 19. PLATE NO. 10-31-47A, 4000 V. (−)

0-10055

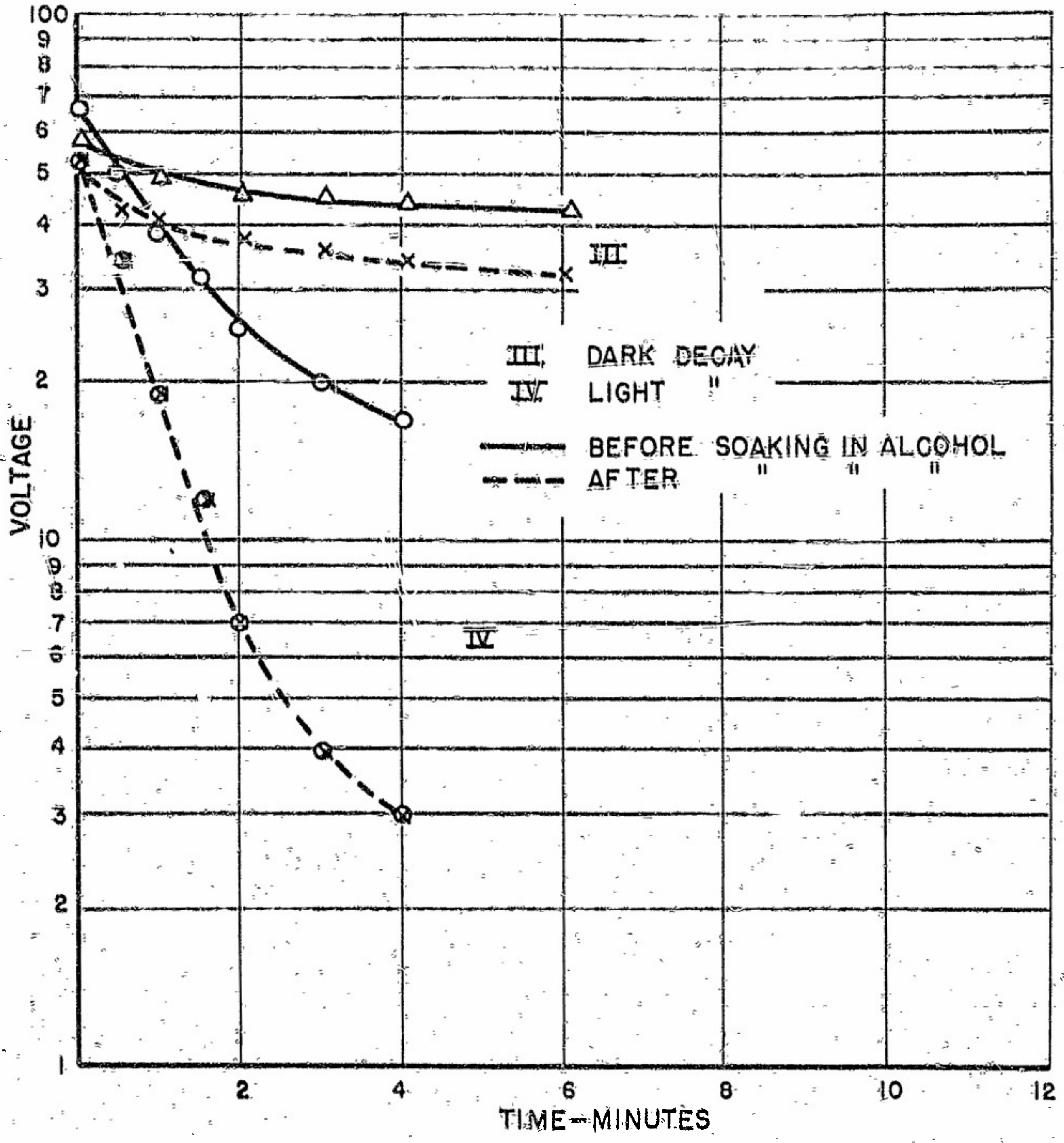

FIGURE 20. PLATE NO. 10—31—47A, 4000V.(—)

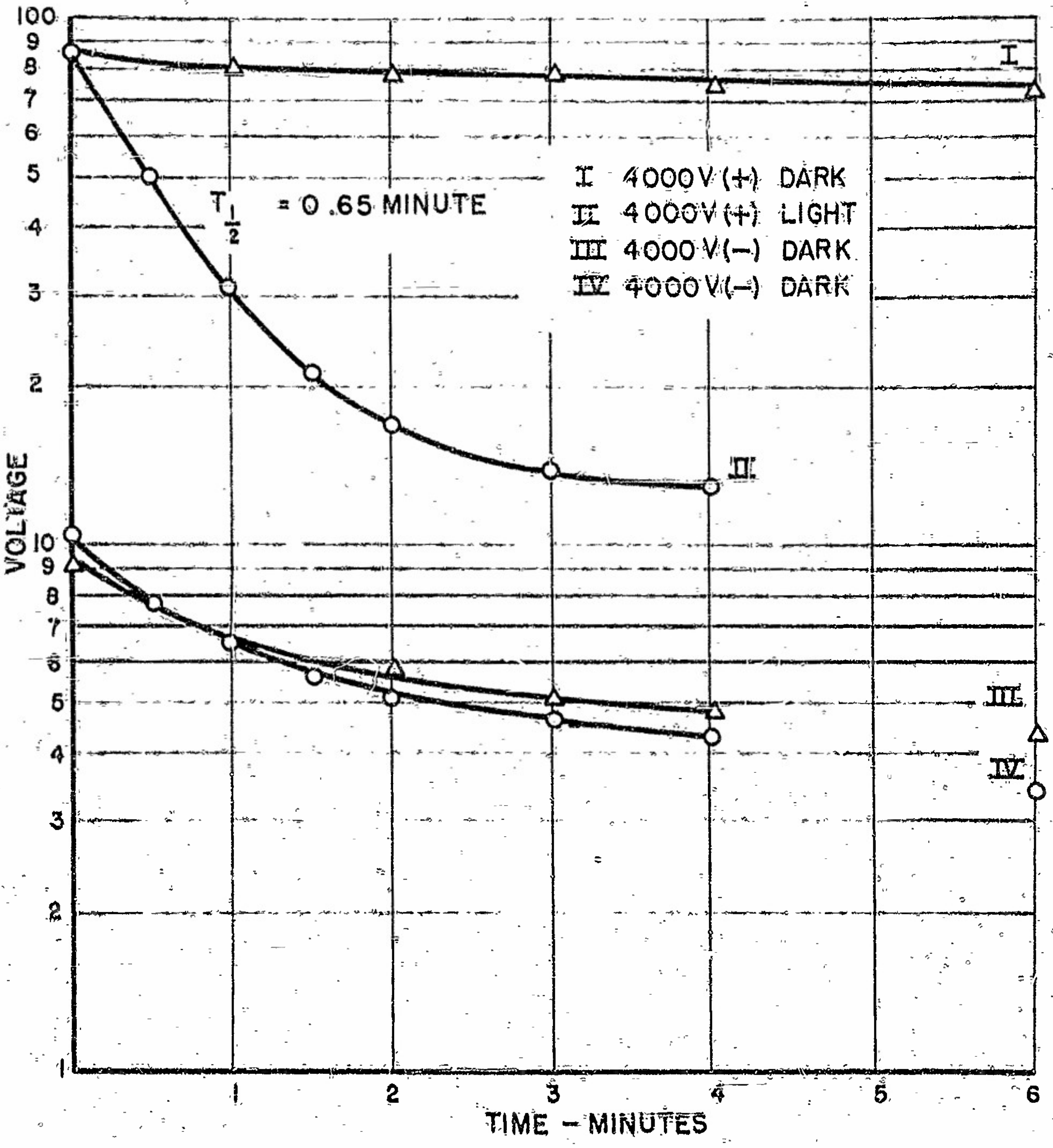

FIGURE 21. PLATE NO. 10-29-48 A II (STAINLESS STEEL BACKING PLATE)

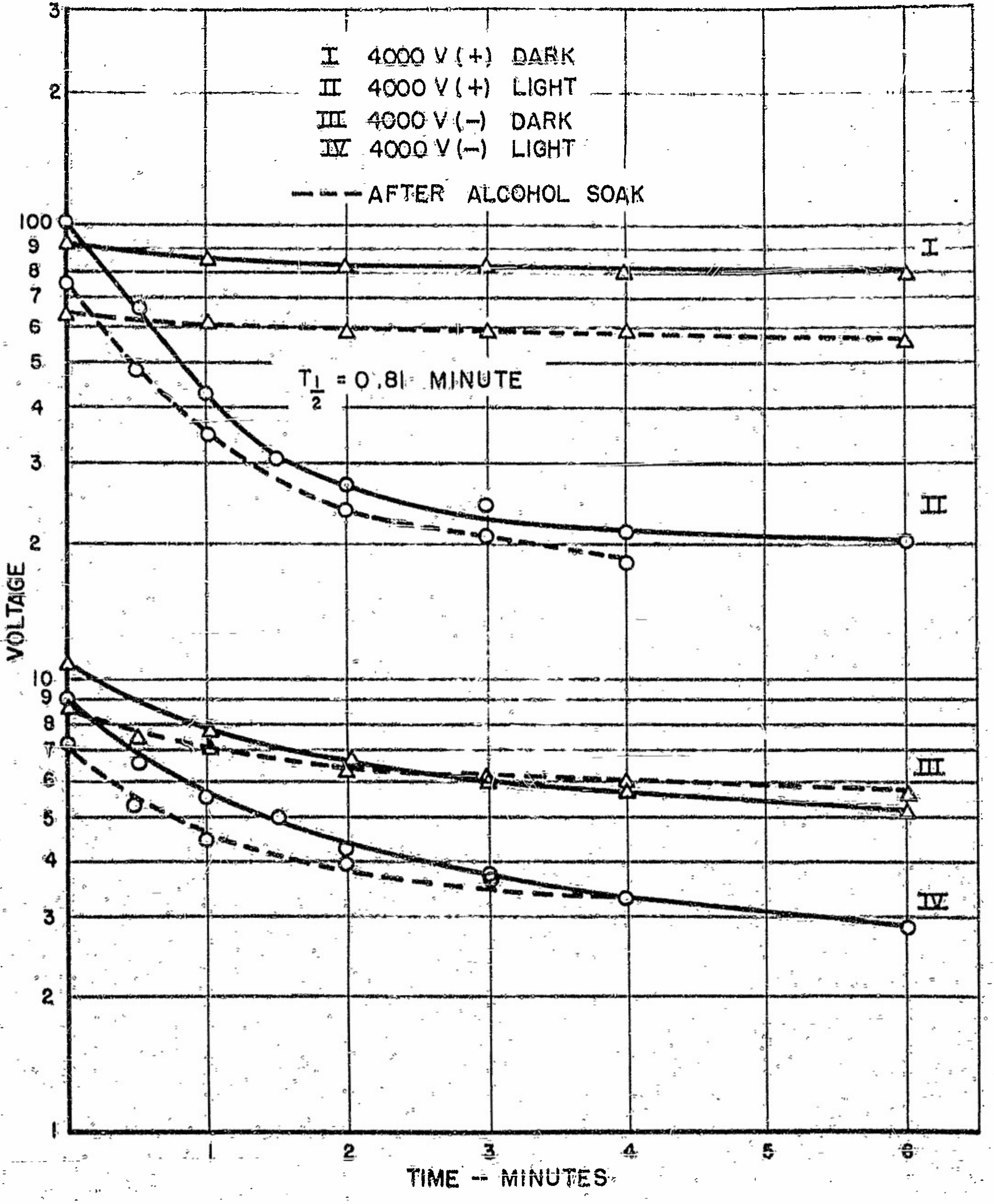

FIGURE 22. PLATE NO. 10-29-48A IV (NICKEL BACKING PLATE)

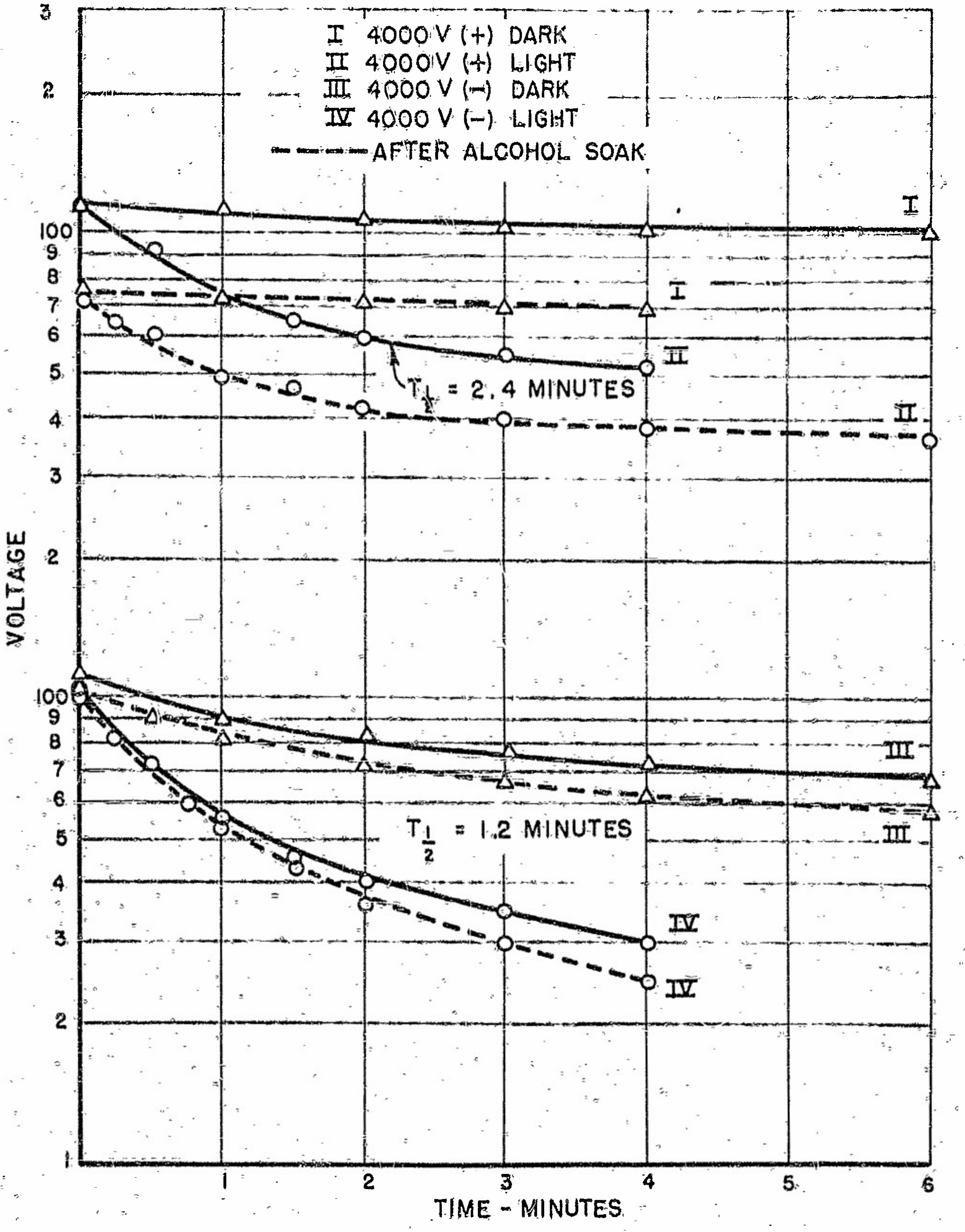

FIGURE 23. PLATE NO. 10-29-48AI (STEEL BACKING PLATE)

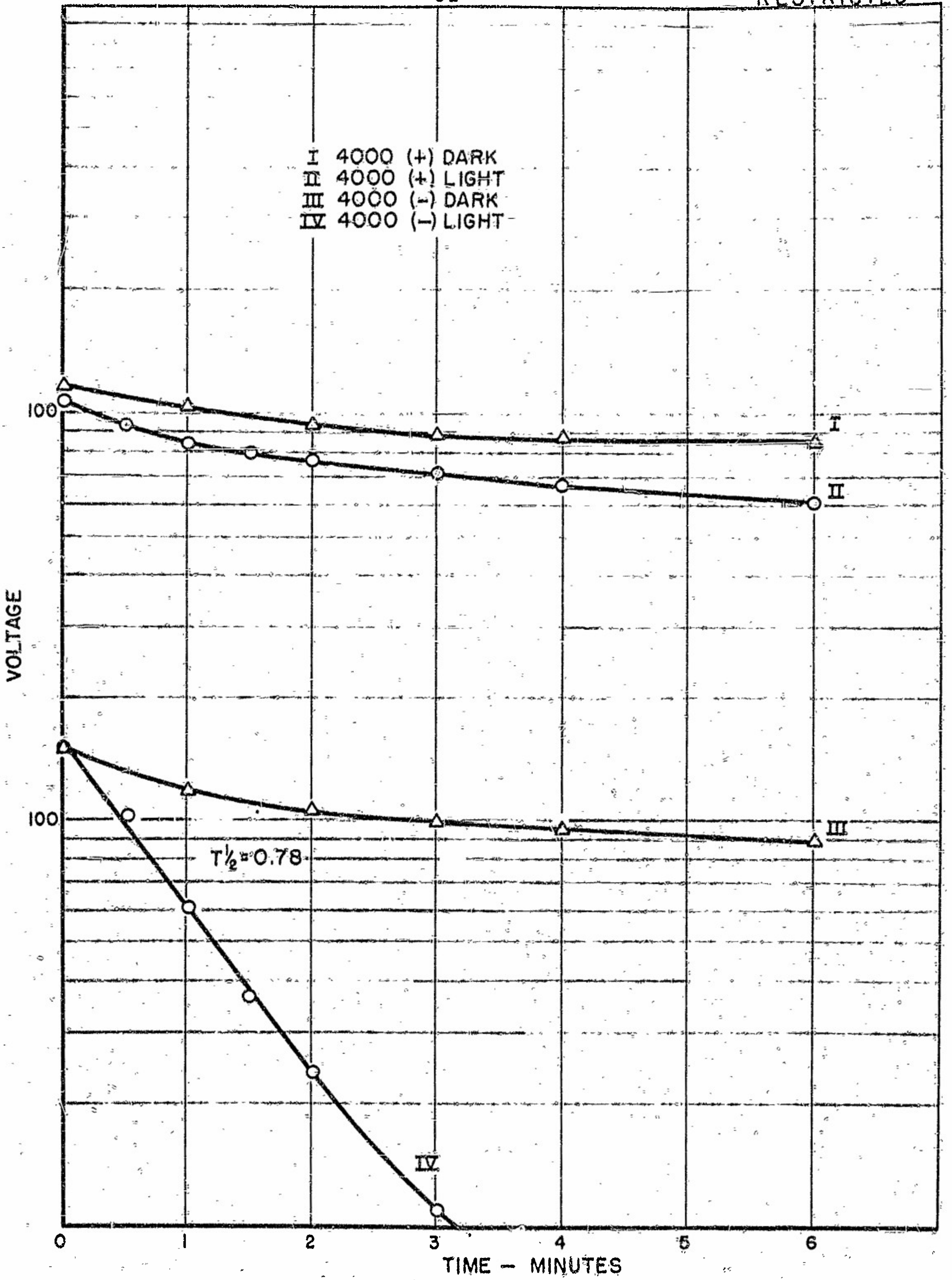

FIGURE 24. PLATE NO. 10-29-48 A III (COPPER BACKING PLATE.)

plates in the order, stainless steel, nickel, steel, and copper. This order, incidentally, is also the order of decreasing thermal conductivity of the four materials.

The original purpose of the experiment here was to see if there is a barrier to charge flow at the selenium-backing plate interface. This point must apparently be tested by use of the same backing material, but with a thin layer of different metals, in order that the bulk properties of the plates may not mask the effect of initial interest.

An X-ray examination of the four plates described revealed only the lines of the base material and a background indicating amorphous selenium. Measurement of the resistivity of the selenium layer on the plates showed resistances of 2.8×10^{11} and 4.1×10^{11} ohms./cm.^{2} for positive and negative upper electrodes, respectively. There was no perceptible difference from plate to plate.

EXPERIMENTS ON SELENIUM ELECTROPHOTOGRAPHIC FILMS MADE BY OTHER METHODS THAN EVAPORATION

Methods Used in Applying Films

In order to have suitable methods available for carrying out the large variety of examinations to be made, as well as in the interest of finding new ways of preparing selenium films, a number of ways of applying films were surveyed. Table 9 shows the results of this survey. It will be specifically noted that:

1. Spraying molten selenium provides a rapid means of studying effects of controlled impurity additions to selenium.

TABLE 9. RESULTS OF INVESTIGATING VARIOUS METHODS OF APPLYING SELENIUM PHOTOACTIVE FILMS

Nature of Method	Pertinent Facts Concerning Film Formation	Electrometer and Other Tests for Photoactivity	Image Tests	Comments on Usefulness as a Method of Manufacture
Molten selenium spraying	Requires controlled temperature of molten Se, base plate, and pressurized gas; critical control of base plate temperature, comparatively thick film inclined to wavy, glassy surface, can be done with and without quenching; requires a modified, low-temperature metallizing gun.	Films show decay rates comparable to those for evaporated plates if selenium purity is controlled.	Good images, time of exposure, background, and other conditions very similar to those for evaporated plate.	Good for studies of impurity effects; must be further developed to determine extent of usefulness.
Platen pressing (stick-coat or powder-coated plates)	Base plate cold for powder method; base plate temperature greater than selenium M.P. for stick coated; rub stick or spread powdered, vitreous Se on base; surface yields glassy layer in stick case; surface and film thickness are functions of temperature of press, pressure, and type of platen surface; adherence good.	Takes no charge; resistance across layer less than 10^9 ohms; indicates crystallinity.	--	Appears promising if crystallinity can be eliminated; plate size only limited by size of press; however requires excellent press and base tolerances.
Spinning method	Rotating, heated base plate, drop molten selenium on base; surface wavy; surface nature and film thickness functions of speed of rotation, temperature of base, and flaming of surface	Films photoactive. No detailed information.	--	Only useful for small plates; not too promising.
Dipping	Very thick films; no control over uniformity and thickness; because of poor wetting of base; adherence poor.	--	--	Not promising, viscosity of selenium too high.
Pigmented selenium paint spraying	Common paint spray methods used; acceptable control of film thickness and uniformity controlled by pressure, modifying paint viscosity by highly volatile solvent, and speed of spray sweep; surface nature flat--not glossy.	Films show decay rates somewhat lower than evaporated films; -- variations in selenium purity, selenium pigment-binder ratio, perhaps particle size and type of binder cause changes in light decay rate.	Good contrast (not so good as evaporated plate for 1-mil. film thickness) high uniform background.	Very promising; plate 4 size almost unlimited; useful for any plate geometry; has flexibility, provides means of shielding selenium from atmosphere, can be used for studying impurities in selenium.
Drawing down selenium-pigmented paint	Film thickness function of flatness of base; surface character function of most of the same factors listed above for spraying.	Same as for sprayed paint.	Same as for sprayed paint.	Limited size, restrictions on base-plate curvature.

2. Platen pressing as done in the selenium rectifier industry fails because under conditions for which a selenium film can be produced, the film resistance is too low(10^9 ohms). The presence of considerable grey hexagonal selenium in such layers is noteworthy. This method, however, appears promising for several purposes if crystallization to grey hexagonal crystals can be minimized.

3. Spraying selenium pigmented paints apparently has considerable promise as a production method if the high background common to the prints obtained from such plates can be eliminated.

Evaporated plates are considered in another section of this report.

The Role of Refinement and Treatment of Selenium

Selenium purity and the nature of its structure as it is received from the supplier is known to be important in obtaining consistent results in the rectifier and photocell industry. When using either the selenium paint or molten spraying methods, in contrast to evaporation, for forming electrophotographic selenium films, the quality of the selenium as received becomes an important factor for consideration. In the interest of determining (a) whether any or all the commercial grades of selenium could be used for electrophotographic purposes when using these methods, and (b) what role the methods of preparing the selenium and applying films of these types of selenium played, tests on the various types of selenium were made. Table 10 shows the compiled results of these tests. It will be particularly noted that:

1. ARQ selenium is apparently consistently satisfactory from batch to batch.

TABLE 10. ELECTROPHOTOGRAPHIC AND OTHER PROPERTIES OF VARIOUS COMMERCIAL AND TREATED COMMERCIAL SELENIUM

No.	Lot of Se	Treatment of Se	Method of Applying Se Film	Electrophoto-activity	Comments
1	ARQ - no inoculation, melted in stick form.	Melted, shotted, and ground.	Se pigmented parlon-rezyl paint film	Satisfactory	Image was formed. Se came from B-L-Co. No aging of paint.
2	CCR - Ref. Se (A) powder form.	No treatment.	Ditto	Unsatisfactory. No charge.	Obtained from source within B.M.I.
3	CCR - Ref. Se (A) powder form.	Melted, shotted, and ground.	"	Satisfactory	Image formed. No sludge formation during shotting.
4	CCR - Ref. Se (2A) powder form.	Melted, shotted.	"	Unsatisfactory.	Molten Se (220°C. readily shotted)
5	Ditto	Ditto	Hot molten Se sprayed	"	Gummy mass appeared 250°C.; this persisted and grew more pronounced, also viscosity increased up to 300°C.; viscosity decreased up to 400°C. where it could be shotted. This shot was brittle and porous.
6	CCR - Ref. Se (1A) powder form.	Melted	-	-	Same as (2A), but gummy mass appeared at 2[illegible]°C. and remained to 370°C.; not able to shot at higher temperature, but could underpour.

TABLE 10. Continued

No.	Lot of Se	Treatment of Se	Method of Applying Se Film	Electrophotoactivity	Comments
7	CCR - Ref. Se (2B)	Melted	-	-	Same as (1A).
8	CCR - Ref. Se (1B)	Melted, shotted.	-	-	Molten Se (220°C.) no gummy mass up to 380°C. This Se was easily shotted - could be compared to Lot A.
9	CCR-ARQ Se No. CP-54-10-8.	Melted, shotted.	-	-	No sludge formation during heating Se for pouring.
10	Ditto	None	Hot molten Se sprayed	Satisfactory	Images obtained.
11	"	None	Se-pigmented parlon-rezyl paint film	"	Images obtained. Made 1 gallon of this paint for various experiments.
12	CCR-DDQ Se No. 5-51	Melted, shotted.	-	-	No sludge formation during heating Se for pouring.
13	CCR-DDQ Se No. 5-51	None	Hot molten Se sprayed	Satisfactory	Images obtained. No background.
14	Ditto	"	Se pigmented parlon-rezyl paint film	Fair	Poor images. High background.
15	CCR-ARQ Se No. 56-11-8	None	Ditto	Satisfactory	-

2. Presence of grey hexagonal selenium in C. C. R. refined selenium is probably one cause for its failure since remelting and shotting the powder sometimes is sufficient to make this selenium satisfactory. However, thermal cycling indicates that certain impurities in the selenium are perhaps more often the cause for failure. Table 11 shows a spectroscopic analysis of a batch of refined selenium which was not satisfactory. Thermal cycling tests on several batches of the refined selenium indicate through their different trends of viscosity that the undesirable impurity content varies from one batch to another.

3. D. D. Q. selenium may be satisfactory. Further tests must be conducted to be certain, however.

Effects of Controlled Impurity Additions in ARQ Selenium

Using ARQ selenium, under the assumption that it is reproducibly the same (as shown in the above tests) and quite pure, and employing the molten selenium spraying method of applying films (see Appendix for discussion) the effects on electrophotographic action of controlled amounts of impurities were studied. Table 12 shows the results of these studies. The manner in which the recorded data in this table were obtained is discussed in the Appendix under "Methods of Testing". Owing to the non-uniformity of film thickness among the plates of this series, resulting from inadequate equipment for controlled spraying, and some variations in the sprayability of the contaminated seleniums, comments on these results must be limited at the moment. However, the following trends are to be noted:

TABLE 11. SPECTROGRAPHIC ANALYSIS OF ONE BATCH OF REFINED SELENIUM (CCR)

Batch of Selenium	Impurities and Estimated Percentages of Them Present in the Selenium		
IIA Selenium, melted and shotted	Fe .05-.5	Ca < .03	Si .01-.1
	Al < .01	Mg < .03	Cu .01-.05
	Sn < .01	Pb < .01	Mn < .005
	Ag < .005	B < .005	

TABLE 12. EFFECTS OF CONTROLLED ADDITIONS OF VARIOUS IMPURITIES IN ARQ SELENIUM ON PHOTOACTIVITY AND IMAGE FORMATION OF HOT MOLTEN SPRAYED SELENIUM FILMS

			Electrometer Test						Image Formation			
			Positive Polarity			Negative Polarity						
	Type	No. of Plates Tested	Total Charge, Volts	Light Decay, %/min.	Dark Decay, %/min.	Total Charge, Volts	Light Decay, %/min.	Dark Decay, %/min.	Time of Exposure	Light Intensity	Quality of Image	Background
Controls	Evp. plate	1	120	306	50	98	400	28.6	1/4 sec.	90 volts	Very good	Low
	Sprayed DDQ	5	160-510 267	108-220 177	31-61 48	190-550 352	270-376 353	37-60 51	1/2 sec.	70 volts	Ditto	"
	Sprayed ARQ	7	105-600 361	167-350 243	18-45 30	190-590 351	142-337 240	22-42 32	1/4 sec.	90 volts	"	"
Impurity Contaminated Selenium	ARQ + 1% LiCl	4	40-305 115	160-256 222	65-160 120	130-360 221	233-379 337	41-126 95	1/4 sec.	90 volts	"	"
	ARQ + 2% Te	5	550-670 613	58-109 87	14-31 23	455-723 571	76-103 86	14-29 21	1 sec.	90 volts	Faint	"
	ARQ + 2% CeI_2	4	0-37	-	- Practically no charge observed.	0-39	-	-	-	-	None	-
	ARQ + 1% Bi	5	229-640 524	55-117 75	27-50 33	270-495 411	69-250 124	19-67 37	-	-	-	-
	ARQ + 1% HgS	7	190-712 510	100-164 119	14-44 28	200-860 595	97-166 129	13-28 23	1/4 sec.	90 volts	Poor	High
	ARQ + 1% $BiCl_3$	4	0-23	-	- Little or no charge observed.	-	-	-	-	-	None	-
	ARQ + 1% Cd	2	47-95 71	120-124 122	75-86 82	100-150 125	350-388 369	71-114 93	-	-	-	-
	ARQ + 1% $CdCl_2$	3	-	-	- Little or no charge observed.	-	-	-	-	-	None	-

NOTE: 1. These plates have wide thickness variations over their surfaces (0.002 - 0.022 inches). This may account for the wide range of values among the samples of each group. The maximum and minimum values are shown above the average values.
2. Image data are for one plate only.
3. 4000-volt potential used in electrometer test.
4. 7000-volt positive potential used in image tests.

1. Considerable variation in the charge accepted by the plate occurs as a result of impurity additions. Note that Tellurium definitely increases the level of charge accepted while CeI_2, $BiCl_3$, and $CdCl_2$ decrease it to zero. Because of the differences in Bi and $BiCl_3$, and Cd and $CdCl_2$ action in this regard, it appears that halogens are detrimental to retaining the required insulating properties of the film.

2. In general, the dark decay increases when the light decay increases as a result of impurity additions. See for example the Li case.

3. There appears to be a correlation between light decay rates and image formation. This can be seen by comparing the Li, Te, and CuS addition cases.

4. Because of the large difference in thickness between the evaporated selenium control plate and the observed fluctuations among the several plates of separate groups, which also varied in thickness, one can only make comparisons to evaporated films in a rather superficial manner since film thickness appears to be an important variable.

5. Qualitatively it is observed speed and quality of image formation from evaporated, selenium sprayed DDQ, ARQ, and Li contaminated selenium are comparable.

6. The difference between the amount of charge accepted and the light decay rates with positive and negative polarity is quite variable. In particular, it will be noted in the Cd case that as much as a factor of three difference in positive and negative light decay rates with very little accompanying difference in positive and negative dark decay rates

is observed. In no case was the positive light decay larger than the negative although with tellurium and CuS the two were approximately equal.

In general, a dependancy of electrophotographic nature of plates on type of impurity content is to be expected according to these results.

Effects of Binder Material

Using ARQ selenium and the selenium pigmented paint method, a study was made to acquire information on the effect of type of binder material on paint film appearance, photoactivity, image formation, and X-ray structure. Table 13 shows the results of this study to date. Because of the better control of film thickness with the paint than in the hot Se spraying method, these data can be discussed with greater freedom than those in the previous section.

The following types of trends can be seen in the table:

1. The type of binder or solvent does not strongly control the electrophotographic properties of the film. However, the image formation apparently varies with binder type. Owing to the lack of information on effects of powder developer in the presence of different binders this difference cannot be attributed to the change in photosensitive properties of the incorporated selenium since it might be accounted for by the powder developer.

2. The binder or solvent does control the structure of the selenium. Apparently some binders can promote the formation of alpha monoclinic selenium.

3. The binder or solvent does affect the color of the film.

TABLE 13. EFFECTS OF BINDER MATERIAL AND PAINT SOLVENT ON THE APPEARANCE, PHOTOACTIVITY, IMAGE FORMATION, AND X-RAY STRUCTURE OF ARQ Se-PIGMENTED PAINT FILMS

Binder Material	Solvent Used for Spraying as Paint	Color	Photo-activity	Image Formation			X-ray Structure
				Time of Exposure	Light Intensity	Image	
Parlon-rezyl	Toluene	Chocolate red	Yes	3 sec.	90 volts	Very good medium uniform background	Amorphous with some alpha monoclinic Se
Silicone DC-804 air dry	"	Black with red cast	Yes	1.5 sec.	90 volts	Good medium uniform background	Alpha monoclinic selenium
Silicone DC-2103 (oven dry 5 min. 400°F.)	"	Grey	No	—	—	No image	No analysis probably grey hex. (owing to heat treatment)
Acryloid A-10	Cello-solve acetate	Chocolate red	Yes	1.5 sec.	90 volts	Faint with high uniform background	Alpha monoclinic plus grey hex. as minor phase
Acryloid B-72	Toluene	Light chocolate red	Yes	.75 sec.	90 volts	Good medium low background	—

TABLE 13. Continued

Binder Material	Solvent Used for Spraying as Paint	Color	Photo-activity	Image Formation			X-ray Structure
				Time of Exposure	Light Intensity	Image	
Vinylite Co polymer	Methyl iso-butyl kentone plus toluene	Grey black	Yes	1 sec.	90 volts	Very faint high uniform background	Amorphous selenium
Polystyrene	X-ylane	Grey black	"	1 sec.	90 volts	Ditto	Alpha mono-clinic selenium

NOTE: 1. All film thickness approximately 1 or 2 mils thick.
2. "X" structure = alpha monoclinic.

4. Binders, which require high-temperature heat treatment to set the paint, fail because of formation of grey hexagonal selenium.

In general, it appears parlon-Rezyl and silicone (air dry) are the best binders used to date.

The outstanding result of these studies in regard to gaining an understanding of film structure is the information that selenium may be observably crystalline (alpha monoclinic) and still be photosensitive in the sense of electrophotographic needs.

Effects of Post Heat Treatments of Electrophotographic Films

Owing to indications that (1) binder or solvent causes changes in selenium structure, and (2) heat treatment to set a paint is detrimental if grey hexagonal selenium is formed and because of the known dependence of selenium structure on its treatment, post heat treatments were made on various types of selenium paint films. Information on the effects on appearance, photoactivity, image formation, and X-ray structure were sought. Table 14 shows the results of heat treating for 5 minutes at 220°C., followed by water quenching.

The following trends are to be noted in this table:

1. Selenium films, exhibiting grey hexagonal selenium, amorphous, and "I" crystalline structures and various colors before heat treatment, all turned a red brown color and showed an unknown structure denoted as "Y" crystalline after heat treatment. Because of the distinction between this and the "X" or alpha monoclinic structure, the independence of its occurrence on the starting structure, and its not being observed without a binder

TABLE 14. EFFECTS OF HEAT TREATMENTS (AFTER PRODUCTION OF PLATES) ON THE APPEARANCE, PHOTOACTIVITY, IMAGE PRODUCTION AND X-RAY STRUCTURE OF VARIOUS TYPES OF ELECTROPHOTOGRAPHIC FILMS

Type of Film	Before				Type of Treatment	After			
	Appearance	Photoactivity	Image	X-ray Structure		Appearance	Photoactivity	Image	X-ray Structure
Refined Se powder in parlon-rezyl binder	Grey-black flat surface	No	No	Grey hex. Se	5 min. 220°C., water quenched	Red-brown	Yes	Yes	"Y" crystals
Remelted shotted refined Se in parlon-rezyl binder	Chocolate red	Yes	Yes	Amorphous Se	Ditto	Red-brown	Yes	Yes	No analysis, probably "Y"
Chemically precipitated red Se in parlon-rezyl binder	Bright red	No	No	"T" Crystals some background indicating amorphous (red?)	"	Red-brown	Yes	Yes	"y"*
Lab.-crystallized Se in shellac	Black	No	No	Grey hex. Se	"	Chocolate red	Yes	Yes	"y"
ARQ Se in DC-2103 oven dry silicone 420°F. - 5 min.	Grey-black	No	No	-	"	Black shot on clear background	No	No	-

NOTE: "Y" has not been identified; it may be an organic selenium compound.

* During treatment color changed from red-black to deep brown.

encompassing the selenium, it appears some interaction of the binder and selenium produces it.

2. "Y" crystalline structure films are photoactive and will give images.

3. The type of binder is also important in another way in determining the effect of heat treatment, as indicated by the marked difference in results for the silicone 2103 case. Apparently the selenium preferred to coagulate out of its dispersed state indicating some bonding exists between selenium and binder in other paint films.

It appears that post heat treatments of paint films should be considered as a means of making poor films into good ones.

These results have given further insight into film structures, which have electrophotographic properties, through discovering a new crystalline structure which is photoactive.

Effects of Various Surface Treatments of Electrophotographic Films

In the course of the work on electrophotography, it has been observed that surface roughness controls image background to some extent. Owing to the high background in prints from most paint films and the rather flat, not glossy, surface nature of these films, it appeared that one could not conclude background was caused by the binder until effects of varying surface properties were investigated. Also indications of mottled background in the prints from hot sprayed selenium films and the complimentary observation of somewhat wavy surfaces were believed to be related. In addition, since the formation of an electrostatic image and the resultant transfer of it by powder must be a function of surface properties of the film, it appeared that surface treatments of various types might reveal new information.

Therefore, various types of surface treatments of electrophotographic films have been made. Table 15 shows the results of polishing, coating, and chemical attacks on the surface.

In particular it is to be noted:

1. Polishing will eliminate the spots in the background on prints made from hot molten sprayed selenium films.

2. Polishing has no effect on the background in prints from paint films, thus indicating the binder and not the surface roughness is responsible for this background.

3. Lacquer films on pressed selenium plates having unsuitable properties are not effective in inducing photoactivity although they serve as a means of holding a charge on the surface. Also lacquer films will smooth a rough surface of a usable plate so an image can be obtained.

4. Rectifier barrier layer chemical treatments on unsuitable presse plates do not change the response of the plate in an observable way.

Film Structure Versus Photoactivity

Because of the nature of the structural data obtained on the plates produced in the above survey and the basic role an understanding of film structure plays in development of electrophotography, further studies of selenium structure were made. Table 16 records all new and previous data on selenium structure and their relationships to photoactivity or image formation.

TABLE 15. EFFECTS OF VARIOUS TYPES OF POST TREATMENTS (AFTER PRODUCTION OF PLATE AND OTHER THAN HEAT TREATMENTS) ON THE APPEARANCE, PHOTOACTIVITY AND IMAGE FORMATION OF VARIOUS TYPES OF ELECTROPHOTOGRAPHIC FILMS

Type of Plate	Before			Type of Treatment	After		
	Appearance	Photoactivity	Image		Appearance	Photoactivity	Image
ARQ Se hot molten sprayed	Wavy black	Yes	Good image, some background and spots	Polished by metallographic method GRO polish	Mirror glass surface	Yes	Very good. No background.
ARQ Se pigmented parlon-rezyl paint	Red-brown flat surface	Yes	Good image with medium uniform background	Ditto	Smooth, almost mirror surface	Yes	Good image, some background
ARQ Se stick coated on hot base	Wavy and glossy	Yes	-	Rough polished with 600 grit paper and lacquer film applied	Smooth, scratches evident, glossy.	Yes	Very fast image.
ARQ Se stick coated on hot base, platen pressed	Smooth glossy surface	No (no charge taken)	No	Applied thin lacquer film	Smooth glossy surface	No (took a charge)	No
GCR refined Se in parlon-rezyl; heat treated 220°C. for 5 min.	Red-brown, rough	Yes	Evidence of image, but difficult to transfer powder	Applied thin lacquer film	Red-brown glossy somewhat less rough	Yes	Very faint image powder transferable
ARQ Se stick coated and pressed	Smooth surface	No	No	Treated with tergitol penetrant to establish a rectifying barrier	No change	No	No

TABLE 16. COMPARISON OF STRUCTURAL NATURE AND PHOTOACTIVITY OF VARIOUS FILM TYPES

Number	Type of Film or Powder	Color	X-ray Structure	Photoactivity or Image Formation	Remarks
1	ARQ lab. ground powder	Grey with red cast	Alpha monoclinic selenium	No data; assumed photoactive.	--
2	ARQ lab. ground powder in parlon-rezyl film	Grey ↓ * red	Alpha monoclinic selenium	Yes	Heat treatment at 220°C. for 5 min. gives chocolate-red, "Y" structure, photoactive film.
3	ARQ shot (as received from COR)	Black	Amorphous selenium	No data; assumed photoactive.	--
4	ARQ shot milled with parlon-rezyl as film	Chocolate red	Alpha monoclinic	Yes	--
5	Crystalline ARQ lab. ground powder with and without binder	Grey	Grey hex. selenium	Nonphotoactive with binder, assumed nonphotoactive without binder	--
6	ARQ Se hot molten sprayed	Black	Amorphous selenium	Yes	--
7	ARQ Se stick coated and hot pressed (150°C.)	Black	Grey hex selenium	No	--
8	ARQ Se evaporated	Black reddish cast possibly result of thinness	Amorphous selenium	Yes	--
9	DDQ shot (as received from COR)	Black	Amorphous selenium; slight evidence of crystals	No data; assumed photoactivity.	--
10	DDQ shot milled with parlon-rezyl	Chocolate red	Alpha monoclinic	Yes	--
11	Refined Se (as received)	Grey	Grey hex. selenium	No data; assumed not photoactive.	Gives same as (2) when heat treated.
12	Refined Se powder in parlon-rezyl and all other binders tried.	Grey to Black	Grey hex. selenium	None	--

TABLE 16. Continued

Number	Type of Film or Powder	Color	X-ray Structure	Photoactivity or Image Formation	Remarks
13	Remelted and shotted refined selenium in parlon-rezyl	Grey → red	Amorphous selenium	Yes	Gives same as (2) when heat treated.
14	ARQ Se + 1% $BiCl_3$ hot molten sprayed	Black	Amorphous selenium no Bi lines	No	—
15	Chemically precipitated red selenium (reduced selenous acid by So_2) in parlon-rezyl.	Red	Crystal "T" and back ground amorphous (red?)	No	Gives same as (2) when heat treated.
16	Fibrous ~~mat~~ layer with grey appearance collected on cold plate from Se smoke.	Red surface grey underneath	Grey hex. Se	Yes	—

NOTE: "T" structure = Alpha monoclinic.

* ↓ After paint aged the paint changed color from grey to red.

→ When ball milling with steel balls in place of glass balls, the paint turned reddish color. The analysis was made on the glass ball milled material.

In reviewing this table, it will be noted that:

1. Any selenium or selenium-binder film with an appreciable amount of grey hexagonal selenium will not be photoactive for electrophotographic purposes.

2. Crystalline alpha monoclinic selenium, amorphous selenium and "Y" type (may be an organic compound of selenium) structures support photoactivity.

3. As a function of method and extent of refining of selenium, it appears refined selenium processing is undesirable owing at least partially to the presence of grey hexagonal selenium in the product, since remelting and shotting of some batches will give amorphous selenium.

4. In regard to the method of application, it appears any method which involves appreciable temperatures during processing is undesirable because of grey hexagonal selenium formation.

5. Chemically precipitated red selenium gives the only other observed structure different from grey hexagonal selenium which is not photoactive in the sense of electrophotography. (This test will be repeated, since the failure was due to not accepting charge and this seems somewhat unreasonable in view of the fact that red selenium should be an insulator.)

6. Some methods of grinding selenium and the incorporation of selenium in a binder tend to give alpha monoclinic selenium. Evaporation and hot spraying methods give amorphous selenium.

7. In most cases, the occurrence of alpha monoclinic selenium is associated with a reddish film color.

5. The undesirable effects of impurity addition, such as $BiCl_3$, do not arise from production of grey hexagonal selenium since only amorphous selenium can be found in such cases by X-ray methods. Thus, it appears that impurities, independent of structural configuration, have a role in controlling photoactivity.

Conclusions

Through considerations of (1) the results of the above correlations of methods of film production, properties of the refiners' selenium, effects of controlled impurities, the role of binder materials, effects of heat treatments and surface treatments of experimental films and X-ray structure of selenium, (2) associated information on other photoactive materials, and (3) data from rectifier studies, with photoactivity and image formation one begins to realize the following:

1. Materials usable as electrophotographic films need not be amorphous, but can be crystalline as long as possessing crystallinity still gives them electrically insulating natures. This follows from the above data and knowing that grey hexagonal selenium films are photoconductive even though they are not photoactive in the electrophotographic sense.

2. A similarity between the structures of photoactive organic compounds and electrophotographic selenium may be present in their molecular natures since monoclinic structures are found among organic compounds and the "Y" structure is only formed by melting selenium in binder materials of certain types.

3. Many of the impurity effects might be explained in terms of molecular attachments.

As a result of these realizations, advanced work has been done which has been based on molecular theory and associated data in the literature.

PRELIMINARY THEORY RELATING ELECTROPHOTOGRAPHIC SENSITIVITY WITH MOLECULAR STRUCTURE OF SENSITIVE FILMS

Considerations of Chemical Bonds in Solids

All materials owe their physical properties to the type and strength of bonding between their atoms or molecules. There are four recognized types of interatomic bonds, namely: ionic or polar*, homopolar or covalent*, metallic*, and Van der Waals or residual*.

Evans** has tabulated the mechanical, thermal, electrical, optical, and magnetic, and structural properties these bonds would produce in a material. (See Table 17.)

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* Explanation of Bond types:

1. The ionic bond is that produced by electrostatic attraction between electropositive and electronegative ions; alkali halides are examples of materials with such bonds.
2. The homopolar bond arises from the sharing of electrons between atoms. One can distinguish such a bond from an ionic bond in that the number of homopolar bonds by which a given atom is linked to others is limited. Diamond is an example of a material having only homopolar bonds.
3. A metallic bond is one which can best be expressed as the attraction between an electron gas and positive ions in the electron gas, that is, this attraction gives the coherence of the structure.
4. The residual or Van der Waal's bond is similar formally to a metallic bond in that it can tie an indefinite number of neighbors together. While it resembles a metallic bond in being able to bond an indefinite number of neighbors, it differs from the metallic bond in that there are no electrons shared, also, it is very weak and can only tie together molecules with no external fields. Rare gases in the solid state have molecules bonded by Van der Waal's forces.

** "Crystal Chemistry," by R. C. Evans, p. 40.

TABLE 17. PHYSICAL AND STRUCTURAL PROPERTIES ASSOCIATED WITH THE FOUR INTERATOMIC BONDS

Property	Ionic	Homopolar	Metallic	Van der Waal's
Mechanical	Strong, giving hard crystals	Strong, giving hard crystals	Variable strength	Weak, giving soft crystals
Thermal	Fairly high M.P., low coefficient of expansion ions in melt	High M.P., low coefficient of expansion, molecules in melt	Variable M.P., long liquid interval	Low M.P., large coefficient of expansion
Electrical	Moderate insulators conduction by ion transport in melt. Sometimes soluble in liquids of high dielectric constant	Insulators in solid and melt	Conduction by electron transport	Insulators
Optical and magnetic	Absorption and other properties primarily those of the individual ions, and therefore similar in solution	High refractive index absorption profoundly different in solution or gas	Opaque, properties similar in liquid	Properties those of individual molecules, and therefore similar in solution or gas
Structural	Nondirected, giving structures of high coordination	Spatially directed and numerically limited, giving structures of low coordination and high density	Nondirected, giving structures of very high coordination and high density	Formally analogous to metallic bond

Seitz* schematically classifies solid types as shown in Figure 25. Evans' table can be correlated with Seitz's schematic diagram in the following sense. Seitz is classifying solid types by their chemical bonding while Evans is showing what properties a material would have if its atoms were bonded together solely by one of the four basic bond types. An outstanding revelation one gains from Seitz's diagram, after he realizes monatomic metals have metallic bonding, valence crystals have homopolar bonding, molecular crystals have Van der Waal's bonding of the molecules and homopolar bonding internally in the molecules, and ionic crystals have ionic bonding, is that all materials do not fall in one of these specific categories, but some represent mixtures of bond types.

It is to be noted that structures with only homopolar bonds are confined to tetravalent atoms. For other valences, such as divalent atoms, one can only form a solid by means of other bonds between the molecules. These bonds are usually Van der Waal's bonds or some modification of them.

Inspection of Table 17 in the light of the requirements that an electrophotographic film be an insulator, shows that such films should only occur if they have homopolar and/or Van der Waal's bonds between molecules and homopolar bonds between atoms of the molecules. Also, it appears that since optical properties of materials having such bonds are properties of the individual molecules, an understanding of why both crystalline and vitreous selenium could have similar optical properties begins to appear (assuming vitreous and crystalline selenium both have this type of bonding between molecules).

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* "The Modern Theory of Solids," by F. Seitz, p. 75.

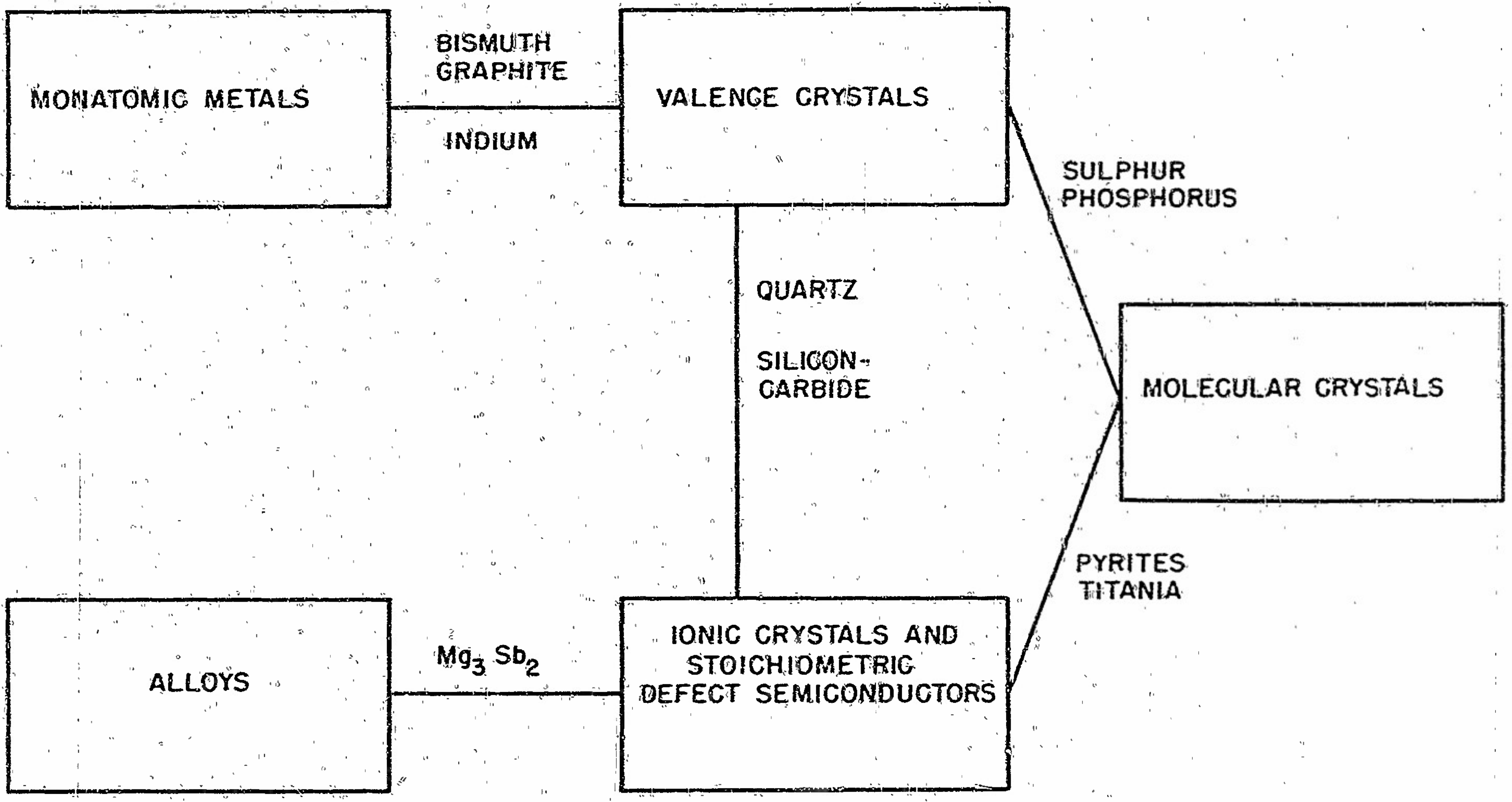

FIGURE 25. THE INTERRELATION OF THE SOLID TYPES

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Seitz classifies hexagonal selenium as a transition between a molecular and valence crystal, which also has impurity semiconductor properties. Evans classifies hexagonal selenium, Te, and Sb_2S_3 as having metallic heterodesmic chain crystals (heterodesmic means that very weak metallic bonding is present). Therefore, it appears that crystalline selenium can be considered as a modified molecular crystal.

Common Structural Characteristics Among Known Photoactive Materials

Because of the above classification of grey hexagonal crystalline selenium, one might imagine that vitreous selenium could consist of extremely small long molecular crystals or just unaligned chain molecules bound by Van der Waal's forces.

If this is the case, it is interesting to note the anthracene has a very similar molecular structure to that of selenium. Evans classifies it as having long flat molecules bound primarily by Van der Waal's forces. Also plastic sulphur is claimed by Evans to consist of long chain molecules bound primarily by Van der Waal's forces.

Providing the above assumptions are true for vitreous selenium, it is evident that one common characteristic among structures of photoactive materials could be their long molecules internally linked by homopolar bonding and bound to other molecules or lined up ordered aggregates of molecules (beginnings of a crystal formation) primarily by Van der Waal's bonds.

In such a case, the Van der Waal's bonds would provide the insulation between chain molecules or chain molecular aggregates.

By assuming each chain molecule has an electron band system, one could expect to obtain photoelectrons in empty bands of the individual molecules under incident light. The separation of the energy bands in each long molecule or molecular aggregate would determine whether electron excitation to the empty band by visible light could occur (if the energy of the light quanta were the same as that of the band separation, the maximum efficiency of the photoexcitation process would be obtained). It is to be noted, however, that one would expect the efficiency of photoexcitation for visible light would vary as the atoms of the molecules are changed to other types.

At this point, it is pertinent to point out that diamond should possess photoactivity, but maybe not for visible light (this depends on the energy separation of the full and empty bands) since its optical properties have dependencies of a similar nature to that of chain molecules and it is an insulator. The major differences between diamond molecules and organic chain molecules or the proposed chain molecules in vitreous selenium is that the carbon atoms forming diamond form single bonds in each of three dimensions because it has four electrons to share, while a selenium atom only has two valence electrons so it can only grow in a chain. Thus, diamond is a three-dimensional array of long chain molecules.

On the basis of the postulation that organic chain molecules will inherently possess photoelectric characteristics if diamond molecules do, (because of the same C-C chains in both the organic and diamond molecules) it might be expected that if a Si-Si chain were formed into a long molecule, separated from other like molecules as in the organic cases and bound primarily by Van der Waal's forces, it would possess photoactive characteristics in the sense of electrophotography because silicon shows photoconductivity. Therefore, it appears both organic and perhaps silicone materials should be photoactive if certain other conditions can be satisfied.

Although the above classification and correlation of structures of photoactive materials indicates:

1. Two requirements for photoactive material structures are that (a) the structure consist of molecules bound primarily by Van der Waal's forces and (b) the molecules be long chains of atoms.

2. The sources of photoelectrons are the individual molecules or perhaps molecular aggregates (beginnings of crystals); the efficiency of the excitation process is a function of the energy band separation.

3. The Van der Waal's binding contributes the electrical insulating nature and allows each molecule to act separately under light.

4. All known photoactive materials are assumed to have or are identified as having this type of structure or a slight modification of it, it is not yet apparent how the photo electrons could release the charge at the surface of an electrophotographic plate.

Structure, Conductivity, and Photoconductivity in the VI Group of the Periodic System

Considerations of some experimental data and structural models given by Von Hippel* for selenium structures relative to that of the elements in the sixth group of the periodic system can be helpful in

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* A. Von Hippel, Journal of Chem. Phys., April, p. 372, 1948.

(1) demonstrating that the assumption made about the structure (in the previous section) for vitreous selenium has had considerable verification and (2) giving further insights which can form a basis for theorizing on the photoaction in the electrophotographic plate. Also, some understanding of the transition from single molecules to crystals can be obtained. In addition, an understanding of the reason for Te and hexagonally crystalline selenium failing to be photoactive in the sense of an electrophotographic plate is made evident.

Structure

Oxygen, sulphur, selenium, tellurium, and polonium atoms have two Porbital electrons which are available for covalent binding. Therefore, they have possibilities of combining to form diatomic molecules, ring molecules, or chain molecules (see Figure 26). The preference, in regard to whether the double or single bond is used, is determined by the amount of energy gained in forming these bonds. For O-O, 34.9 kcal/mole is required as compared to 96 kcal/mole for O=O: so diatomic molecules are expected. For S, the corresponding values are 63.8 and < 88 kcal/mole, showing ring molecules are more favorable, that is, utilizing two single bonds will net an energy gain of 127.6 as compared to 88 kcal/mole for a double bond. For selenium the large size and polarizibility gives single and double bonds of about equal strength (57.6 compared to 59 kcal/mole) so single bonds will also be expected in this case.

Ring molecules will break into chain segments at high temperatures which may polymerize into chain molecules, giving the resulting material

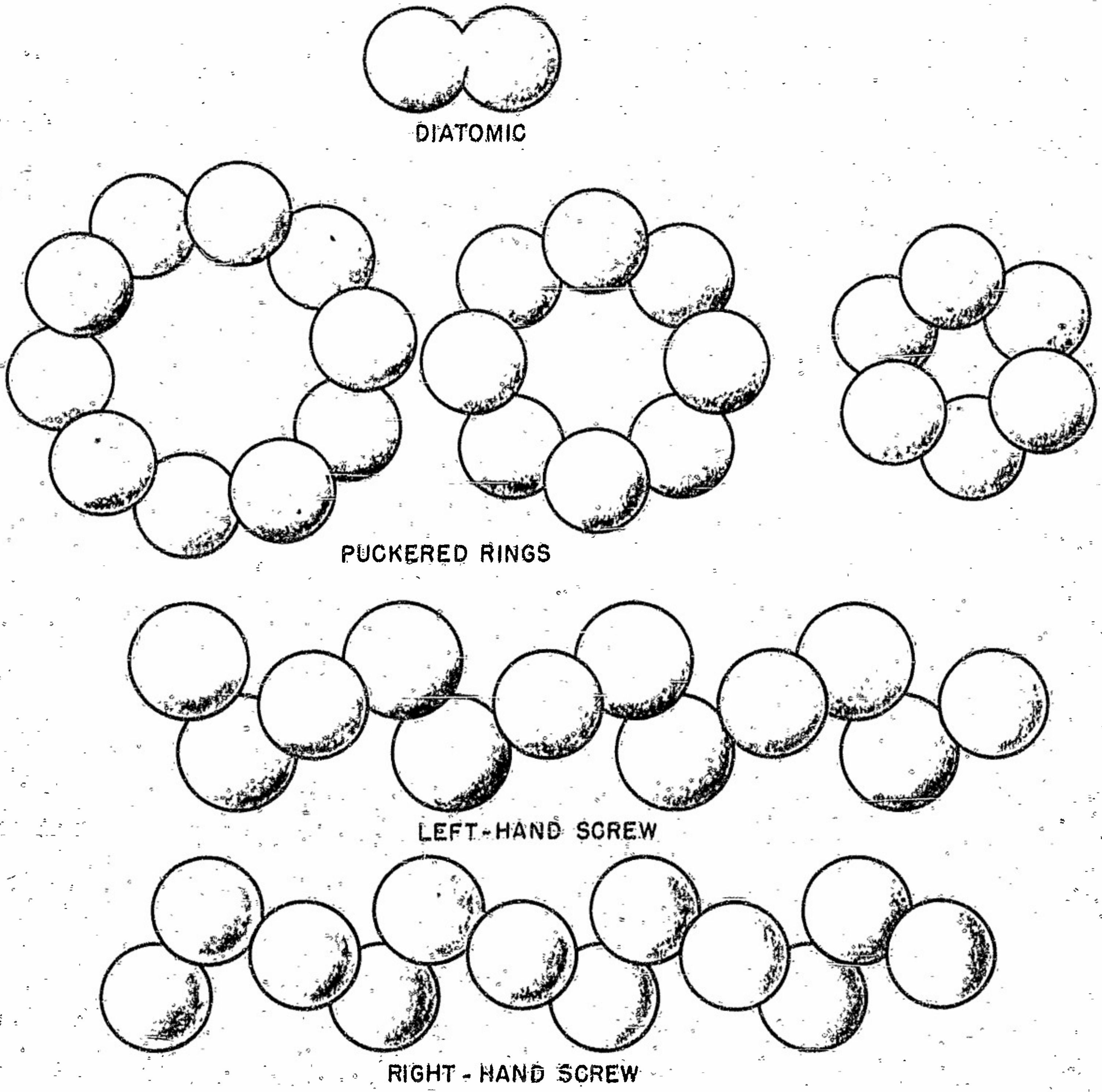

FIGURE 26. SULPHUR MOLECULES

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plasticity, for example, plastic sulphur. It is known that stability of chain molecules depends on the status of their end groups and on binding forces acting between neighboring chains. Oil, sulphuric acid, or halogen can act as chain terminators and prevent polymerization as has been shown by viscosity measurements on sulphur with such additions present.*

The binding forces acting between the molecules of oxygen, sulphur, selenium, tellurium, and polonium are indicated by the crystal structure of these elements. Solid oxygen consists of diatomic molecules only bound by Van der Waal's forces. In sulphur, S_8 ring molecules are packed together at a distance somewhat closer than their Van der Waal's spacing. Te and Se have hexagonal structure composed of chain molecules and Po presents a simple cubic lattice. Therefore, a progressive decrease in the distance between molecules takes place in going from O to Po. Se represents a case where the intermolecular binding forces have increased enough that it has a choice, as a function of cooling rate, of remaining in a disordered chain and ring molecule stage or going over into an orderly chain molecule arrangement which is the hexagonal structure. Incidentally an orderly arrangement of ring molecules gives an orthorhombic structure for sulphur and a monoclinic (red) selenium structure. In Te the binding forces between molecules is too great to allow the disordered condition to exist in the solid state. Figure 27 shows the structures of S, Se, Te, and Po. One can see here the way in which the chain molecules fit together to form the hexagonal structure of Se or Te. From a knowledge of the atom spacings and angles in these structures, it can be shown that the seeds of the cubic structure of polonium exist in Te and Se. The appearance of the

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* R. F. Bacon and R. Fanelli, J. Am. Chem. Soc., 65, 639, 1943.

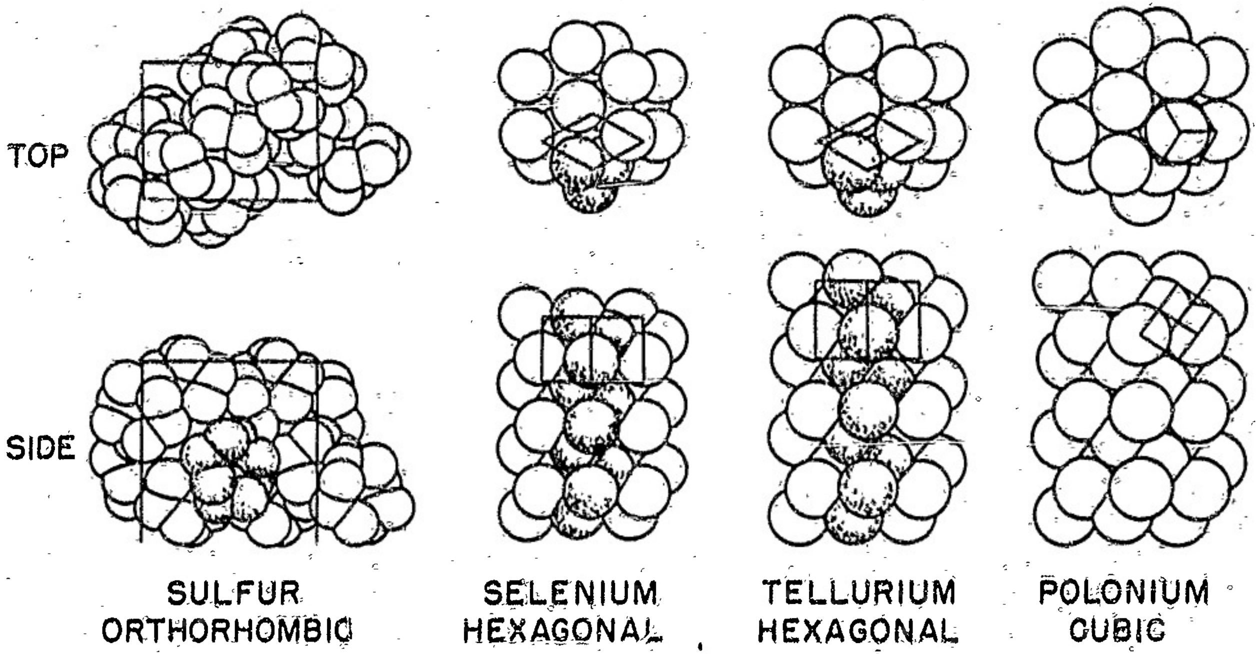

FIGURE 27. STRUCTURES OF SULFUR, SELENIUM, TELLURIUM, AND POLONIUM

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cubic structure in Po is the cause of the drop in the melting point in going from Te to Po.

Electronic Conductivity

As the above molecule and crystal structure develop in going from O to Po, a gradual evolution of electronic conductivity occurs. In O, electron transfer can only occur between atoms of diatomic molecules. In sulphur, the ring molecules have the beginnings of electron band structure. The formation of long chains by polymerization in S, Se, and Te makes electron conductivity along the individual molecules possible. However, as a result of the homopolar bonding between atoms of the molecules, the electrons are shared between atoms, therefore, giving a filled band and making conduction at room temperature within a molecule impossible unless excitation of electrons by other means to higher electron levels occurs.

Light or temperature can serve as the energy of excitation to excite electrons from the filled bands in these molecules. When these electrons leave the filled band of the molecule, they leave a positive hole behind. Under an applied electric field, the excited electrons in the formerly empty band, and also the positive holes in the full band can move. (See Figure 28.) The excited electron proceeds toward the anode and the positive hole migrates by electron exchange toward the cathode. The width of the gap between the filled and empty band determines the energy needed for electron excitation. Evidence that this band separation in S, red monoclinic, and gray hexagonal selenium is approximately that of the quanta of visible light has been given by various investigators* as shown

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* R. F. Bacon and R. Fanelli, J. Am. Chem. Soc., 65, 639, 1943.

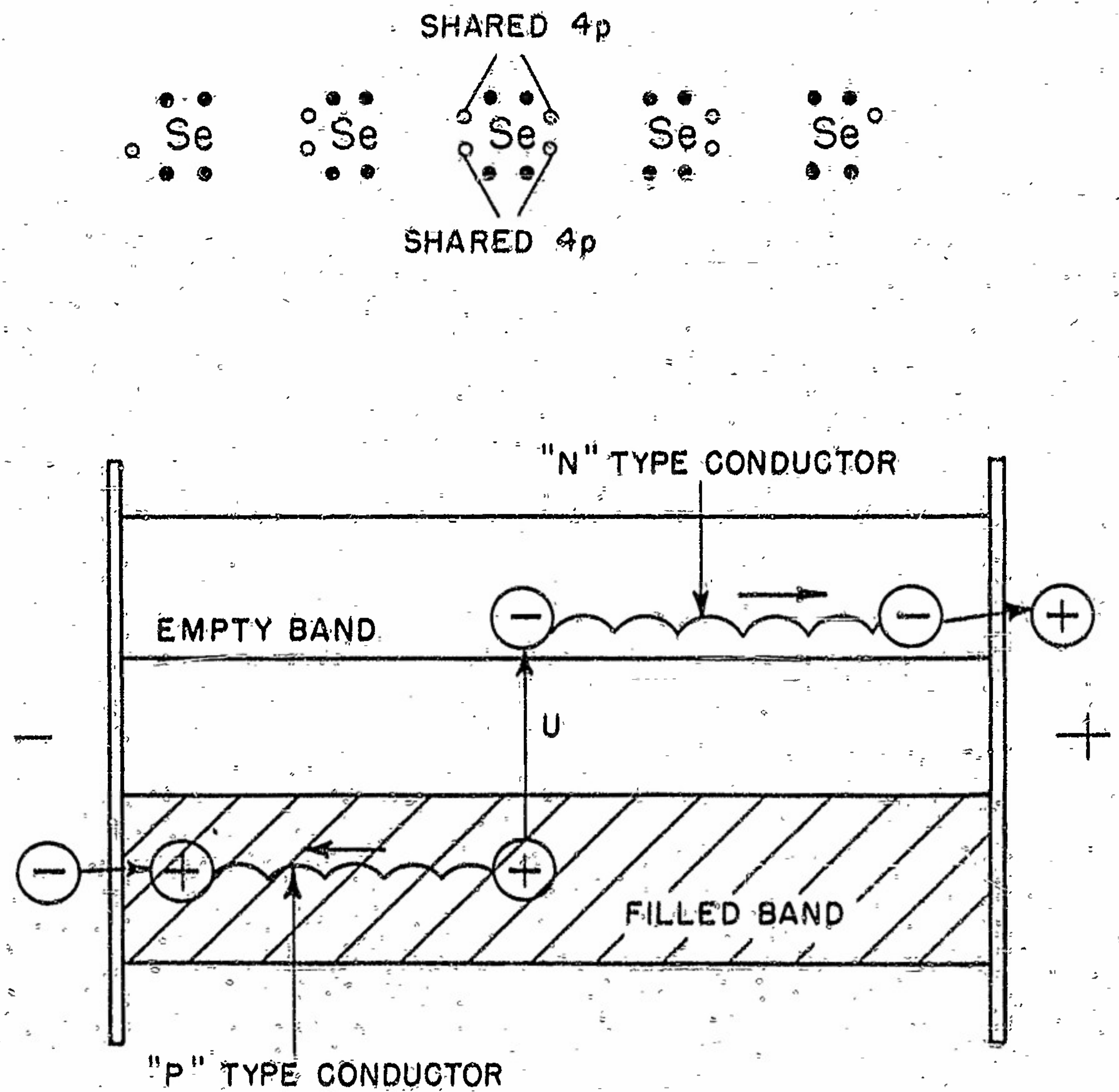
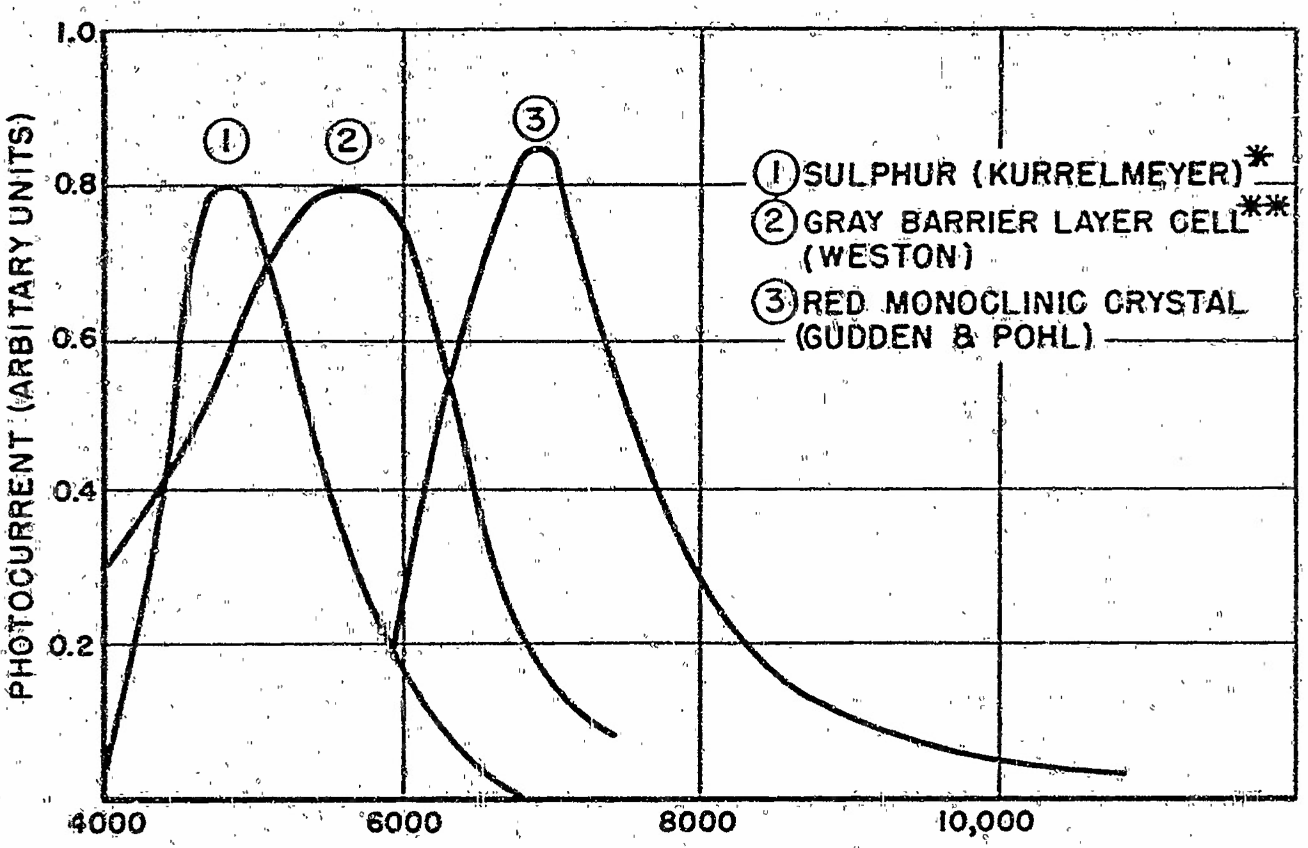


FIGURE 28. BOND AND BAND PICTURE FOR SELENIUM AS A MOLECULE

in Figure 29. It is to be noted that this evidence in Figure 29 was obtained from solids made up of many molecules. One must, therefore, explain how the electrons move from one molecule to the next. One would expect that the excited electron leaving a positive hole behind would create a positive space charge. The force of the positive space charge left behind, plus the low probability of an electron passing the Van der Waal's gap between molecules, should trap the electron. If, however, a high field were applied to overcome these two influences, one might obtain conduction of the excited electrons through the body of the material. Experimental evidence that photocurrent in sulphur and monoclinic selenium is a function of applied voltage, as shown in Figure 30, shows that the combination of high field and the high energy level of the excited electrons allows conduction in such a molecular medium.

The differences between electrical conductivity of grey hexagonal selenium, red monoclinic, amorphous selenium, and sulphur can now be understood by considering their structures and the process of exciting electrons and creating holes. In S, monoclinic selenium, and amorphous selenium, the holes left behind by the excited electrons, which move between molecules only under high applied fields can not move from the molecule in which they are produced because of the higher potential barrier between molecules presented at this lower energy level than at the energy level of the excited electrons. As soon as the hexagonal selenium structure evolves by formation and lining up of chain molecules, the stronger intermolecular forces resulting from the tendency toward metallic bonding like that in Po lowers the barrier between molecules and



* B. KURRELMEYER, PHYS. REV., 30, 893 (1927)

** B. GUDDEN AND R. POHL ZEITS. f. PHYSIK, 35, 243 (1926)

FIGURE 29. PHOTOCURRENT AS FUNCTION OF WAVELENGTH (A)

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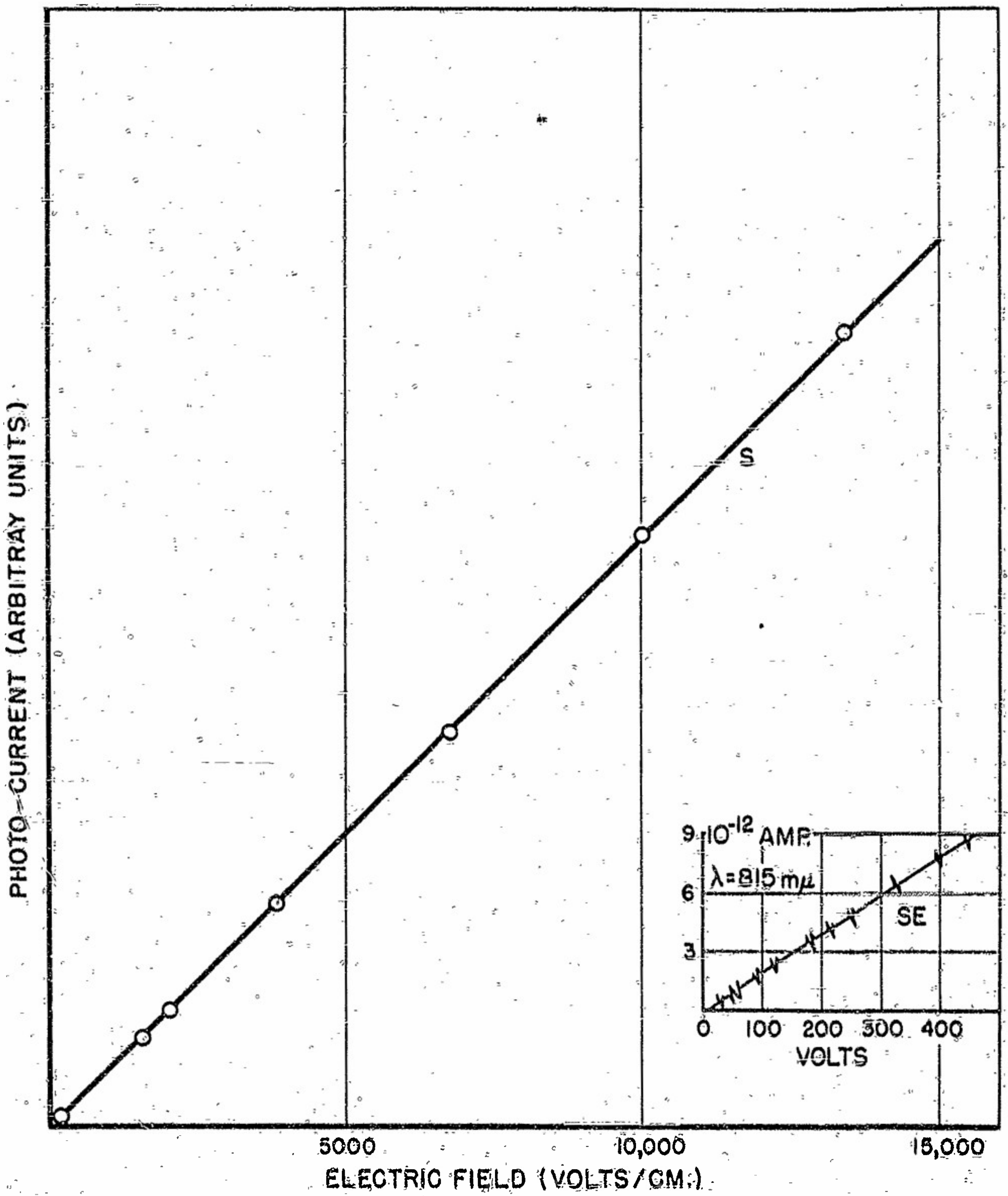

FIGURE 30. LINEAR RISE OF PRIMARY PHOTO-CURRENT WITH VOLTAGE IN SULPHUR AND MONOCLINIC SELEMIUM

allows the holes to migrate. Evidence that this explanation is valid is given by Hall effect measurements, thermoelectric power measurements and rectifier action of grey hexagonal selenium, since positive holes are indicated as providing the conduction in these cases. One may ask why one observes a Hall effect, since equal number of holes and electrons should be moving, thus seemingly cancelling out any effect. This can be answered by noting that there is a difference in the mobility of holes and electrons and also noting that if impurity levels of the acceptor type are present, the excited electrons may be trapped.

Therefore, a model for electrophotographic selenium structure composed of isolated chain molecules (amorphous selenium) or ring molecules in crystals (monoclinic selenium) is feasible and the reason for the inability to use completely grey hexagonal selenium, having similar photoelectric properties, can be seen. The mechanism by which photoexcited electrons can pass through a medium composed of chain or ring molecules bound together by Van der Waal's forces is shown and supported by experimental data. Also the reason and supporting data for the insulating nature at room temperature in the dark of a material built like this model is apparent. Further the assumptions made, in the previous section, where a possible common structural nature for photoactive materials was discussed, are supported and elucidated.

The Formation of an Electrostatic Image

The explanation of the formation of an electrostatic image can be readily made using the above structural model and considering the conditions under which conduction can occur in such a structure.

Charge, either on the surface or induced in the film surface at room temperature by the charging device, sets up an electrical field through the film. No appreciable current will flow while the specimen is in the dark in this condition (however, there is undoubtedly an upper limit to the field which can be withstood) because any positive hole present in the full band can not move from one molecule to another and the energy separation of the full and empty energy bands for the molecules is great enough that thermal excitation of electrons to the empty band only results in a few such transitions.

On exposure to light, photoexcitation of electrons occurs so that electrons rise to the empty bands of the molecule. The electric field pulls them to the anode providing the field is large enough to overcome the force of the positive hole attraction and the potential barrier between molecules. If the film surface is the anode, the plus charges there will be neutralized by the electrons. If the film surface is the cathode, the negative charges there will be neutralized by the bound positive holes in the molecules at the surface (it will be recalled that the previous discussion indicated holes can not move from molecule to molecule in monoclinic or amorphous selenium). Since light quanta must hit individual molecules in order for electrons to be released, it is obvious that only those areas of the surface on which light impinges will lose their charge. Also, since the number of quanta per unit area increases with the intensity of light and molecules are very small, areas hit by the greater light intensities will lose more charge than those hit by lower light intensities, that is one expects a statistical increase with light intensity in the number of charges neutralized per unit area.

A simplified diagram of one concept of the effect of charging and light on the molecules or crystals of an electrophotographic film is shown in Figure 31.

Discussion

A critical examination of the above explanation of the formation of an electrostatic image relative to accumulated knowledge on electrophotography, details of the structural model, and the dependencies of its electrical conduction characteristics brings out a large number of considerations pertinent to development and understanding of electrophotographic plates and also other possibilities in explaining the details of image formation. At the moment, some of these considerations have been made. In the following, some of these are discussed and in a following section some pertinent experiments are reviewed.

For the present, it is to be noted that:

1. Since a positive hole space charge can be developed in the film by incident light in the presence of an electric field, one may expect to find that a film will degenerate on subsequent charging with the same polarity.

2. One could imagine the charging process as developing a positive hole space charge either near the base or surface of the film (depending on the charging polarity), which would persist after removing the charging field.

3. Under high field strengths, one would get electron field emission from the molecules composing the film. Also, positive holes would have a greater probability of penetrating the intermolecular barriers under

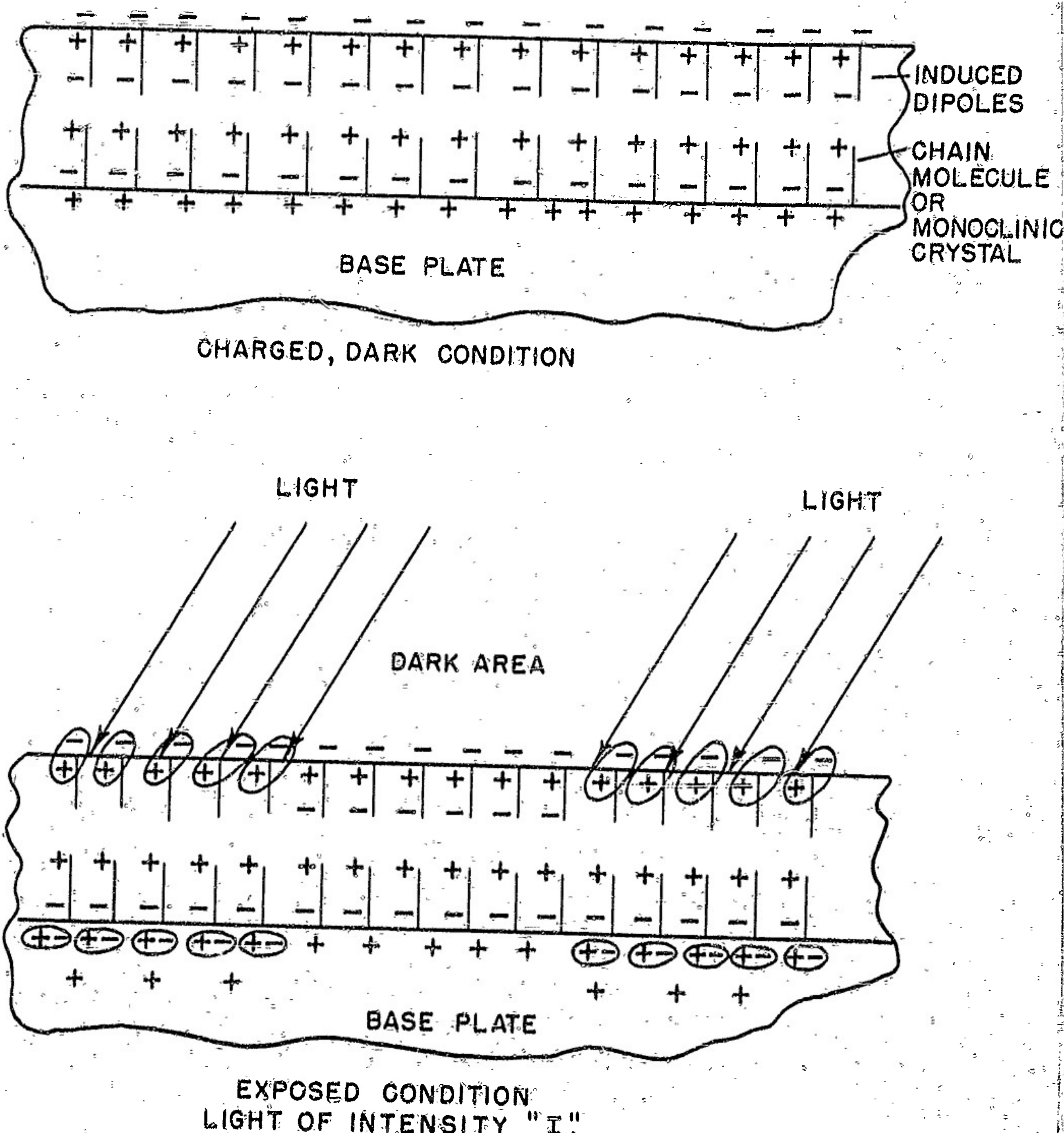

FIGURE 31. A SIMPLIFIED SCHEMATIC DIAGRAM OF THE ACTION OF ELECTROSTATIC CHARGING AND INCIDENT LIGHT ON THE STRUCTURE OF AN ELECTROPHOTOGRAPHIC PLATE (SIDE VIEW-SPECIAL CASE WHERE MOLECULES ARE ORIENTED)

higher applied electrical fields. It follows that the amount of charge able to be retained on the surface of a film after the charging operation may be a function of field thresholds for flow of these charge carriers. Further, owing to differences in mobility of electrons and holes, one might expect asymmetry of charge built up using different polarities.

4. Dark decay may be accounted for by assuming a finite probability of positive hole flow between molecules in the dark and assuming some electrons are thermally excited to the empty band in the molecules at room temperature. It would be expected that impurities in the selenium would have different effects depending on where they were positioned. They might act to increase the probability of positive hole conduction and increase dark decay. They could also increase light decay if they lowered the potential barriers impeding photoelectron flow.

As was noted previously, there is an apparent increase in dark decay rate associated with illumination. One possible explanation of this might be based on the assumption that during illumination some electrons are raised to excited states which are not, however, in conducting bands. The extra energy possessed by these electrons will make it easier for thermal agitation to raise them into conduction bands in the dark. Until the number of these excited electrons is exhausted, there will be an apparent increase in dark decay rate. While this explanation may account for the effect, it is only considered tentative since, as noted in section 1, there is some doubt as to whether the effect is real.

5. The effect of orientation of molecules relative to the film surface is of strong interest since when chain molecules are involved,

conduction along their lengths only is possible. One would expect that at a position where all the molecules were lined up end-to-end from surface to base, the greatest rate of light decay would be observed and also the greatest probability of positive hole migration would be presented.

6. On considering the data in Figure 29 for sulphur and selenium and the difference in the electrophotographic action of a plastic sulphur and vitreous selenium film, one begins to wonder why there is such a large difference in light decay rates between them. This might be explained by differences in potential barrier heights between molecules owing to differences in Van der Waal's spacing and then again it could be explained if one assumes that in selenium molecular aggregates (seeds of crystals) are more common than in sulphur. The aggregation of molecules into a preferred array would tend to decrease the difficulty of moving electrons or positive holes. Support for some additional considerations such as these is given by observations of alpha monoclinic selenium in paint films, some hexagonal selenium in a few usable films and the simultaneous increase of light and dark decay in going from S to Se.

7. Owing to the characteristics which could be ascribed to films by variations in molecular orientation and aggregation and in view of the importance of the field strength in obtaining photoconduction, one can easily see that film thickness should be a very important factor in determining the action of an electrophotographic film.

8. It would appear that electrophotographic action could be a strong function of film temperature during charging (owing to the role played by thermal excitation) as well as the effects of light exposure.

ADVANCED EXPERIMENTS PERTINENT TO VERIFYING AND EXTENDING THE THEORY AND ADVANTAGEOUSLY USING THE STRUCTURAL CLASSIFICATION TO FIND NEW ELECTROPHOTOGRAPHIC MATERIALS

Effects of Thickness of Selenium Pigmented Paint Films On Their Electrophotographic Properties

Table 18 and Figure 32 show the results of electrometer and image formation tests on selenium pigmented parlon-Rezyl paint films of controlled thicknesses varying from 0.0004 to 0.015 inch, made from one batch of paint and prepared under controlled conditions.

One visualizes a paint film as containing molecular aggregates of selenium in monoclinic crystal array, probably dispersed in particles of molecular selenium which in turn are dispersed in an insulating organic medium which separates the selenium particles by thin barriers. On the basis of theory and structural characteristics for selenium, one would expect that thinner films would therefore take less charge and show greater light and dark decay rates. This type of trend is observed for films less than 0.002 inch thick and continues with some modification to 0.005 inch thicknesses. At the moment, it is believed that unexplained trends at larger film thickness are caused by paint flow (perhaps giving molecular alignment).

No attempt was made at this early date to explain the details of the curves. If the same characteristics persist in future tests, the detailed trends will then be considered.

It is noteworthy also to point out that light decay rates for the thinnest films approach those for evaporated films of similar thicknesses

TABLE 18. EFFECTS OF VARIATIONS OF FILM THICKNESS ON CHARGE ACCEPTED, LIGHT AND DARK DECAY RATES AND IMAGE CHARACTERISTICS FOR ARQ So PIGMENT PARLON-REZYL FILMS MADE FROM ONE BATCH OF PAINT

			Positive			Negative			Image Formation		
Number Samples	Thickness, In.	Base Material	Charge, Volts	Light Decay, %/min.	Dark Decay, %/min.	Charge, Volts	Light Decay, %/min.	Dark Decay, %/min.	Time of Exposure	Light Intensity	Quality of Image
6	0.0005	Aluminum and Steel	120-170 146	107-154 134	25-42 32	70-145 115	294-362 322	72-119 88	- 1/2 sec.	- 90 volts	Good High uniform background
6	0.001	Aluminum and Steel	350-470 382	42-148 120	40-53 47	130-270 195	200-274 226	78-100 90	- 1/2 sec.	- 90 volts	Good Medium uniform background
6	0.002	Aluminum and Steel	510-600 560	91-117 105	50-64 59	260-400 327	159-213 184	80-96 87	- 1/4 sec.	- 90 volts	Good Medium uniform background
3	0.005	Aluminum	490-525 500	66-97 83	38-55 47	323-380 356	143-167 153	59-74 67	- -	- -	- -
3	0.010	Aluminum	500-540 525	140-172 154	76-100 91	325-358 336	200-244 218	119-130 123	- -	- -	- -
3	0.015	Aluminum	103-120 109	240-290 278	141-143 142	62-84 71	313-324 317	158-180 169	- -	- -	- -
1	0.0003	Aluminum	51	200	52	45	355	118	-	-	-
1	0.0004	Aluminum	-	-	-	-	-	-	1/8 sec.	90 volts	Good Medium uniform background

NOTE:
1. Base plates wire brushed before painting.
2. Paint used was No. 4165-1.
3. Plates charged with 4000 volts on needles.
4. Values are averages - extreme range is shown.
5. 7000 volts on wire for image charge.
6. One image for each thickness - using optimum conditions.

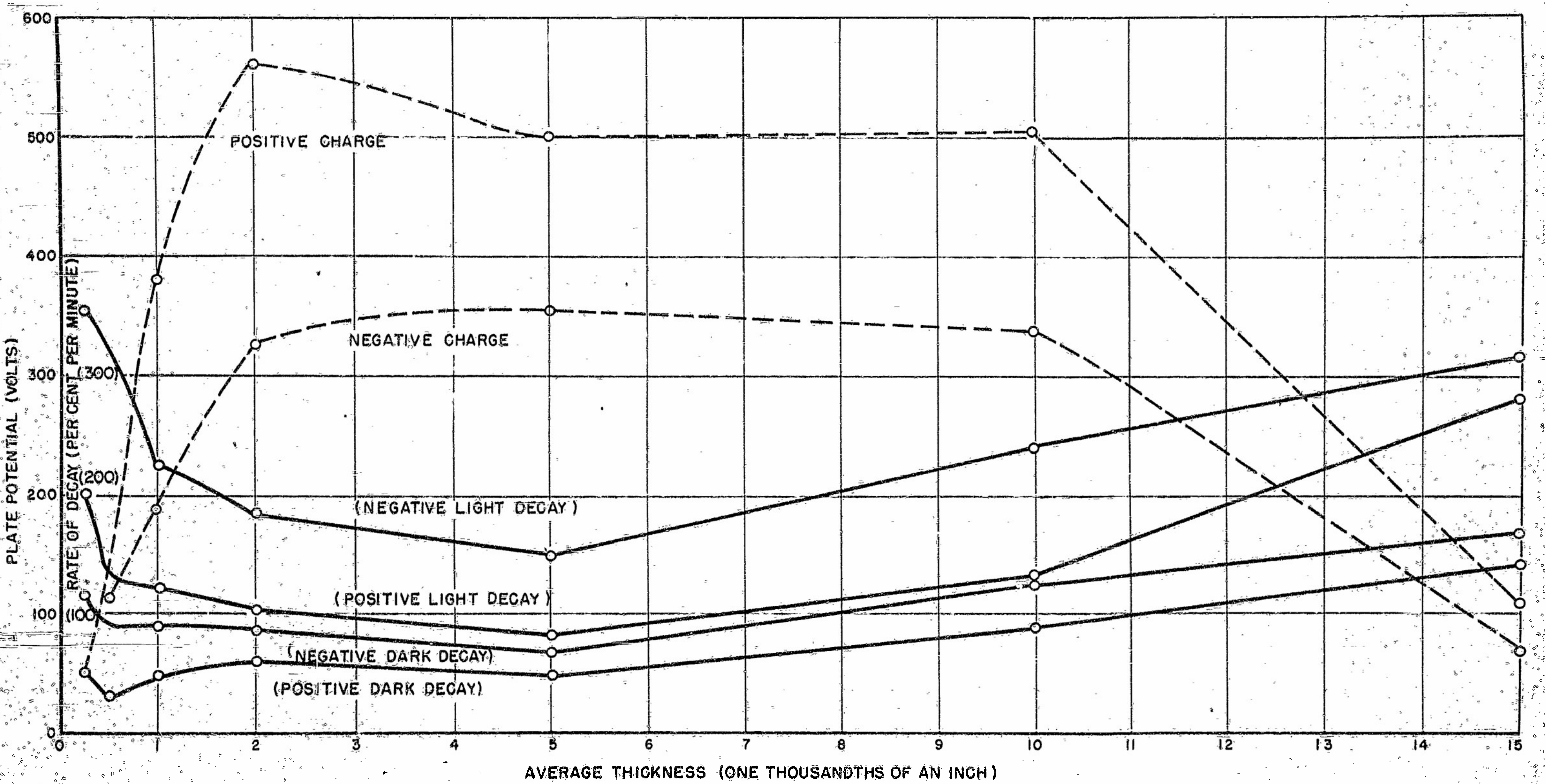

FIGURE 32. EFFECT OF THICKNESS ON ELECTRICAL AND PHOTOELECTRICAL CHARACTERISTICS OF PHOTOACTIVE SELENIUM PAINT SPRAYED PLATES

0-10106

and images can be obtained in shorter times (1/8 second for thinnest plate). However, background persists on the prints from the thinnest films.

Effects of Sulphur Additions in Selenium

On the basis of structural diagnoses of selenium and sulphur one expects that sulphur added to selenium might retard formation of its hexagonal structure. Therefore, it should be possible to hot press selenium with sulphur additions without crystallizing the selenium during the process. As a result, it should be possible to use the hot-press method to make electrophotographic films.

Also, one expects that since sulphur molecules have larger Van der Waal's spacing than selenium molecules and sulphur shows a lower light decay than selenium, sulphur will lower the sensitivity of selenium.

Attempts to hot press selenium with sulphur additions and retain electrophotographic properties were successful, using 1 per cent or greater additions of sulphur. Figure 33 shows the trends of accepted charge, light decay, and dark decay with the percentage of sulphur additions. It is to be noted that positive and negative dark and light decay rates and accepted charge are similar with sulphur additions (this has been noted as not the case with selenium alone). Also, the anticipated trend is obtained.

On attempting to obtain images from these plates, however, an unexpected effect was observed. (See Table 19) The low percentage sulphur plates which showed the best decay characteristic would not produce a powder image. However, after removing the surface layer from the plates

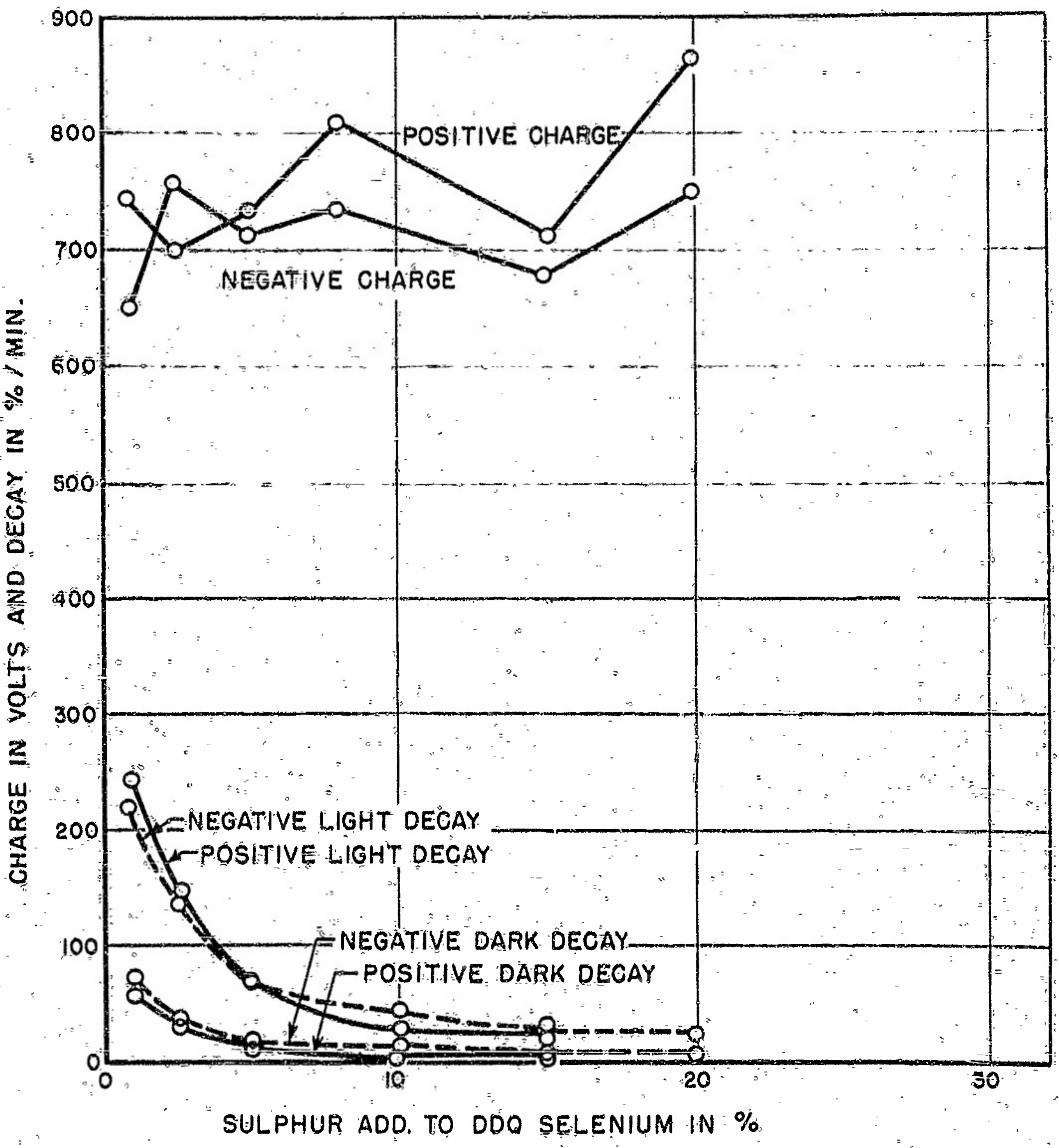

FIGURE 33. THE EFFECT OF ADDITION OF SULPHUR IN DDQ SELENIUM USING THE PLATEN PRESSING METHOD

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TABLE 19. ELECTROPHOTOGRAPHIC DATA ON HOT PRESSED SELENIUM PLUS SULPHUR FILMS

Per Cent of Sulphur ~~Addition to~~ DDQ Selenium Lot 5-51	Material Application to Base	Type of Platen Used in Pressing	Photoactivity by Electrometer	Image Formation			Surface Treatment	Image Formation After Treatment	Comments
				Time of Exposure	Light Intensity	Quality of Image			
0	Sprayed shot	Polished chrome	None	-	None	-	Scratched with sandpaper	No	Mirror surface.
0			-	-	-	-		-	Surface becomes wavy and selenium flows. Presence of gray hex. So probably reason for no charge.
1	Poured on as a liquid	Ditto	Yes	15 sec.	110 volts	None	-	-	Mirror surface - readily pressed - approximately 0.020 inches film thickness.
2.5	Ditto	"	"	Ditto	Ditto	"	Scratched with sandpaper	Yes	Physical nature like 1 per cent case - image fair with high background probably owing to scratching.
5	"	"	"	"	"	"	Ditto	Yes	Physical nature like 1 per cent case - image faint with low background.
5	"	Glass	"	10 sec.	"	Yes	-	-	Surface poor because glass shattered - image fair with high, mottled background.
5	Sprayed	Polished chrome	"	Ditto	"	Yes	-	-	Pitted surface - fair image - with very high, mottled background.
5	"	No pressing	"	"	"	Yes	-	-	Surface wavy and glossy - faint image - very high background.
10	Poured on as a liquid	Polished chrome	"	"	"	Yes	-	-	Mirror surface with spots - faint image - high background.
10	Ditto	Ditto	"	"	"	Yes	-	-	Mirror surface - somewhat better image than above plate pressed at 300°F. instead of 200°F.
15	"	"	"	"	"	None	-	-	Reddish colored, poor surface.
20	"	Mica	"	"	"	Faint	Scratched with sandpaper	Yes	Faint image, high background.

NOTE: Platen pressed plates at 200°F, unless otherwise noted.

1. 7000 volts on wire for image test;
   4000 volts on needles for electrometer test.
2. One plate each.
3. DDQ selenium (see technique in Appendix I.)
4. For charge level, decay rate, etc. See Figure 33.

they did. Also when using a glass or mica platen or spraying the liquid selenium on instead of pouring it before pressing with a chromium platen, one could obtain an image for 5 per cent additions of sulphur. Using 10 per cent sulphur addition and a chromium platen, one could obtain a faint image.

An explanation of the lack of image formation in some of these cases can be given when the molecular structure of selenium and the effects of platen pressing are considered and it is realized that a scattered deposit of chromium particles is present on the selenium surface. Apparentl the surface was made conducting enough by the chromium in the cases of small percentages of sulphur that the surface charge either leaked off or was pulled off by the powder developer.

These results have repercussions on theory of charging a plate with an electrostatic charge, if they are verified by further experiments, since they could support the idea that a positive hole space charge in the bulk of the material is induced which remains even if the charge leaves the surface as shown by electrometer data. On the other hand, the electrometer results are accounted for if it is assumed the powder developer removes the surface charge owing to the nature of the surface not being such that charge will adhere to it strongly. Further, investigations of these phenomena will be made.

Photoactivity of Materials Selected on the Basis of Their Fundamental Chemical Structure

After finding that photoactive material structures are related through their molecular nature and type of binding forces tying the atoms of the molecules and the molecules together, tests were made on materials chosen on the basis of their having this structural character.

Table 20 shows the results of these controlled searches for new materials as far as they have been carried at the present time. These materials with molecular structures characterized by having long chain or flat molecules or crystals with a preponderance of Van der Waal's bonding between molecules and able to be obtained in thin layers all showed photoactivity thus supporting the classification for photoactive materials.

These tests have not been in progress for long enough to find out whether any anomalies can be found.

Because of other factors besides molecular structure being important such as, for example, the energy levels in the molecules, it can not be assumed that this classification is complete. However, it appears to be good enough that considerable time may be saved by using it to look for new materials.

Effects of the Temperature and Temperature Treatment of the Selenium Film on Photoactivity

Since the theory of conduction in electrophotographic films and consideration of the habits of selenium structure indicates temperature of the film should affect its response and also since temperature treatment is known to be important in changing selenium structure, tests were initiated to determine what type of effects temperature treatments of 50 and 70°C. would have at temperature and following the treatment.

Table 21 shows the results for a selenium pigmented parlon-rezyl film, a hot-pressed selenium plus 5 per cent sulphur film, and a hot-

TABLE 20. PHOTOACTIVITY DATA ON MATERIALS SELECTED ON THE BASIS OF THEIR FUNDAMENTAL CHEMICAL STRUCTURE CLASSIFICATION

Type of Material	Form of Material	Fundamental Structural Nature	Results of Electrometer Tests for Photoactivity	Remarks
		Known Photoactive Materials		
Selenium	Paint film evap., hot sprayed powder alpha.	Chain molecules aggregated to some extent; molecules bonded by Van der Waal's and other forces	Highly photoactive	Semi-plastic material
Sulphur	-	Ditto	Slightly photoactive	Plastic
Anthracene	Film	Flat long molecules	Ditto	"
	New Photoactive Materials Chosen for the Nature of Their Molecular Structure			
Sb_2S_3	Powder	Flat long molecules	More than slightly photoactive	-
SeS	Platen pressed or sprayed	Ditto	Ditto	Plastic
Diamond	Diamond dust in paste polishing material	Three-dimensioned homopolar crystal	Very slightly photoactive	Requires analysis of paste and tests thereon to verify diamond photoactivity
Naphthalene	Melted on plate and quenched; film	Flat long molecule	Slightly photoactive	Semicrystalline plastic-like wax

TABLE 20. Continued

Type of Material	Form of Material	Fundamental Structural Nature	Results of Electrometer Tests for Photoactivity	Remarks
Long chain paraffins (multiwax W-445)	Melted and dispersed in toluol and sprayed as paint	Long chain molecules	Slightly photoactive	Fully microcrystalline and plastic: dist. by Petroleum Specialites, Inc.
Other Materials Chosen for Their Closely Associated Natures				
Vitreous quartz	Glass plate 7/32" thick	-	Took a charge no observable light action	-
Natural rubber	Smoked sheet 1/16" thick	-	Took high charge (1010 volts) no observable light action	-
SiO_2	Powder	-	No charge	-
Wallastinite (impure $CaO \cdot SiO_2$)	-	-	Took charge no observable light action	-

TABLE 21. TEMPERATURE EFFECTS ON ELECTROPHOTOGRAPHIC FILM CHARACTERISTICS

Plate and Temperature	Charging Voltage	Positive Charge, Volts	Positive Light Decay, %/min.	Positive Dark Decay, %/min.	Negative Charge, Volts	Negative Light Decay, %/min.	Negative Dark Decay, %/min.
Paint Plate							
Room temp.	4000	175	165	56	210	327	60
50°C.	4000	125	167	62	130	314	83
Room temp.	5000	205	166	55	205	290	62
60° - 70°C.	3000	10	0	40	31	320	200
Pressed Plate							
Room temp.	4000	575	33	7	740	32	11
50°C.	4000	530	20	16	495	21	14
Room temp.	5000	690	39	13	1165	34	13
60° - 70°C.	4000	555	133	70	725	71	37
Sprayed Plate							
Room temp.	4000	550	150	63	130	150	70
50°C.	4000	420	156	107	220	200	100
Room temp.	5000	620	104	56	820	490	40
60°-70°C.	3800	495	179	135	380	246	190

NOTE: Paint Plate - ARQ Selenium Parlon-Rezyl
Pressed Plate - DDQ + 5% S addition
Sprayed Plate - DDQ Selenium

sprayed DDQ selenium film. Thicknesses were variable and the experiments were crude so only a brief discussion of these results is possible at this time.

The light decay or dark decay of a paint film is not appreciably affected by temperature treatment at 50°C. or a temperature of 70°C. In contrast the light decay of the pressed sulphur-containing selenium and the hot-sprayed selenium is affected. However, the effects appear to be somewhat different in the latter two cases. For the sulphur contaminated plate, it appears 50°C. decreases light and increases dark decay while 70°C. increases light and decreases dark decay. For the sprayed plate, the response for the negative and positive polarities is different. In this case, it is to be particularly noted that after the 50°C. treatment, the negative light decay was increased to extraordinarily high values and the dark decay was decreased.

Investigation of Materials Known or Suspected to be Photoactive as Selected from Literature Survey on Basis of Photoconductivity, Fluorescence, and Phosphorescence

The list of materials known or suspected to be photoconductive was extended and forty-four additional materials were tested for photoconductivity.

The extended list of possible photoconductive materials appears in Table 22. A summary of the results obtained in the testing of these materials appears in Table 23.

The test methods used in checking the materials for photoconductivity were as follows: (1) Break up the material using a mortar and pestle;

TABLE 22. MATERIALS KNOWN OR SUSPECTED TO BE PHOTOCONDUCTIVE

Material	Chemical Formula	Status Ordered	 Received	 Tested
Acenaphthene	$C_{10}H_6(CH_2)_2$			X
Acridine	$C_6H_4 \cdot CH \cdot C_6H_4$			X
Aluminum oxide	Al_2O_3			X
Aluminum selenide	Al_2Se_3	X		
Aluminum telluride	Al_2Te_3	X		
Anthracene (Kodak)	$C_6H_4(CH)_2C_6H_4$			X
Anthracene (Reilly)	$C_6H_4(CH)_2C_6H_4$			X
Anthraquinone	$C_6H_4(CO)_2C_6H_4$		X	
Antimony metal	Sb			X
Antimony trisulfide	Sb_2S_3			X
Auramine O				X
Barium selenite	$BaSeO_3$	X		
Barium tellurite	$BaTeO_3$	X		
Barium titanate				
Benzidine	$(NH_2C_6H_4)_2$			X
Bismuth metal	Bi			X
Bismuth trisulfide	Bi_2S_3	X		
Boron	B	X		
Boulanzerite	$Pb_3Sb_2S_6$			
Bournonite	$PbCuSbS_3$			

TABLE 22. Continued

Material	Chemical Formula	Status Ordered	Status Received	Status Tested
Brilliant green				X
Cadmium selenide	$CdSe$	X		
Cadmium sulphide	CdS	X		
Cadmium telluride	$CdTe$	X		
Calcium flouride	CaF_2			X
Calcium selenide				X
Calcium tungstate	$CaWO_4$			
Cerium tungstate	$Ce(WO_4)_2$			
Chrysene	$C_{18}H_{12}$			X
Crystal violet				
Cupric oxide	CuO			X
Cuprous iodide	CuI	X		
Cuprous oxide	Cu_2O			
Cuprous selenide	Cu_2Se			
Diphenylamine	$(C_6H_5)_2NH$			X
Diphenylcarbazide	$(C_6H_5NH \cdot NH)_2CO$			X
Diphenylene oxide	$(C_6H_4)_2O$			X
Erythrosin B				X
Fluoranthrene	$C_{15}H_{10}$			X
Fluorene	$C_6H_4 \cdot CH_2 \cdot C_6H_4$			X
Fluorescent 2205*				X
Fluorescent 2210*				X

TABLE [illegible]. Continued

Material	Chemical Formula	Status Ordered	 Received	 Tested
Fluorescent 2215#				X
Fluorescent 2220#				X
Fluorescent 2225#				X
Fuchsine				
Germanium	Ge			
Indium sulfide	In_2S_3			
Indium sulfide (sulfur added)	$In_2S_3(S)$			
Indium selenide	In_2Se_3			
Iron selenide	$FeSe_3$			X
Jamsonite	$Pb_2Sb_2S_5$			
Lead Chromate	$PbCrO_4$			X
Lead selenide	PbSe	X		
Lead sulfide	PbS			X
Lead telluride	PbTe	X		
Lithium selenide	Li_2Se			X
Magnesium selenite	$MgSeO_3$			X
Magnesium titanate	$MgTiO_3$			X
Malachite green				X
Mercuric iodide	HgI_2			
Methyl violet				X
Molybdenum disulfide	MoS_2	X		

TABLE 22. Continued

Material	Chemical Formula	Status		
		Ordered	Received	Tested
Napthalene	$C_{10}H_6(SO_3H)_2$			X
Nitrophenol	$HO \cdot C6H4 \cdot NO2$			X
Nickel Rubeanate				X
Phenanthrene	$(C_6H_4CH)_2$			X
Pinacyanol				
Phenosafranine				
Pinaverldoe				
Potassium bromide	KBr			X
Potassium chloride	KCl			X
Potassium iodide	KI			
Potassium	K			
Nickeledithiooxylate				X
Phosphorescent 2304"				X
Phosphorescent 2310"				X
Phosphorescent 2330"				X
Phosphorescent 2469"				X
Potassium selenate	K_2SeO_4			X
Pyrene	C_6H_{10}			X
Pyrogalloe	$(CH_3O)_2C_6H_3 \cdot OH$			
Quinone	$CH(CH_2)_3CO \cdot CO$			
Rhodamine B				X
Rhodamine 6G				X

TABLE 22, Continued

Material	Chemical Formula	Status Ordered	 Received	 Tested
Selenium	Se			X
Selenium sulphide	SeS			
Selenium tetrabromide	$SeBr_4$			X
Silicon dioxide	SiO_2			
Silver bromide	$AgBr$	X		
Silver bromide (thallium added)	$AgBr(th)$			
Silver chloride	$AgCl$			X
Silver oxide	Ag_2O			
Silver sulfide	Ag_2S	X		
Silver thioantimonite	Ag_3SbS_3			
Silver thioarsenite	Ag_3AsS_3	X		
Stephanite	Ag_5SbS_4			
Sodium chloride	$NaCl$	X		
Sodium iodide	NaI			
Strontium selenide	$SrSe$			
Sulphur	S		X	
Sulphur anthracene			X	
Tartaric acid	$(CHOHCO_2H)_2$	X		
Tellurium tetrabromide	$TeBr_4$			X
Tellurium tetrachloride	$TeCl_4$			X
Tellurium tetraiodide	TeI_4			X

TABLE [illegible]. Continued

Material	Chemical Formula	Status Ordered	 Received	 Tested
Thallous sulfide	Tl_2S	X		
Tin sulphide	SnS	X		
Titanium oxide + barium titanate	$TiO_2 + BaTiO_3$			X
Titanium oxide + magnesium titanate	$TiO_2 + MgTiO_3$			X
Titanium oxide + zinc titanate	$TiO_2 + ZnTiO_3$			X
Triphenylmethane	$(C_5H_5)_3CH$			X
Tungsten trioxide	WO_3			
Vanadium pentoxide	V_2O_5			
Zinc	Zn			
Zinc beryllium silicate	$ZnBeSiO_4$			X
Zinc orthosilicate	Zn_2SiO_4			
Zinc oxide	ZnO			X
Zinc silicate	$2ZnOSiO_2H_2O$			X
Zinc sulphide	ZnS			X
Zinc titanate	$ZnTiO_4$			X
Zirconium oxide	ZrO_2			X

\# Procured from the New Jersey Zinc Company.

TABLE 23. MATERIALS TESTED FOR PHOTOCONDUCTIVITY

Material	Initial Charge	Photoconductive*	Remarks
Acenapthene	Very large	Yes (6)	Slow decay of charge in darkness
Acridine	Large	No	-
Aluminum oxide	None	-	-
Anthracene (Kodak)	Medium	Yes (5)	-
Anthracene (Reilly)	Large	Yes	-
Antimony metal	None	-	-
Antimony trisulfide	Small	Yes (?)	Rapid decay of charge in darkness
Auramine O.	None	-	-
Barium tellurite	None	-	-
Barium titanate	Small	No	-
Benzidine	Large	Yes (4)	-
Bismuth metal	None	-	-
Brilliant green	None	-	-
Calcium flouride	None	-	-
Calcium selenide	None	-	-
Chrysene	Large	Yes (7)	Extremely slow decay of charge in darkness
Cupric oxide	None	-	-
Diphenylamine	None	-	-
Diphenylcarbazide	Large	No	Extremely slow decay of charge in darkness
Diphenylene oxide	Large	No	-
Erythrosin B.	None	-	-
Fluoranthrene	Large	?	-
Fluorene	None	-	-
Fluorescent 2205**	None	-	-

TABLE 23. Continued

Material	Initial Charge	Photoconductive*	Remarks
Fluorescent 2210**	None	-	-
Fluorescent 2215**	None	-	-
Fluorescent 2220**	None	-	-
Fluorescent 2225**	None	-	-
Iron selenide	None	-	-
Lead chromate	None	-	-
Lead selenide	None	-	-
Lithium selenide	None	No	-
Magnesium titanate	Small	-	-
Magnesium selenite	None	-	-
Malachite green	None	-	-
Methyl violet	None	-	-
Napthalene	Large	No	-
Nickelodithiooxalate	None	-	-
O-Nitrophenol	Medium	No	-
P-Nitrophenol	Medium	No	-
Nickel rubeanate	None	-	-
Phenosafranine	None	-	-
Phosphorescent 2310**	None	-	-
Phosphorescent 2330**	None	-	-
Phosphorescent 2469**	None	-	-
Potassium Bromide	None	-	-
Potassium chloride	None	-	-
Potassium selenate	None	-	-

TABLE 23. Continued

Material	Initial Charge	Photoconductive*	Remarks
Pyrene	Medium	No	-
Rhodamine B.	None	-	-
Selenium	Medium	Yes (1)	-
Selenium tetrabromide	None	-	-
Silver chloride	None	-	-
Tellurium tetrabromide	None	-	-
Tellurium tetrachloride	None	-	-
Tellurium tetraiodide	None	-	-
Triphenylmethane	None	-	-
Zinc beryllium silicate	None	-	-
Zinc oxide	None	-	-
Zinc silicate	None	-	-
Zinc sulfide	None	-	-
Zinc titanate	Very large	Yes (3)	-
Zirconium oxide	None	-	-

NOTE: The test method, for all materials except barium titanate, magnesium titanate, and zinc titanate, was as follows: Break up the material using a mortar and pestle; spread a thin layer of the material onto a metal plate; pass the coated plate under a corona discharge; place the charged plate near an electrostatic electrometer; record initial charge and the rate of decay of this charge when the plate is in darkness and when the plate is exposed to a white light. (For the method used in testing barium titanate, magnesium titanate, and zinc titanate, see Progress Report No. 1, page 29.)

* The numbers appearing in this column show roughly how the materials which exhibited photoconductivity rank with one another, selenium exhibited the most photoconductivity; chrysene exhibited the least.

** Procured from the New Jersey Zinc Company.

spread a thin layer of the material onto a metal plate; pass the coated plate under a corona discharge; place the charged plate near an electrostatic electrometer; record the initial charge and the rate of decay of this charge when the plate is in darkness and when the plate is exposed to a white light (a No. 2 photoflood, 6 inches from the plate). (2) Compress the material to a thin disc; fire; evaporate or spray a conductive coating on one side; sensitize, record initial charge, and measure rates of charge decay as set forth in (1) above.

EXPERIMENTAL WORK ON PLATE PREPARATION BY VACUUM EVAPORATION

The object of this work is to determine the factors in the preparation of plates which affect the characteristics of plates to any important extent. Both the electrical characteristics and the image reproducing ability are being studied. In order of importance, the following factors are to be investigated: (1) cleaning method preparatory to evaporation, (2) temperature of plate during and after evaporation, (3) thickness of selenium, and (4) pressure during evaporation.

Factors such as plate material, presence of oxide or other films, either conducting or semiconducting, between the base metal and the selenium, rate of evaporation, and others will be investigated as time permits or need dictates.

Preparatory to carrying out this plan, the question of plate surface quality was investigated. Certain necessary improvements in the vacuum apparatus have been planned and other contemplated. (See Appendix IV.)

Cleaning Procedure Preparatory to Evaporation

The cleaning procedure whose final step consists of a degreasing in commercial-grade isopropyl alcohol vapor was tried out because of the success with which this method has been used in other similar applications. The preliminary steps are a thorough wash by hand with soap or detergent and water, followed by cleaning with methyl alcohol or acetone on a clean cloth. If the plates are fairly clean to start with, the soap and water step may be eliminated. Two features of this vapor cleaning are (1) that as the vapor condenses on the cold plate, it produces a clean, particle-free liquid which washes dirt and dust off the plate and (2) that the vapor will not become contaminated with greases, etc. This method has been used successfully to prepare the base material for evaporation and has eliminated the occurrence of water or alcohol drop marks and cleaning streaks. An example of a plate not cleaned by the degreasing method which exhibits alcohol drop marks much in evidence is shown in Figure 34. A degreaser has been constructed which will take a plate 10" x 12" (see Figure 35).

The normal boiling point of isopropyl alcohol is 82.3°C. Consequently, if a xerographic plate is immersed in this vapor for several minutes (longer depending on the specific heat and mass of the backing material) it can be made to lose its photoconductive property as it changes to the gray crystalline form. Hence, finished xerographic plates cannot be cleaned by degreasing with this vapor, but a lower boiling point liquid might be used successfully.

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Figure 34. Photograph of xerographic print showing spots on print resulting from alcohol drops on plate after cleaning before evaporating the selenium film onto the plate surface. Several of the marks are indicated by arrows. The plate was cleaned by hand and not vapor degreased.

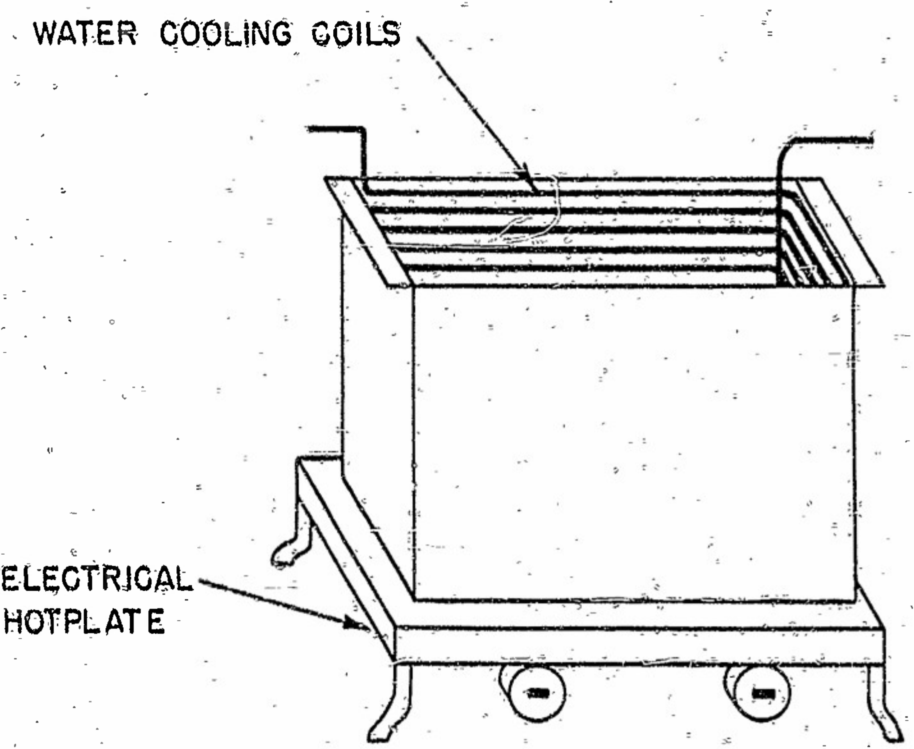

FIGURE 35. DEGREASING TANK FOR CLEANING XEROGRAPHIC PLATES BEFORE EVAPORATION.

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Temperature Control of Plate During Evaporation

Though no cold trapping is in use as yet on the system, preliminary tests were made on maintaining the plate below room temperature during evaporation. The plates were clamped at 4 points to a platen having cooling coils passing through it. The temperatures recorded in Table 24 are those of the coolant leaving the platen and not of the plate itself. Some of these plates were also made in nearly total darkness. Table 24 lists the cooled plates made in this series. As is to be expected, the cooler the plate, the thicker the selenium film is for given conditions of firing distance and weight of charge. All of the plates maintained at or near room temperature during evaporation have a bluish gray cast; i.e., the surface scatters light rather than reflecting it specularly. This cast is different from the strong gray scattering which one sees from crystalline selenium. These cooled plates are photoconductive, acting much as the uncooled plates do as far as making line copy and continuous-tone reproductions are concerned. There are, however, two features about the electrical characteristics that should be noted. When the plates are moderately cooled and prepared in near-total darkness, they take a much lower positive voltage than uncooled plates do. Also, they have practically zero residual charge after 1 minute of light decay test. Whether this is primarily a function of the temperature or the lack of light (a fatigue effect) or both has not been ascertained. Reference to the theory presented in an earlier part of this report suggests that this effect is to be expected, however. Doubt concerning the specific roles played by temperature and light during the preparation of the plate prevents an

TABLE 24. SELENIUM-COATED ELECTROPHOTOGRAPHIC PLATES PREPARED BY VACUUM EVAPORATION UNDER TEMPERATURE-CONTROLLED CONDITIONS

Plate Designation	Weight of Charge, Grams	Thickness, Microns	Heater Type	General Appearance	Coolant Temperature, °C.	Average Pressure, Microns	Made and Handled in Darkness or Light	Positive Charge			Negative Charge		
									Light Decay, 1 Minute			Light Decay, 1 Minute	
								Maximum	Loss	Final	Maximum	Loss	Final
10-13-48-A	20	10	Double rost.	Blue scatter	+ 26	1.1	Semidarkness	300	150	150	355	155	200
10-13-48-B	"	16	Ditto	Ditto	- 10	1.1	"	340	185	155	470	175	295
10-15-48-A	"	8	"	"	~+ 8	>5	Dark	52	22	30	135	36	99
10-28-48-A	10	10	Hotplate	"	+ 15 to 20	8	Light	200	130	70	330	125	205
10-28-48-B	15	17	"	"	+ 18 to 24	8	"	435	230	205	555	230	325
10-29-48-B	"	"	"	"	17 - 27	5 - 8	Dark	65	55	10	275	120	155
11-1-48-A	"	"	"	"	16	"	"	160	160	0	375	185	190
11-2-48-A	"	15	"	"	16	"	"	26	26	0	315	130	185
11-3-48-A	"	17	"	"	16	"	"	215	185	30	550	245	305
11-3-48-B	"	18	"	"	16	"	"	80	80	0	535	200	335
11-4-48-A	"	"	"	"	16	"	"	130	130	0	400	175	225

NOTE: Plates all 18-gauge aluminum (mirror finish) 8-1/2" x 11".
Selenium - ARQ brand
Distance - source to plate - 24 cm.
Vacuum system - RCA
Cleaning method - Methanol, H_2O rinse, Duranol, H_2O rinse, blown dry.
Charging voltage - 4000 volts.

accurate interpretation of these results on the basis of the theory at the present time. It is suspected, however, that differences in the relative ability of excited electrons and positive "holes" to move from their molecular confinement will be involved in the explanation.

Plates Prepared in Darkness

At the suggestion of the Signal Corps representative, several experiments were conducted wherein plates were prepared by vacuum evaporation in total darkness and kept in darkness until the light decay curves for negative voltage were run. These tests were conducted in conjunction with the tests on plate preparation at reduced temperatures. Results of these tests are tabulated in Table 24. As stated in the above section on "Temperature Control of the Plate During Evaporation", the notable points are the low value for the positive charging voltage and the low value of the positive residual charge.

Importance of Surface Quality

To investigate the effect of the base material surface quality on the grain in continuous-tone images and the background in line copy reproductions, several plates were prepared on plate glass and several on metal surfaces of high polish. The size of these plates was 4" x 5". Plate glass was selected as having a higher degree of surface smoothness than any other surface available. Thin brass plates having a very high surface polish were chosen as having a surface quality intermediate between the glass and the commonly used mirror-finish aluminum sheet.

To provide a conducting surface on the glass, but still not impair the quality of the surface (presumably), a film of aluminum was evaporated onto the glass. For some of the specimens, the aluminum and selenium films were deposited in the same evacuation. For other, the aluminum film was prepared beforehand. There was much better adhesion between the selenium and the aluminum films when they were prepared in the same evacuation. The aluminum films ranged in thickness from approximately 20 per cent transmitting to practically opaque (less than 0.1 per cent transmitting). Neither the time of preparation of the aluminum nor its thickness seem to have any influence on the quality of images the plate will take (as long as the aluminum is thick enough to be conducting). One film of nichrome was used as the conducting layer; it worked as well as aluminum.

The polished plates of brass also have an aluminum film evaporated on before the selenium. This is also true of two regular mirror-finish aluminum plates. The sketch of Figure 36 shows the relative positions of the aluminum sources, selenium source and receiving surfaces. Figure 26 also shows the release mechanism used to shield a portion of one end of the glass plates from the selenium so as to allow making electrical contact to the conducting layer during charging. It is operated by means of a magnet from outside the bell jar after the aluminum has been deposited.

Figure 37 shows a comparison of the standard mirror-finish aluminum and a glass-backed plate from the standpoint of powders, both positive and negative, which adhere to the plate in both exposed and unexposed portions. For both positive and negative powders, the aluminum

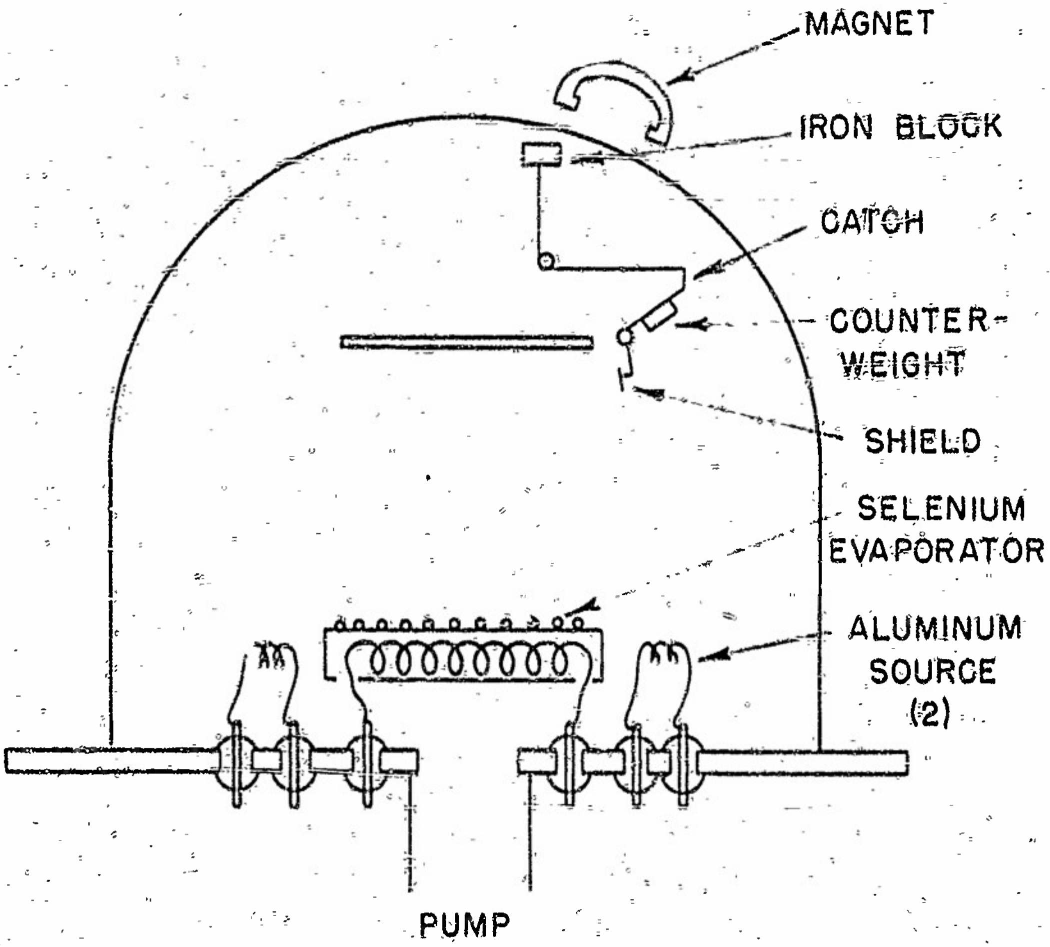

FIGURE 36. SCHEMATIC VIEW OF SET-UP FOR APPLYING ALUMINUM AND SELENIUM FILMS IN ONE EVACUATION SHOWING SHUTTER ARRANGEMENT TO SHIELD PORTION OF PLATE FROM SELENIUM.

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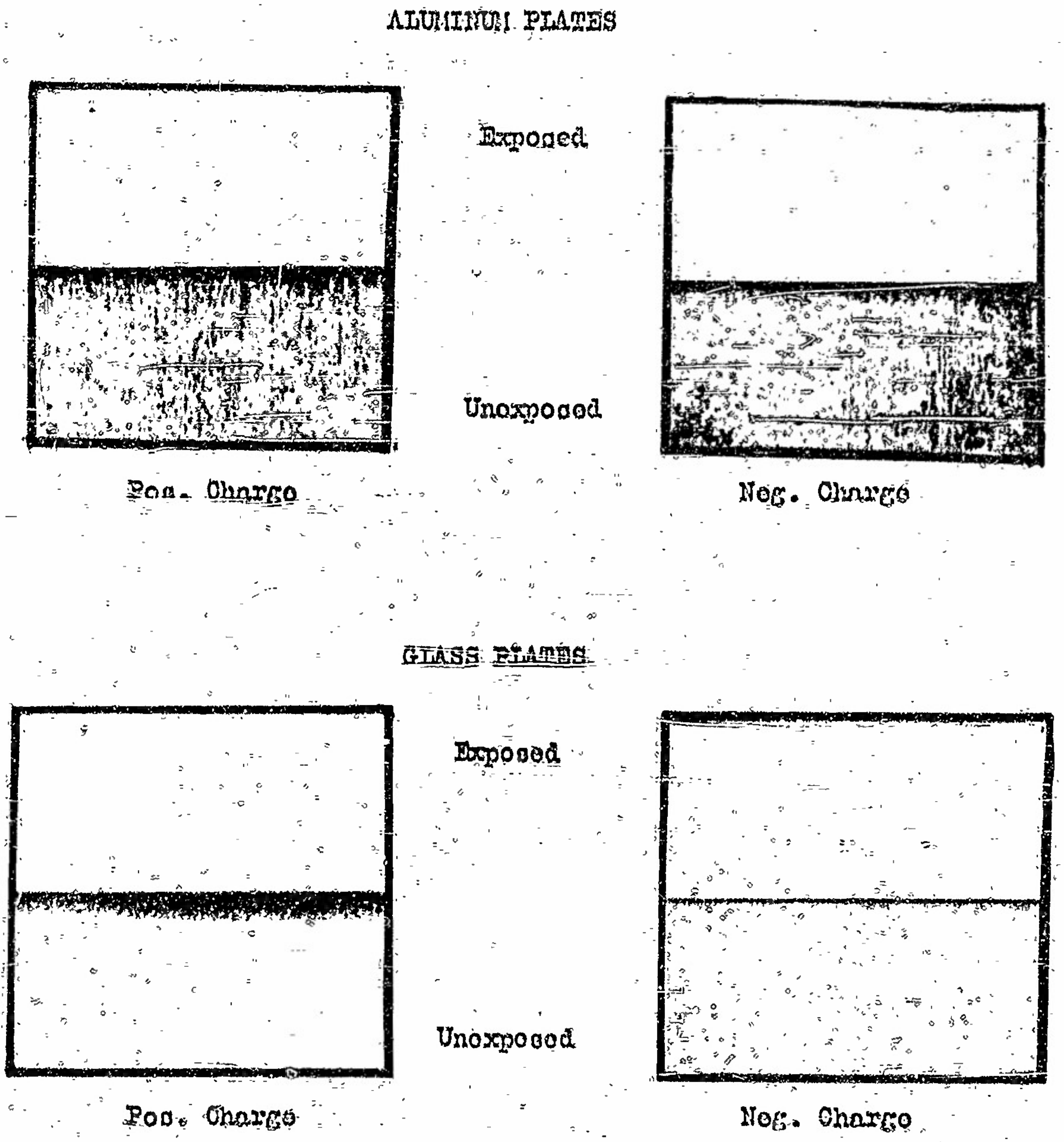

Figure 37. Comparison of backgrounds on aluminum and glass-backed plates. Positive and negative charging, exposed and unexposed portions.

plate has considerable powder adhering in the unexposed portions, indicating many small discontinuities in the surface. On the other hand, for the glass plate with positive charging, no powder adheres except along the edge between the exposed and unexposed regions---apparently the only place where a charge discontinuity appears for the positive powder. For the negative powder, the situation is entirely different for the glass-backed plate. Here considerable powder adheres both in the exposed and the unexposed areas.

In general, the contrast on the glass-backed plates are very good for positive charging, but low for negative. The few exceptions to this are unexplained. The background on the glass plates is more uniform and homogeneous than for the aluminum; a direct result of scratches and roll marks in the aluminum. The polished brass also gave more uniform background than the aluminum. There was apparently no effect of the aluminum film evaporated on the aluminum.

These plates still must be tested for electrical characteristics. Continuous-tone pictures made with glass plates do not, however, show much less graininess than the mirror-finish aluminum, proving again that all grain is not due to the surface characteristics of the aluminum or selenium. See Table 25 for the data on the preparation of glass-backed plates.

Measurement of Thickness of Coating

Since the method used to date to measure the thickness of the selenium films depends upon the use of a relatively thick conducting

TABLE 25. DATA ON THE PREPARATION OF SELENIUM-COATED GLASS-BACKED ELECTROPHOTOGRAPHIC PLATES

						Undercoating			Line-Copy Reproduction		Background	
Plate Designation	Distance Source to Plate, Cm.	Weight of Charge, Grams	Base Material	General Appearance	Average Pressure, Microns	Material	Same Run as Se Evaporated	Thickness, % Transmission	Negative Charging	Positive Charging	−	+
11-15-48-A-4	24	16	Glass	Specular	>1	Nichrome	No	10	-	Good	-	-
11-24-48-A	20	10	"	"	"	Aluminum	"	"	Poor	Fair	-	-
11-24-48-B	20	10	"	"	"	"	"	"	Fair	Good	-	-
11-30-48-B	22	10	"	"	1	"	Yes	"	None	Very good	-	-
11-30-48-C	"	"	"	"	"	"	"	"	Fair	Good in one corner. None in other corner.	Some	Low
12-2-48-A	"	"	"	"	2	"	"	5	Fair	Fair	-	-
12-2-48-C	"	"	"	"	"	"	"	"	"	Good	High	Low
12-2-48-F-1	21	"	"	Gray in spots, oxide colors in others.	"	"	"	1	Bad	"	Very high	Low
12-2-48-F-2	"	"	Aluminum	Gray scatter	"	"	"	"	None	None	None	None
12-2-48-H-1	"	"	Glass	Specular	"	"	"	"	Poor	Good	High	None
12-2-48-H-2	"	"	Aluminum	Oxide colors	"	"	"	"	Bad	Fair	High	None
12-8-48-J-1	"	"	Glass	Specular	4	"	"	20	Won't print	(?)	-	-
12-8-48-J-2	"	"	Polished brass	"	"	"	"	"	Poor	Poor	High	Low
12-9-48-A-1	"	"	Glass	Slight gray	3	"	"	Opaque	Good	Good	Low	Low
12-9-48-A-2	"	"	Polished brass	Specular	"	"	"	"	Poor	"	High	Low

NOTE: Base material - 1/8"-thick plate glass, size 4" x 5".
Double rectangular heater for Se.
Selenium - ARQ.
Vacuum system - RCA.
Cleaning method - Dupanol, H2O rinse, Methanol, Isopropyl vapor degrease.
All made in light.
Charging voltage - 4000.

backing material. The aluminized glass plates of course do not provide this so another method was used. It consists of using an optical flat laid across the edge of the selenium film so as to form interference fringes on the bare aluminum portion as shown in Figure 38. By counting the fringes with the aid of a vertically illuminating microscope, the selenium layer was found to be approximately 12 microns thick. This is within the range that was expected, judging from the amount of charge and distance between source and plate. The visibility of the fringes from the highly reflecting aluminum surface is enhanced when the lower surface of the test glass has a semitransparent reflecting film on it.

EXPERIMENTAL WORK ON DEVELOPING TECHNIQUES

Use of a Grounded Auxiliary Electrode During Development

An auxiliary, grounded electrode was placed near the surface of an electrophotographic plate during development. The spacing between electrode and plate was varied from 1/16 inch to 7/16 inch.

The electrode consisted of flat sheet metal which was drilled and tapped for four adjustable screws. During development, these screws were in contact with the electrophotographic plate and effected the plate to electrode separation.

The selenium plate, 10-27-48-A, was sensitized by negative corona, exposed to a continuous-tone, positive transparency and then developed with and without the auxiliary electrode using developer 5-28-48-1-A.*

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* Type No. 8 glass beads (coated with Durite X-221, Durez 12763, and Vinylite VYLF) as carrier with powder G1 (20 part Gilsonite to 1 part Raven and carbon black by weight, micronized).

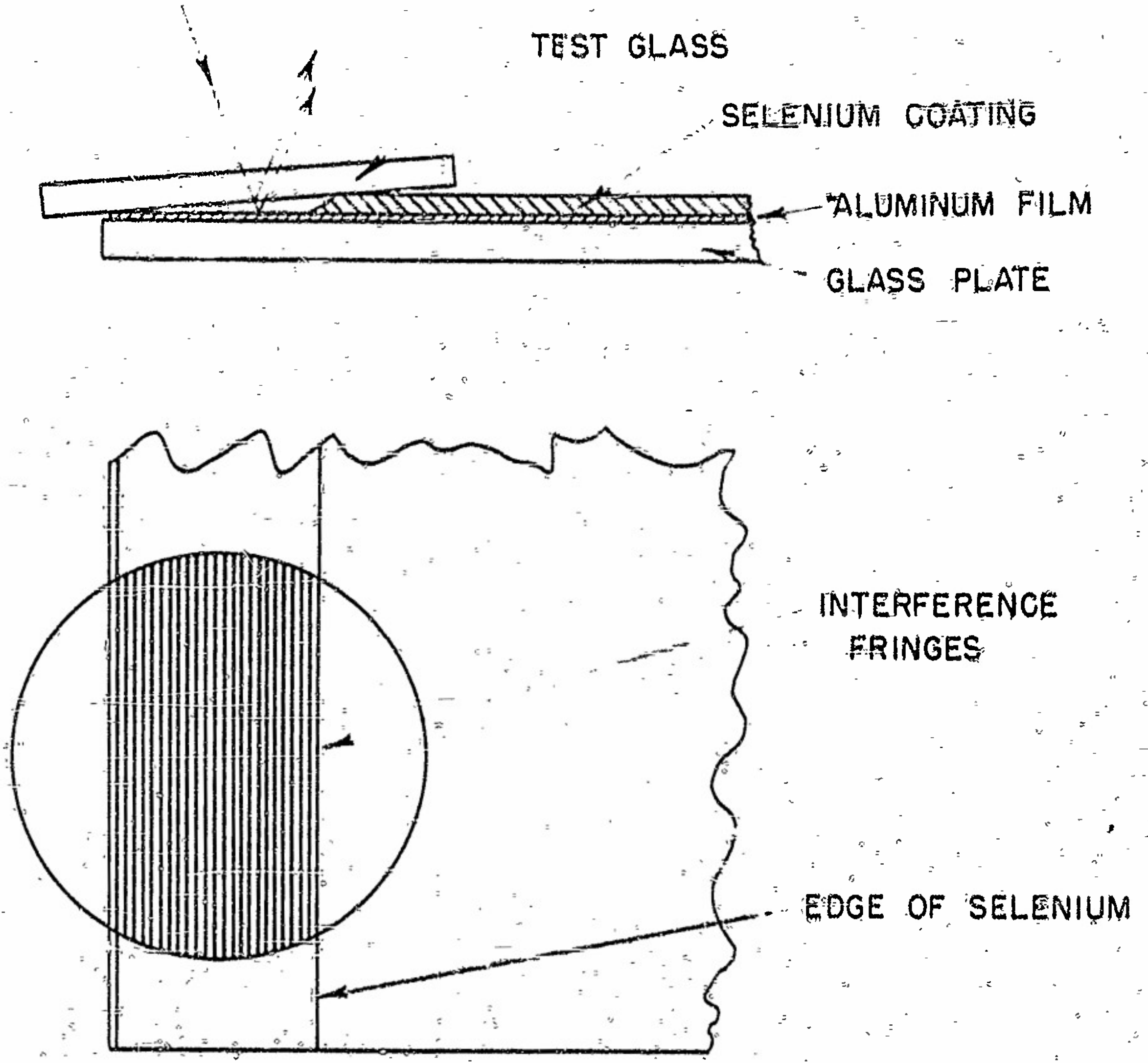


FIGURE 38. INTERFERENCE FRINGE METHOD FOR DETERMINING THICKNESS OF SELENIUM COATING.

0-10,071

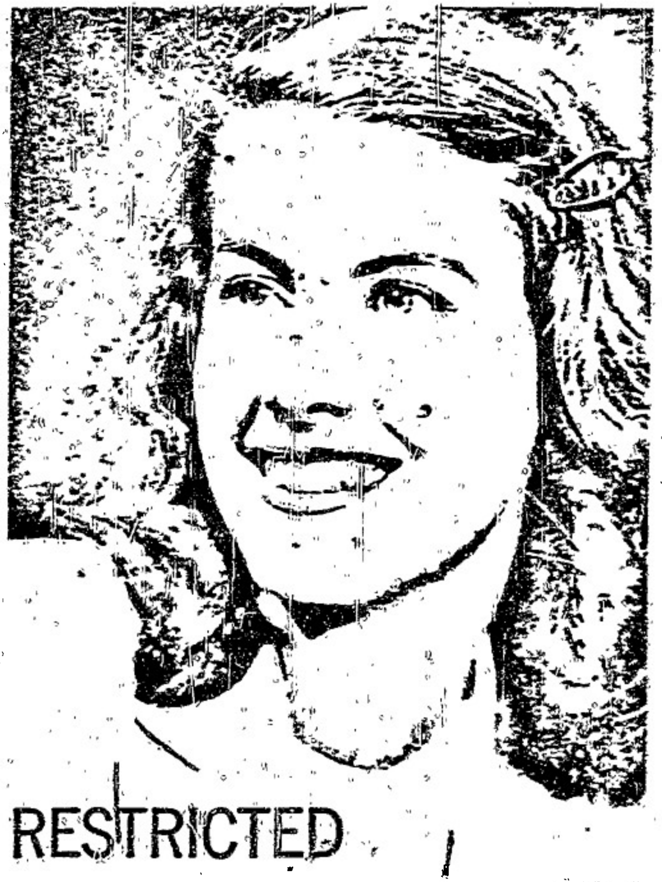
Figure 39 shows a photographic print of the continuous-tone image used in this work. The results, Figures 40 and 41, show an improvement in quality of continuous-tone reproduction with the use of the grounded electrode. It was found that the amount of powder deposited on the image was approximately inversely proportional to the plate-electrode separation (i.e. the smaller the separation the greater the amount of powder deposited). The improvements in results are believed due to an intensification of the electrical field immediately above the plate by the presence of the electrode. Without the electrode, the electrical field immediately above the plate is weak except near the line of demarcation between charged and uncharged areas. As a result, there is little attraction for developer powder except around the edges of image areas. With the electrode in place, however, there exists a much stronger field immediately above the plate and hence developer powder will be more strongly attracted to the plate. In these early experiments, the auxiliary electrode was held at zero or ground potential, however, the adjustment of this potential to other values is contemplated.

Screening of Image in Continuous-Tone Reproduction

A 120-line half-tone transparency of uniform dot area was prepared for use in an attempt to improve the quality of continuous-tone reproduction. The prepared half-tone transparency was 75 per cent opaque. A charged electrophotographic plate was exposed separately to a continuous-tone, positive transparency and to this screen transparency. This procedure served to break up the large electrically charged areas on the

60150

Figure 39. Photographic print of the continuous-tone image used in continuous-tone electrophotography.



59993

Figure 40. Continuous-tone image produced in the normal manner, using a positive transparency, Plate 10-27-48-A, developer 5-28-48-1-A, and negative sensitization.

Figure 41. Continuous-tone image produced when a grounded electrode was placed 0.0625 inch above the charged electrophotographic plate during development. The remaining variables were the same as used in Figure 40.

plate into many small charged areas and to bring into play the electrical phenomena which produce dense images near the edge of charged areas. Figures 40 and 42 show the results produced with and without the screening exposure operation. The screening improves the reproduction of gradations of tones, but at least in these examples, it does not produce dense shadows.

Electrophotographic plate 10-27-48-A, developer 5-28-48-1-A, and a 75 per cent opaque 120-line half-tone transparency was used in this work. The exposure time used for each of the two separate exposures was approximately one-half of the normal exposure time or 5/8 second at 70 volts.

MEASUREMENT OF RESISTIBILITY OF A SELENIUM BINDER WITH VIBRATING PROBE ELECTROMETER

A series of exploratory tests were made to determine the resistivity of selenium binders using the vibrating probe electrometer (see Appendix VI).

Extensive tests were made on only one of the binders, namely, ethyl cellulose*, and the results of these tests only will be presented here.

The ethyl cellulose coated to 21 microns thickness on an aluminum plate was charged by exposure to a needle charged to 7000 volts for two seconds at a needle-to-plate distance of approximately 6 mm. The charged needle was fixed at a position directly above the center of the test area of the plate.

---

* The material used was "Ethocel", Dow Chemical Company.

RESTRICTED

52994

Figure 42. Continuous-tone image produced when the electrophotographic plate was exposed separately to a continuous-tone, positive transparency and a 75 per cent opaque half-tone transparency. Plate 10-27-48-A, and developer 5-26-48-1A was used with negative sensitization to make this print. The separate exposure times were 5/8 second at 70 volts.

Directly after the charging operation, the plate was brought into test position and the voltage induced in the vibrating probe by the charged plate was amplified and viewed on the screen of a cathode ray oscilloscope. In order to increase the accuracy of the plate-voltage measurement as it varied with time, a null method was used wherein a known voltage of same polarity was applied to the shield of the probe until the net voltage induced in the probe was zero as indicated by the pattern on the oscilloscope screen.

Several test runs were made on the ethyl cellulose sample at intervals of approximately 15 minutes and each run was characterized by a decrease in discharge rate over the previous run.

When negatively charged, the plate discharged more slowly than when positively charged; however, a sufficient number of oppositely charged plates have not been tested to determine the significance of this observation.

A typical discharge curve is one shown in Figure 43.

On the assumption that Ohm's law applies, the current that flows between two points of the conductor at a potential difference V is given by $i = \frac{V}{R} = \frac{dQ'}{dt}$; where Q' is the quantity of charge flowing through unit cross section. But $\frac{dQ'}{dt} = -\frac{dQ}{dt}$; where $-\frac{dQ}{dt}$ is the loss of charge per unit area at the surface of the ethyl cellulose. Further, $V = \frac{4\pi x Q}{kA}$; where k is the dielectric constant of the "Ethocell", A the area of the surface, and x the thickness of the coating. Since, by definition, $R = \frac{rx}{A}$ where r is the resistivity we have finally

$$V = V_0 e^{-\frac{4\pi}{rk}t} \tag{1}$$

where V_0 is the initial voltage.

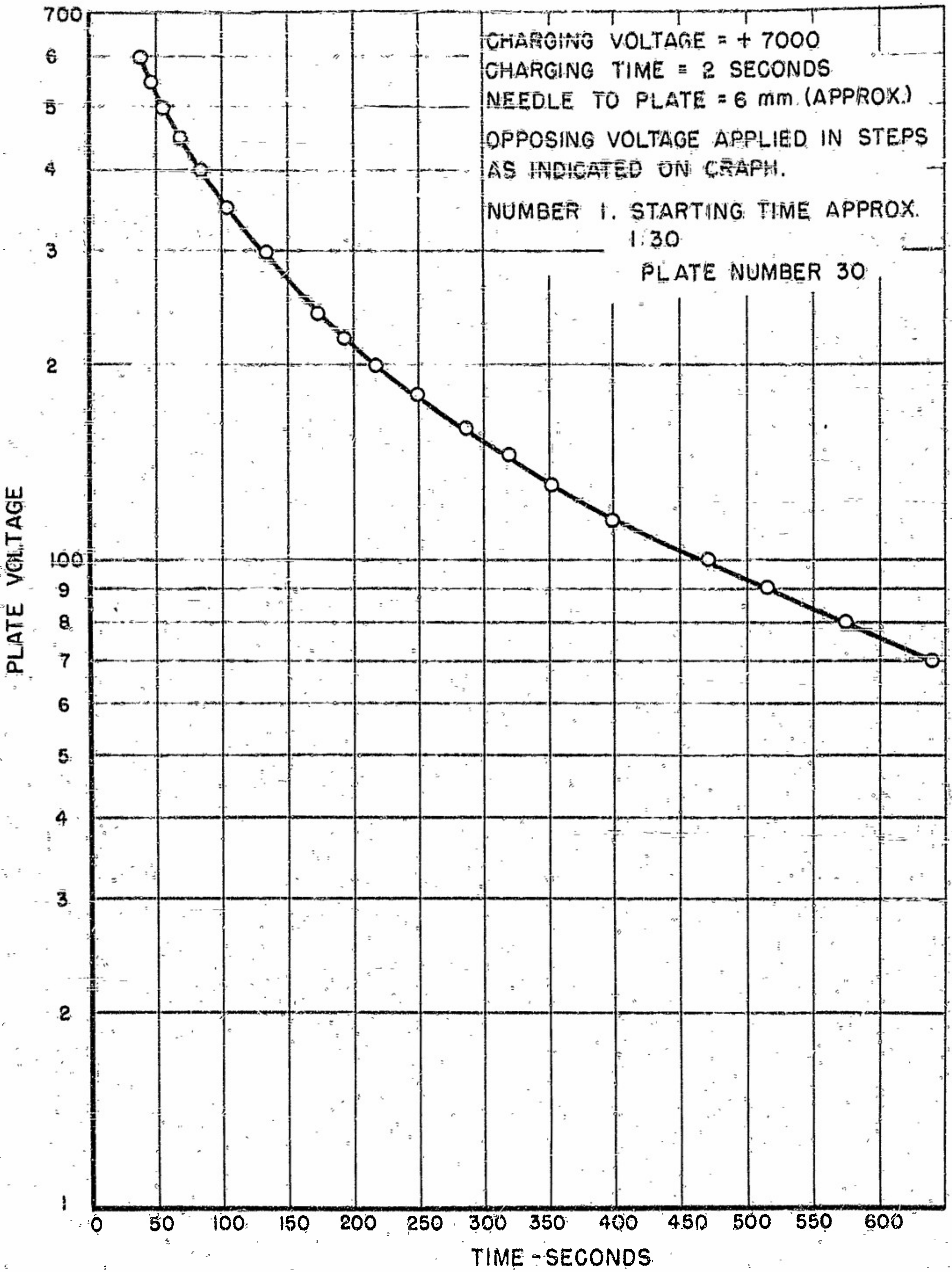


FIGURE 43. TYPICAL VOLTAGE DECAY CURVE FOR ETHYL CELLULOSE INSULATING BINDER.

Since the curve in Figure 43 departs considerably from linearity, it is evident that the assumptions used to arrive at equation (1) are not quite correct. Nevertheless (1) can be used to obtain a value of r of the order of magnitude of the correct value.

From Figure 43, we assume a value of 1000 volts for V_o. Also, since k = 2.5 to 4.0 for ethyl cellulose for 60 to 1000 cycles, the value k = 3.0 was chosen.

Using these values in conjunction with equation (1) and the data from Figure 43, it was found that r varied between 3×10^{14} and 9×10^{14} ohm-cm.

The variation of $\frac{rk}{4\pi}$ was plotted as a function of time, and as shown in Figure 44, the relation is nearly linear; at least in the initial stages of discharge.

Data for this report are recorded in Laboratory Record Books:

No. 3871, pages 52 - 75, inclusive.
No. 3903, pages 1 - 4, inclusive.
No. 3931, pages 1 - 9, inclusive.
No. 3956, pages 6 - 31, inclusive.
No. 3957, pages 1 - 11, inclusive.
No. 3997, pages 19 - 74, inclusive.
No. 4041, pages 40 - 68, inclusive.
No. 4117, pages 1 - 14, inclusive.
No. 4191, pages 1 - 27, inclusive.
No. 4241, pages 1 - 3, inclusive.

RMS/LRJ/AEH/LEW/DTW/JJR/OAU/JS/JFW/PGA/DLF/JRB/KEC/KEJ/CJM/NBO/CDO:swr
December 28, 1948

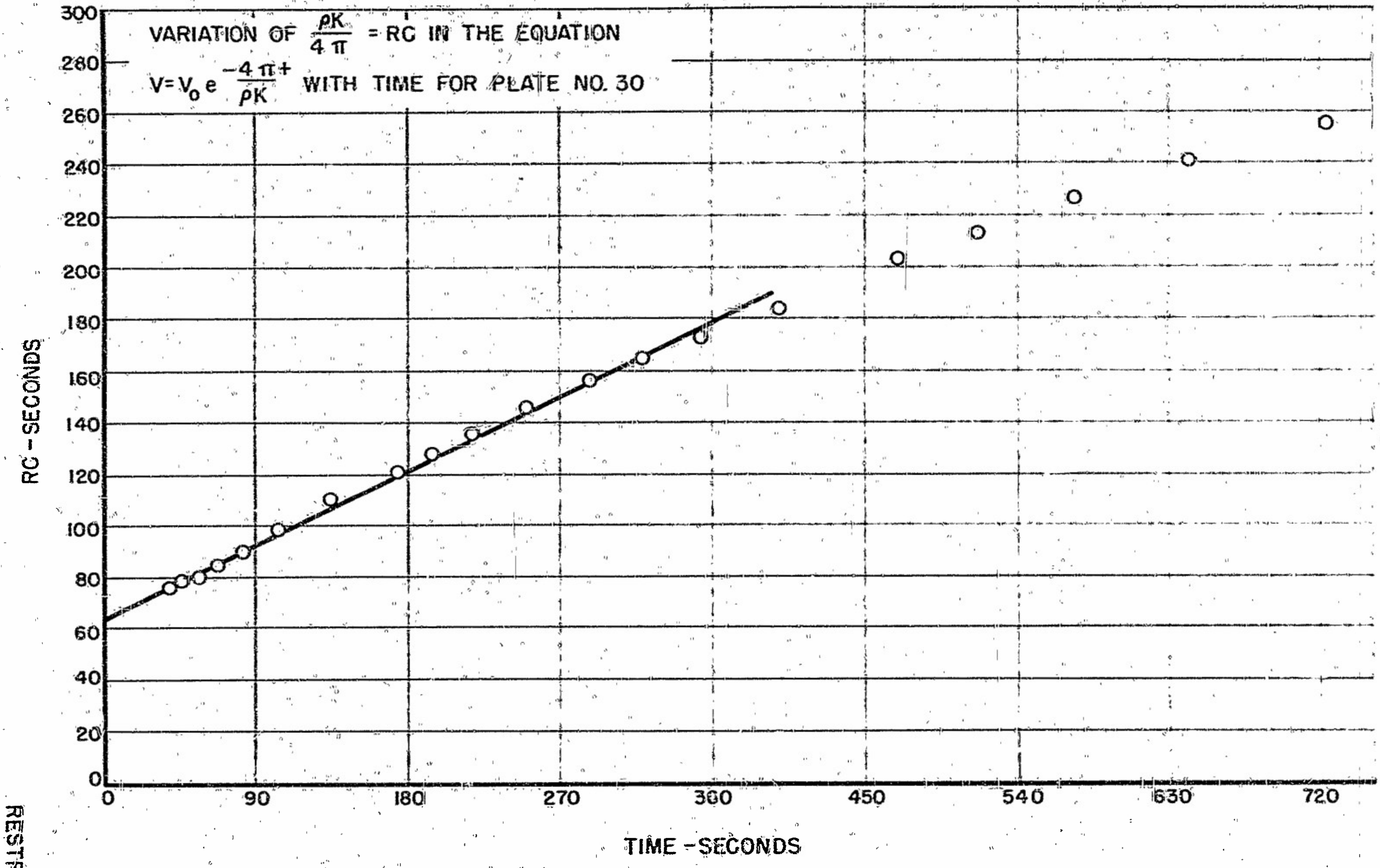


FIGURE 44. VARIATION OF RESISTIVITY WITH VOLTAGE ON AN INSULATOR

0-10,073

APPENDIX I.

Methods Used in the Preparation of Selenium Photoactive Films

APPENDIX I.

Methods Used in the Preparation of Selenium Photoactive Films

Preparation of Selenium

Selenium is obtained commercially in the following forms: (a) OCR refined selenium powder, consisting largely of crystalline selenium in undetermined quantity; (b) DDQ selenium (double distilled in quartz) is a semipure vitreous selenium in which the impurities vary from batch to batch in the processing; (c) ARQ selenium (ammonia reduced in quartz from SeO_2). This is considered the most pure selenium, although it also has variations in impurity content from batch to batch.

Processing of OCR Refined Selenium. The refined commercial grade of selenium, being of crystalline nature, cannot be used as photoactive material; therefore, this form was converted to the vitreous by the following processing:

1. The refined selenium is heated to a temperature of 250°C. The molten selenium at this temperature has a relatively low viscosity.

2. The molten selenium is then slowly poured into cold running water. This forms hard spherical vitreous shot selenium.

3. The selenium shot is then treated with petroleum ether, which removes the excess water still retained on the surface of the shot; the selenium is then allowed to dry at room temperature in an open vat.

The selenium shot, obtained by the above processing of the refined selenium, was sometimes further processed for use in making Se paint. This additional processing consisted of grinding. Grinding was accomplished with a micro-pulverizor, which gives a powder with particle sizes, ranging from 1 micron to 50 microns.

Processing of Selenium for Spraying and Pressing Application Methods. The selenium used for the spraying and pressing methods does not require a definite form; therefore, the ARQ and DDQ commercial-grade seleniums can be utilized satisfactorily, as received from the refinery. The DDQ and ARQ selenium is produced as vitreous shot, and need not be charged from this form unless it is desirable to have it in another form, or to use it for impurity additions. Selenium for spraying can have any form, either crystalline or vitreous, since the selenium must be in the molten state for spraying. The selenium used for pressing also can have either form or state, since the pressing is done with heated platens and pressure. The forms used most are stick selenium, powder, and shot. To obtain stick selenium, the selenium is heated to the molten stage, cast in porcelain boats, and then rapidly cooled in water to inhibit the formation of crystalline material.

Controlled Impurity Additions. To obtain selenium which contains controlled amounts of impurities, it is necessary to process these seleniums in the laboratory, since they are not available commercially. The starting selenium must be nearly chemical pure, since ARQ selenium was the only available selenium with this characteristic, it was utilized for impurity addition studies.

The addition of impurities to selenium batches was completed in the same manner; namely, (a) heating selenium of a prescribed quantity to the molten state, (b) adding the controlled amount of impurity while agitating the selenium to insure obtaining a homogeneous material, and (c) casting the ~~selenium into~~ sticks.

Table 26 lists the amounts and types of impurity-contaminated seleniums which have been produced.

Techniques Used in Preparation of Photoactive Selenium Paints

Initially, the procedure used for preparing selenium paints consisted of charging very finely ground selenium metal, organic binder, and solvents to a pint- or quart-size glass jar, filled approximately to the halfway mark with 1/2-inch glass balls. Glass containers and balls were used in place of the conventional ceramic porcelain or steel jars and balls, to avoid the possibility of contamination of the paint with abraded ceramic or metal particles. Subsequent work has shown that either ceramic, porcelain, or steel jars and mills can be used without any apparent impairment of photoactive properties of the selenium paint.

Also, as indicated above, the selenium was ground in the dry state by suitable techniques, and classified by means of an air classifier, into various particle-size ranges, and the selenium powder, thusly ground and classified, then charged to the ball mill container, as described above. Here, again, subsequent work has shown that relatively large particle-size selenium pellets (1/16 to 3/16 inch in diameter), when charged to a steel ball mill jar, filled approximately 1/2 full with steel balls,

TABLE 26. CONTROLLED IMPURITY ADDITIONS TO SELENIUM-PIGMENTED PAINT FILMS

Weight of ARC Selenium, grams	Weight of Impurity Addition, grams	Type of Impurity	Remarks
350	3.5	Cd	CdSe formation detected in residue. Per cent unknown.
750	10	Bi	Bi_2Se_3 formation detected in residue. Per cent unknown.
500	10	Te	Te enters only as a mixture.
500	10	CeI_2	Iodine vapors released upon addition. ~~Formation unknown.~~
500	5	$CdCl_2$	Formation unknown.
500	5	$BiCl_3$	Ditto
500	5	CuS	Some CuSe formed, checked in residue.
500	5	LiCl	Formation unknown.

along with the organic binder and solvents, can be reduced to satisfactory particle size and dispersed in the paint vehicle simultaneously. This latter step, if production of selenium pigmented photoactive paints should become feasible, represents a real economic advantage in that it eliminates the necessity of grinding and classifying equipment, as well as the time and labor consumed by such operations.

On the basis of the experimental work completed to date, the following conventional ball milling technique seems to be the optimum procedure for preparing a photoactive selenium paint.

A conventional cylindrical steel ball mill jar is filled approximately half full with suitable sized steel balls (usually 1/2-inch-diameter balls). To this mill are then added a suitable sized charge of the following ingredients:

1. Selenium shot or pellets. These pellets may vary in size up to approximately 3/16 to 1/4 inch in diameter.

2. The organic binder being used as the vehicle. This binder can be in the form of a dry solid or a solution in suitable solvent or solvent mixture.

3. Plasticizers for the organic binder, if any are required.

4. Solvents. Sufficient solvent to give good "grinding viscosity" is all that is required.

The jar is then closed, started rotating, and allowed to run for approximately 16 to 20 hours. At the end of this period, the jar is opened, and the paint examined for fineness of grind. If the selenium is judged to be ground finely enough, the paint is then removed from the jar and stored in a suitable container until needed for use.

In the above procedure, a suitable sized charge is considered to be a charge whose solid volume is sufficient to fill the voids of the steel balls, and to cover the steel balls with 1 to 2 inches of solid volume (in a gallon-sized jar; in larger or smaller jars, the height of the solid volume above the balls will be proportionately larger or smaller). Also, a good "grinding viscosity" is such a viscosity that under the operating conditions of the ball mill (i.e. speed of rotation, etc.) the balls are carried up the inner periphery of the ball mill jar until it reaches a point approximately 3/4 the distance along the circumference to the top of the jar, and then fall or "cascade" down the inclined plane formed by the remainder of the balls. Such cascading provides the maximum number of impingements of ball against ball, and hence maximum grinding speed.

The following is a list of the variants in the technique of preparing selenium metal paints, which are felt to be worthy of study at some future date:

1. The effect of varying the length of grinding time. It is felt that this variable should be studied because variation in grinding time will affect the ultimate particle size of the selenium metal in the paint which in turn may influence the photoactive properties of the resultant paint.

2. Determination of the optimum grinding viscosity when the most desirable vehicle or binder is found.

3. Study of the possibility of grinding in part of the resin, and reducing the paste with the remainder to improve grinding.

APPENDIX II.

Methods Used for Applying Photoactive Films

APPENDIX II.

Methods Used for Applying Photoactive Films

Molten Selenium Spray Method

The spraying of molten selenium vitreous films is accomplished by the following techniques:

1. The gas pressure used for the atomization of the selenium liquid is heated to a temperature close to 100°C.

2. The base panel being sprayed is heated to a temperature where the vapors of selenium on contact form a vitreous film; this temperature is in the range of 175°C.

3. The selenium is maintained molten during the spraying operation to insure a continuous flow of liquid to the atomizing section of the gun.

4. To maintain a constant flow of selenium to the gun jet, a back pressure is employed on the surface of the selenium.

This also serves to control the percentage of atomization, since it controls the amount of selenium being fed. Also, the atomizing pressure can be regulated to obtain the optimum atomization of the selenium.

The gun used for the above if a simple venturi-type low-temperature metallizing gun, which contains a reservoir for melting the material being sprayed, and is an integral part of the gun. The jet orifice is 1/32 of an inch, and is mounted such as to allow the gas pressure to escape through a 1/4-inch opening.

The procedure for applying a selenium film to a panel is to heat the panel over an open gas flame to the approximate temperature required (175°C.), and then pass the plate in front of the vapor being released by the gun. If the base plate is not heated to high enough temperature, then the formation on the panel will be gray crystalline selenium. If, however, the temperature of the panel is too high, then the vapors being sprayed on the panel will immediately revaporized, and no coating will be obtained. After the panel is completely coated, it can then be quenched in water or allowed to cool to room temperature; either method seems to be satisfactory and does not appear to have any effect on the final characteristic of the plate.

Hot Pressing Selenium Films

The application of a selenium film to a base material was accomplished in the following manners.

1. The selenium was spread on the surface of the base, as shot or powder. In addition, it was poured on or applied as crude selenium chunks.

2. Pressure is applied to the selenium-coated base placed between two heated platens until the selenium flows over the entire surface of the base. The thickness of the resulting selenium film is a function of the temperature of the platens and the pressure being applied.

3. To obtain a uniform, highly polished, and smooth surface, the selenium is pressed against highly polished metal platens or other materials with similar characteristics. The ones being used at the present time are stainless steel, chromium plated brass, and Mica sheet.

4. The plates, after being pressed, are then quenched into cold water; this being necessary to inhibit the growth of crystalline selenium. Plates produced in the above manner have the following characteristics:

(a) a highly polished glossy surface

(b) uniform thickness over the entire plate

(c) low resistance on the surface of the plate (less than 10^6 ohms)

(d) good adherence of the selenium film to the base material

(e) no photoactivity of the plates is noted

(f) images cannot be obtained.

<u>Techniques Used for Application of Photoactive Paint Films</u>

The initial experimental photoactive paint films were applied, by means of a 0.003-inch Bird Film Applicator, or doctor blade. This technique was soon discarded because of the following considerations: It is not possible with a doctor blade to coat the entire surface of a test plate, because of the end supports of the doctor blade, which must rest directly on the panel surface. Also, in order to obtain uniform films over large test plate areas, extremely flat test plates are required, a condition which is very difficult to achieve in actual practice.

The next technique studied, and the one currently being used, is the conventional spraying procedure used quite widely for application of paints, lacquers, etc. Specifically, the technique presently being used consists of thinning the paint to approximately 17 to 20 seconds viscosity, as measured in a number 4 Ford Cup and spraying with a suction-type spray gun, using twenty to thirty pounds air pressure. The fluid feed is adjusted to permit flow of that amount of paint which will give a uniform film with no tendency to sag. The main advantage of the spraying technique is that it is a widely used procedure for which equipment is readily available. Additional advantages are that it offers great flexibility insofar as size of test plate desired, presents possibilities of conveyorizing with automatic spraying, etc.

The third technique which has been widely used industrially is that of dip coating. Although this method has not been used to apply photoactive paint films, there appears to be no good reason why it should not be applicable.

Still another technique which should merit special consideration is the electrostatic spraying. When it is remembered that the estimated price per gallon of selenium pigmented paints varies between $15 and $20 per gallon (depending upon the amount of selenium used per gallon), this procedure, which is claimed to eliminate approximately 50 to 75 per cent of the paint lost as overspray, becomes especially attractive.

Application by roller-coating should also be investigated, especially on flat surfaces, since the coating loss is also minimized by this technique.

At the present, at least no especially difficult problems are foreseen in regard to methods of applying selenium paints as such. The only problem visualized in this connection is that of preparation of the metal surface upon which the selenium paint is being sprayed, and here, again, the problem should not prove too difficult, if it arises.

APPENDIX III.

Methods of Testing

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Methods of Testing

Electrometer Type Testing

The electrometer is used whenever tests are made concerning charge and discharge characteristics of photoactive plates. Photoactive characteristics of sample plates are checked in a light tight box. There is a door in the lower part of the box, so that samples to be tested may be placed inside on an insulated platform. An electrical charge is placed on the plate by mechanically driven needles at high potential sweeping across the surface. A pickup probe mounted above the sample plate is connected to an externally mounted electronic electrometer.

The upper half of the box is electrostatically shielded from the lower part, and contains four 25-watt incandescent lamps used for exposure lights. These lamps are 3-3/4 inches above the sample, and are symmetrically located, one on each side. The usual voltage used on the four lamps is 40 volts, which causes their radiation to be somewhat in the red region.

In order to measure charge potential, a Central Scientific Electronic Electrometer is connected to the probe through a charge divider system of capacitors. This arrangement gives an electrometer action which is very sensitive, the charge divider being used to increase the readings. Over long periods of time (several minutes), the electrometer is subject to a slight drift. This drift is one reason for adopting a fast method of measuring plate characteristics.

The present methods of plate measurement have been derived from the drawn-out procedure of taking complete discharge curves over a period of several minutes, and rating plate discharge speed as the time for a plate to lose one-half of its charge. In effect, the present method is a measure of the discharge curve initial slope, i.e., if the plate were to discharge at its original rate, what per cent of its original charge would it lose in one minute. This is accomplished as follows:

1. The plate is first charged positive in the closed, dark chamber.
2. Its discharge voltage over a 15-second period (E_L) is recorded for a given exposure light intensity.
3. The plates total charge voltage (E_T) is recorded.

From these two values, the overall slope of the discharge curve can be calculated in per cent per minute.

$$\frac{4 \times E_L}{E_T} \times 100 = 0/0/\text{min. light discharge rate}$$

Negative characteristics may be checked in exactly the same manner.

To complete the photoactive characteristics, it is necessary to determine dark decay rate in a similar manner. This is done as follows:

1. The plate is again charged positive in the darkened chamber.
2. Its dark discharge voltage (E_D) is noted over a 30-second period.
3. The total charge voltage (E_T) is recorded.

From those two values, the average slope of the dark discharge curve is determined.

$$\frac{2 \times E_D}{E_T} \times 100 = \text{per cent/min. dark discharge rate}$$

The negative dark discharge rate is measured in exactly the same manner.

The data sheet on the following page will serve to indicate the nature of the data obtained from a good photoactive plate.

Using the negative polarity data, the percentage per minute decay figure would be calculated as follows:

Since electrometer deflection is directly proportional to voltage, the deflection figures may be used as a ratio without converting to voltage, therefore,

$$E_L \text{ is proportional to } 0.50$$
$$E_T \text{ is proportional to } 0.60$$

Then

$$\frac{4 \times 0.50}{0.60} \times 100 = 333 \text{ per cent/minute}$$
$$= \text{light discharge rate}$$

Dark decay values would be obtained in a similar manner.

The principal advantage of this system is the time required to evaluate a sample plate. Between six and twelve samples can be measured in an hour's time. The calculations are very simple, and no graphs need be drawn for direct comparisons.

Disadvantages of the system are that some fast samples do not lose their charge at a linear rate over a 15-second or 30-second time interval, and therefore appear to have a slower discharge rate. In cases where this occurs, shorter time intervals have been used and the calculation formula constants changed accordingly.

Image Testing

The testing of a plate for its ability to produce an image involves several factors. These are (1) charging or sensitizing, (2) exposure, and (3) developing.

PHOTOSENSITIVE PLATE TESTING

CHARGING DATA

PLATE NUMBER 4165-5-1 DATE 30 Nov. 48

COATING MATERIAL 4165-1 (ARQ Shotted Se in Parlon-Rezyl)

COATING THICKNESS 0.0005" SIZE 4 x 5

PLATE CHARGING VOLTAGE 4000 LAMP VOLTAGE 40

LIGHT DECAY

	Positive			Negative		
	DEFL.	VOLTS	%/min.	DEFL.	VOLTS	%/min.
15 sec.	0.3		141	0.50		333
Maximum	0.85	140		0.60	110	

DARK DECAY

	Positive			Negative		
	DEFL.	VOLTS	%/min.	DEFL.	VOLTS	%/min.
30 sec.	0.2		42	0.22		96
Maximum	0.96	160		0.46	70	

REMARKS Wire brushed, steel base plate

G-1259-1. Form No. 2.

Figure 45. Data sheet used in recording tests on photosensitive plates.

In sensitizing a plate, the amount of charge developed on the plate is controlled by voltage on the sensitizing wires and speed of travel of the plate under the sensitizing wires. In general, speed of plate travel is kept constant at about 1-3/8 inches per minute, and sensitizing wire voltage is used to control the amount of charge developed on a plate. Distance between the sensitizing wires and plate surface is held constant at 0.438 inch.

Exposure of a plate for normal test purposes is by standard contact printing methods. Light intensity and exposure time are controlled to produce the desired (usually optimum) degree of contrast and background. Four symmetrically placed incandescent lamps (usually 60 watt) are placed about 10 inches below the surface of the plate. A variac is used to control line voltages, thus varying light intensity. Below 80 volt light radiation is too much in the red region, and lower wattage lamps must be used for lower intensities so that voltage can be kept above 80 volts.

After the plate has been exposed, it is put into a tray, and developing powder is shaken across its surface. The plate is then placed on the sensitizer with a sheet of paper on the image surface. Passing under the high voltage wires will transfer the image (powder) to the paper. A few seconds between hot platens will fix the image to the paper. At this point, an image may be evaluated. The photoactive plate must be cleaned with grain meal before another image is taken.

To date, practically all image evaluations have been made with positive polarity because positive developing powder is more readily available. Negative images are to be considered as soon as a suitable developing powder is obtained. A line drawing on vellum is used as a standard copy item, in order that images may be readily compared.

Resistance Tests

It was found that a resistance check from base to film surface can be used for determining whether a plate will take a charge. A G. E. Megohmmeter, with a maximum range of 50,000 megohms (5×10^{10} ohms), was used. Tests of a large number of plates have shown the following:

1. Point probes are suitable.
2. A plate will not charge if its resistance is 10^8 ohms or less.
3. Plates which will take a charge have resistances greater than 10^8 ohms, with the best photoactive plates showing resistances greater than the capacity of the instrument, i.e., greater than 5×10^{10} ohms.

The resistance of good photoactive plates has been tentatively set at about 10^{16} ohms, this figure being based on sensitive voltmeter resistance tests.

Reproducibility

Inasmuch as the same personnel are concerned with taking data, a minimum of error should be present in data due to techniques.

The reproducibility of charge and decay rate data for painted plates is fair, being about ±10 per cent. This is probably because thickness of painted plates can be rather closely controlled. Hot-sprayed and pressed selenium plates have shown more deviation in readings because thickness has not been closely controllable with the elementary type of equipment used for producing these plates.

The electronic electrometer shows a tendency to drift. This effect is kept to a minimum by taking readings in as short a time as possible.

APPENDIX IV.

Equipment Revisions on Vacuum Unit

APPENDIX IV.

Equipment Revisions on Vacuum Unit

In the interest of making it possible to attain lower vacua for one phase of the program, new binding posts have been designed and made which will facilitate leak detection. The manner in which the present binding posts are sealed makes it impossible to determine whether they are leaking and also impossible to stop suspected leaks with any assurance. The N.R.C. machine has provision for four large and four small binding posts. Drawings of the new design are shown in Figures 46 and 47. In these designs, the vacuum seal is on the outside of the system instead of inside, thus making it possible to paint leaking points with glyptal. It also eliminates the practice of using rubber inside the system where it is exposed to the heat of the filaments. An adapter for making the vacuum-tight connection, where the cooling platen tubing passes through the base plate, has also been made. A refrigerated trap has been designed to keep oil vapors out of the evaporation chamber, but still to retain fast pumping speed. Figure 48 is a drawing of this trap. The need for a trap comes particularly for the work in which the plate is to be cooled below room temperature during evaporation and in which low pressures are desired. A new double cooling platen is planned which will eliminate possibilities of cooling system leaks in the vacuum chamber by having it consist of one long unbroken piece of tubing. It will be made in two parts, one further from the source than the other to allow deposition of films of two different thicknesses in one evaporation. It is sketched in Figure 49.

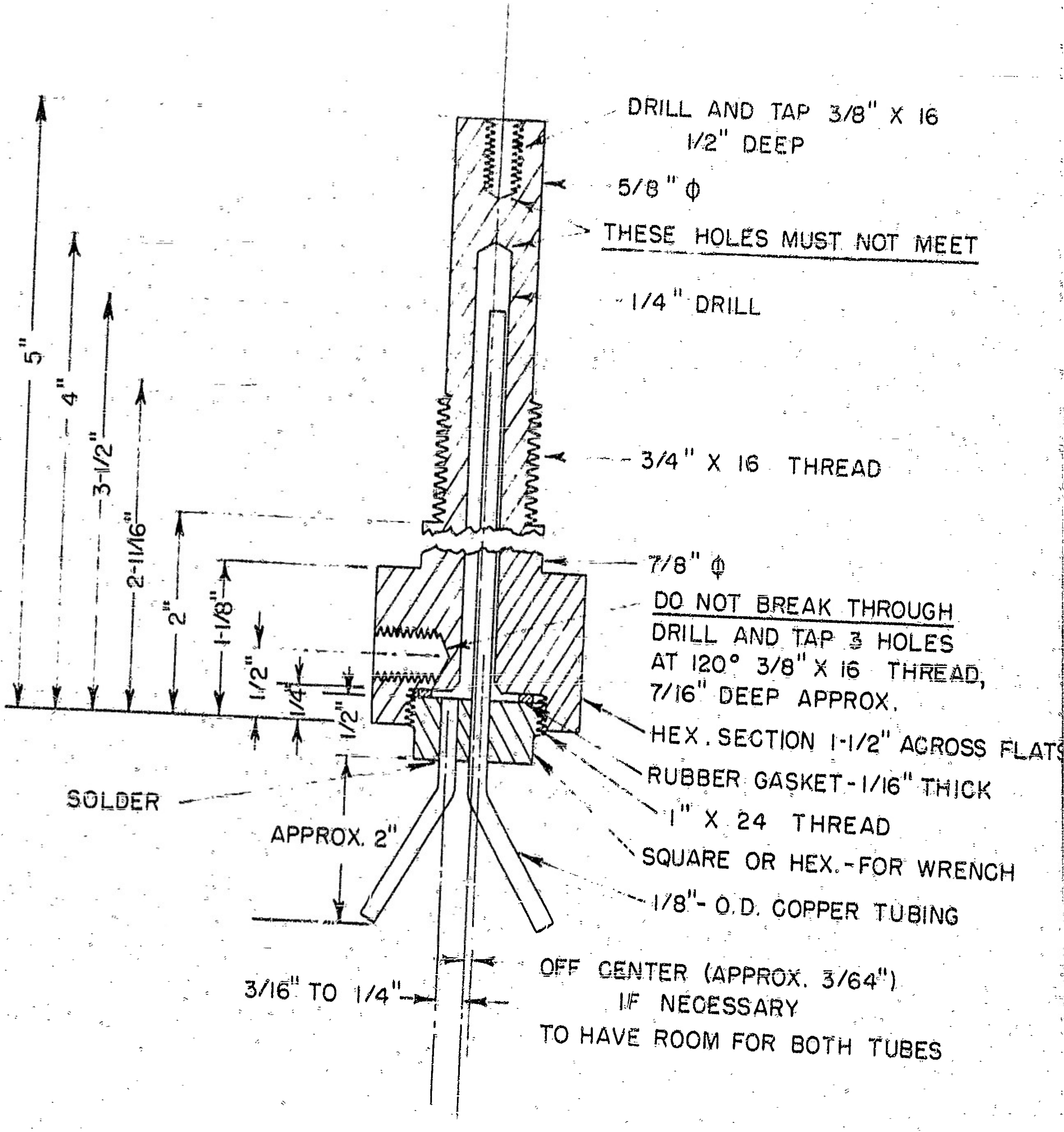


FIGURE 46. WATER-COOLED BINDING POST (STEEL)

0-10,074

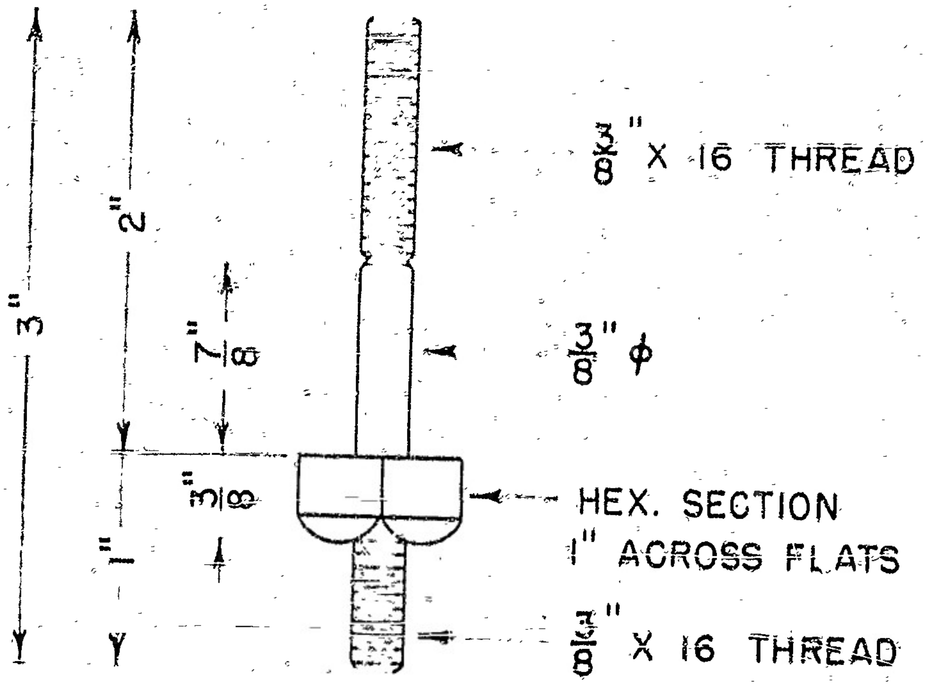


FIGURE 47. SMALL BINDING POST

0-10,075

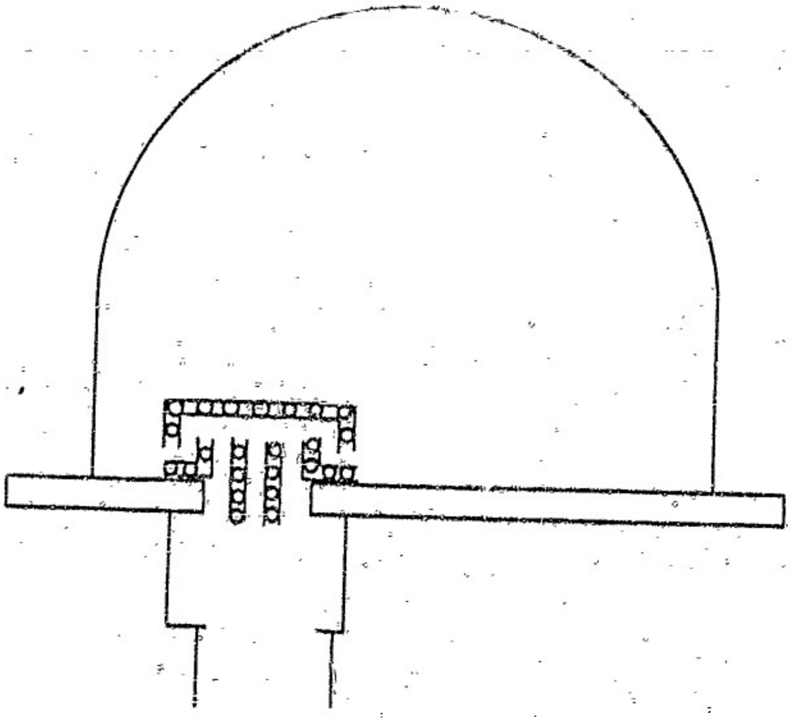


FIGURE 48. TRAP DESIGN

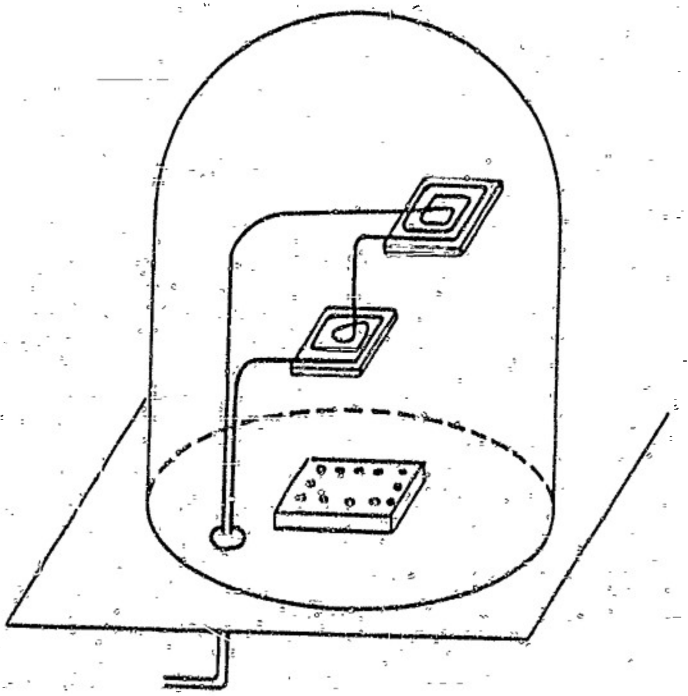


FIGURE 49. DOUBLE COOLING PLATTEN

Two new vacuum gages have been procured. One is a Pirani whose range is 1 to 500 microns covered in two-scale settings, permitting good accuracy in reading. The other is an ionization gage, designated DEM-36 by its supplier, Distillation Products, Inc. This extends the pressure range below that covered by the discharge gage and covers it more accurately.

All of these changes and additions are not only directly applicable to this particular phase of the problem, but make the equipment more convenient to use and more adaptable to other phases of the work.

APPENDIX V.

Power Supply for Sensitizing Plates

APPENDIX V.

Power Supply for Sensitizing Plates

One power supply, wired as shown in Figure 50, has been completed, and the parts for two more power supplies of this type have been procured. Full-scale deflection of the zero centered microammeter will indicate 10 peak kilovolts when a series resistance of 6,380,000 ohms is used. This resistance has been calculated with the assumption that the voltage appearing across the high-voltage transformer secondary winding will be sinusoidal.

The advantages of a power supply based on this particular wiring diagram are listed below:

1. Polarity switching is accomplished in a low-voltage circuit.
2. All component parts are stock items which are readily available.
3. It can be easily and quickly constructed.
4. The polarity is clearly indicated during use.
5. Tube failure can be detected by merely switching polarity.
6. This type of power supply is extremely easy to operate: only one control is necessary for switching both polarity and high voltage.

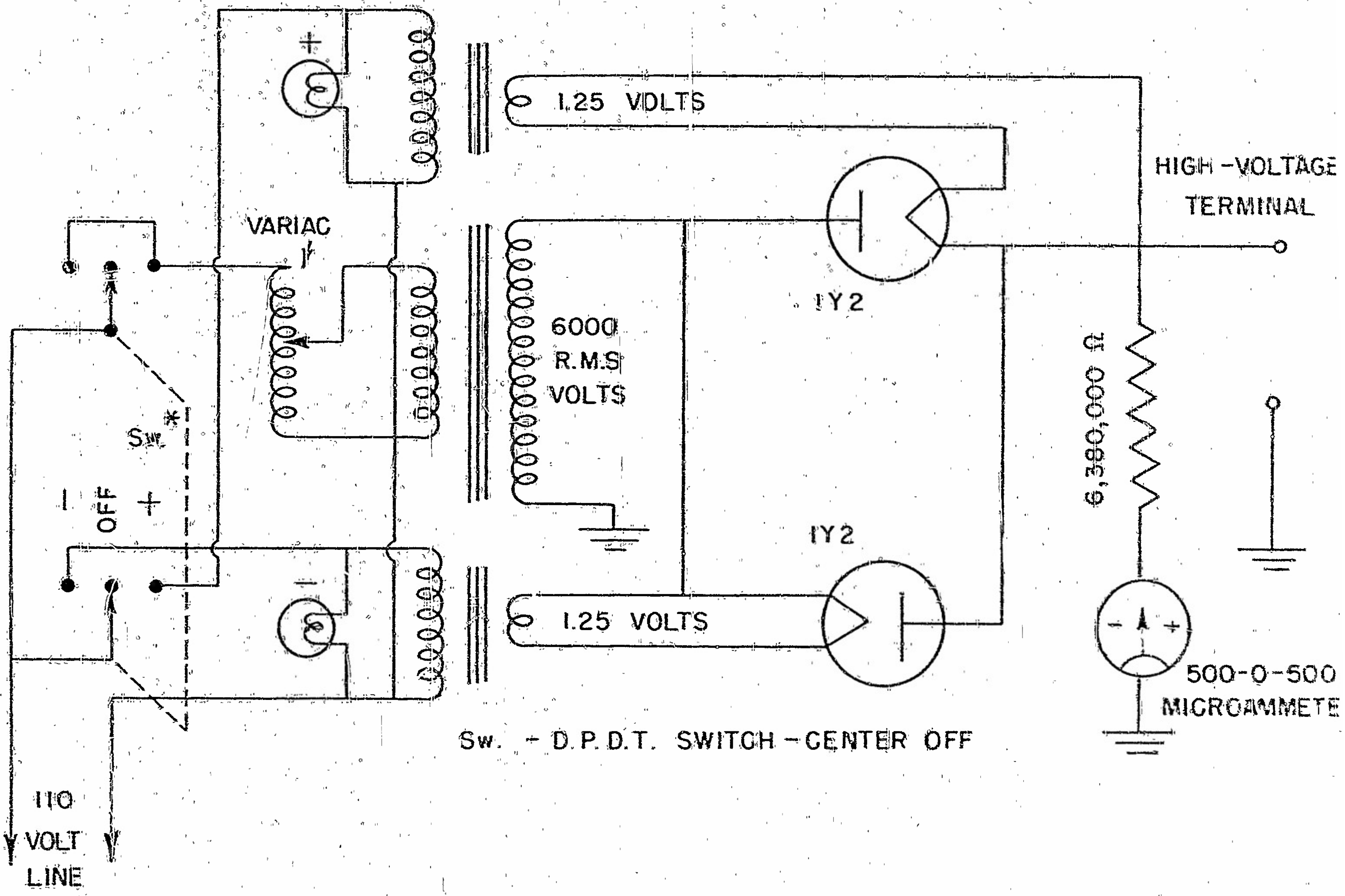


FIGURE 50. POWER SUPPLY CIRCUIT FOR USE IN SENSITIZING XEROGRAPHIC PLAT

0-10,076

APPENDIX VI.

Vibrating Probe Electrometer Design

APPENDIX VI.

Vibrating Probe Electrometer

A vibrating probe type of electrometer was constructed in order to obtain more accurate measurements of the electrical characteristics of electrophotographic plates. The present design of the apparatus makes possible the measurement on a two-centimeter-diameter circular area of the electrophotographic plate, with an accuracy of plus or minus one volt, for slow voltage change rates. The instrument has also been used to measure decay rates of insulating binder materials.

The principle of a vibrating probe type of electrometer involves the vibration of a high impedance probe in the electrical field of the object whose potential on charge is to be measured. The variation in the object to probe distance during the vibration causes a similar variation of the capacitance between the probe and the object. This variation in capacitance between the probe and the object shows up as a variation in the potential of the probe. The probe sensitivity of this type of electrometer (the ratio between the AC voltage on the probe to the voltage on the object) will always be less than the probe sensitivity of non-vibrating types of electrometers (the ratio of the potential on the probe to the potential on the object) if the physical dimensions of the systems are the same. However, the ease with which AC voltages may be amplified, and the fact that the probe may be maintained at ground potential (through a high resistance) overshadow that disadvantage. The ultimate sensitivity of the vibrating type of instrument is determined by the amount of electronic noise developed. The drift of the electrometer is zero.

A general view of the vibrating probe electrometer is shown in Figure 51. For purposes of description, the instrument may be divided into three parts: (1) the vibrating element, (2) the plate holder and charging method, and (3) the electronic portion of the instrument.

An isometric drawing of the vibrating element is shown in Figure 52. The probe cylinder is made of brass shimstock formed as shown and soldered into a rigid unit. The cylinder is supported by two polystyrene Y's, the junction between the polystyrene and the cylinder being surrounded by conducting sleeves to eliminate extraneous triboelectric difficulties. The polystyrene Y's were attached to two permanent magnet speaker voice coils. The physical arrangement as shown in the figure was such as to permit a beam of light to be passed between the two speakers and through the probe cylinder without interference. The probe element is driven by 240 c.p.s. alternating current, and for a 0.15 cm. amplitude of vibration, the system uses about 2 watts of energy. The voice coils are mounted in the speaker permanent magnets by adjustable, flexible plastic spiders (not shown in the drawing). The electrical connection to the voice coils is made through light phosphor bronze springs.

The plate holder and a detailed view of the test area are shown in Figure 53. The test area consists of a two-centimeter-diameter circular hole cut into a 1/2-inch steel ground plate, against which a plate to be tested is held and in front of which the probe element vibrates. The region in which the probe operates is magnetically and electrically

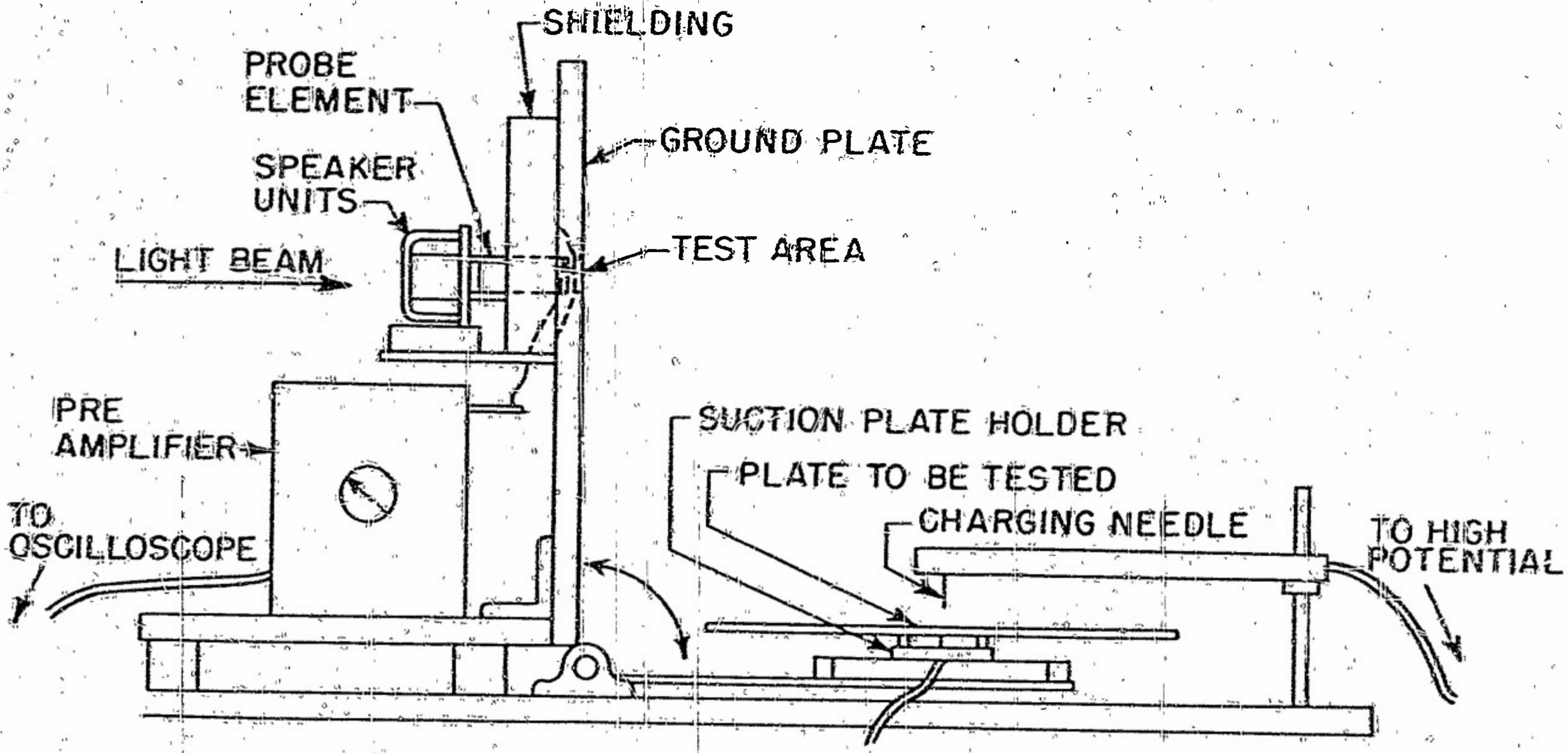
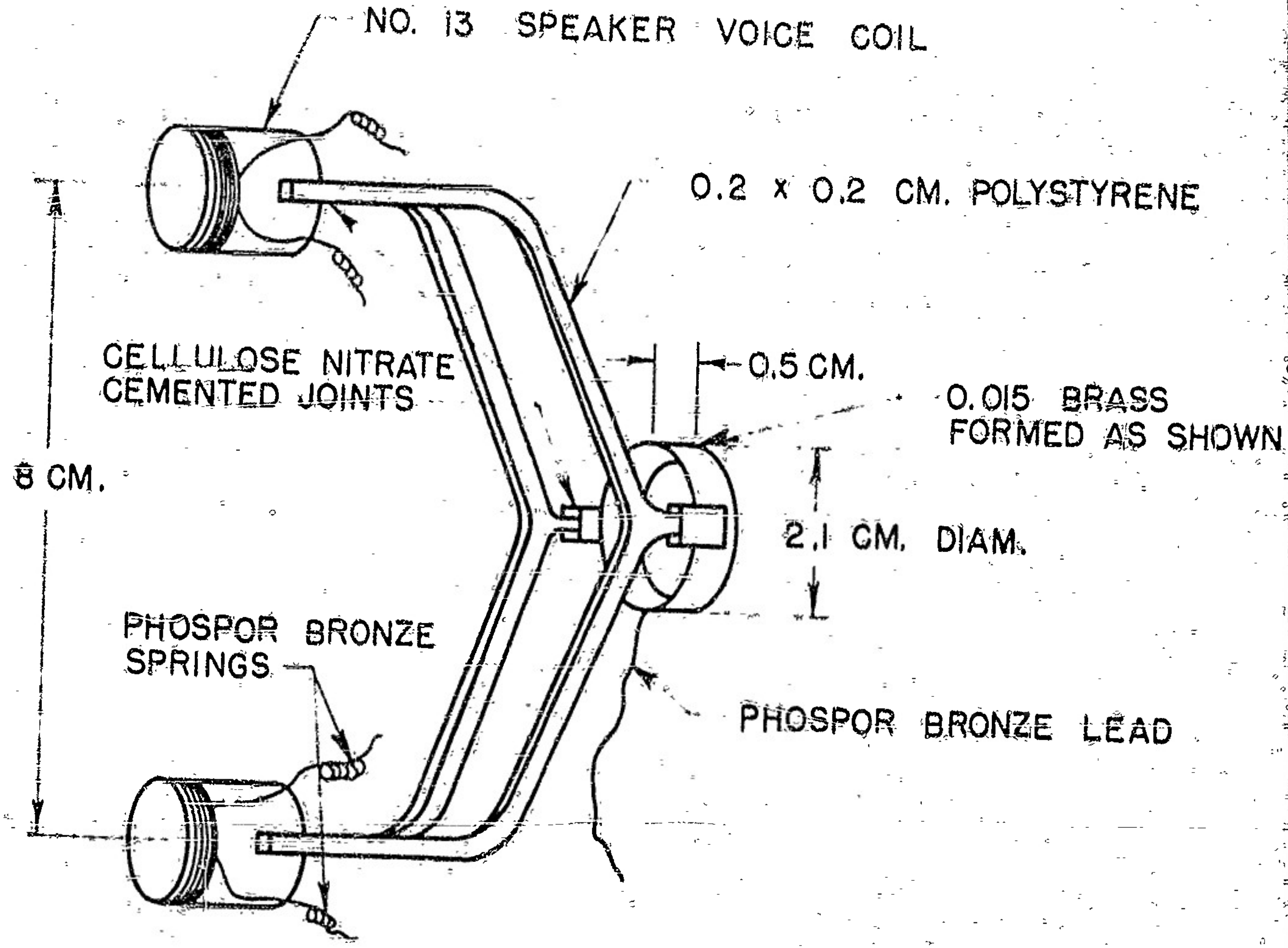


FIGURE 51. ELECTROMETER SETUP: SIDE VIEW (1/4 SCALE)

0-10977



FULL SCALE - ISOMETRIC

FIGURE 52. VIBRATING PROBE ELEMENT

O - 10078

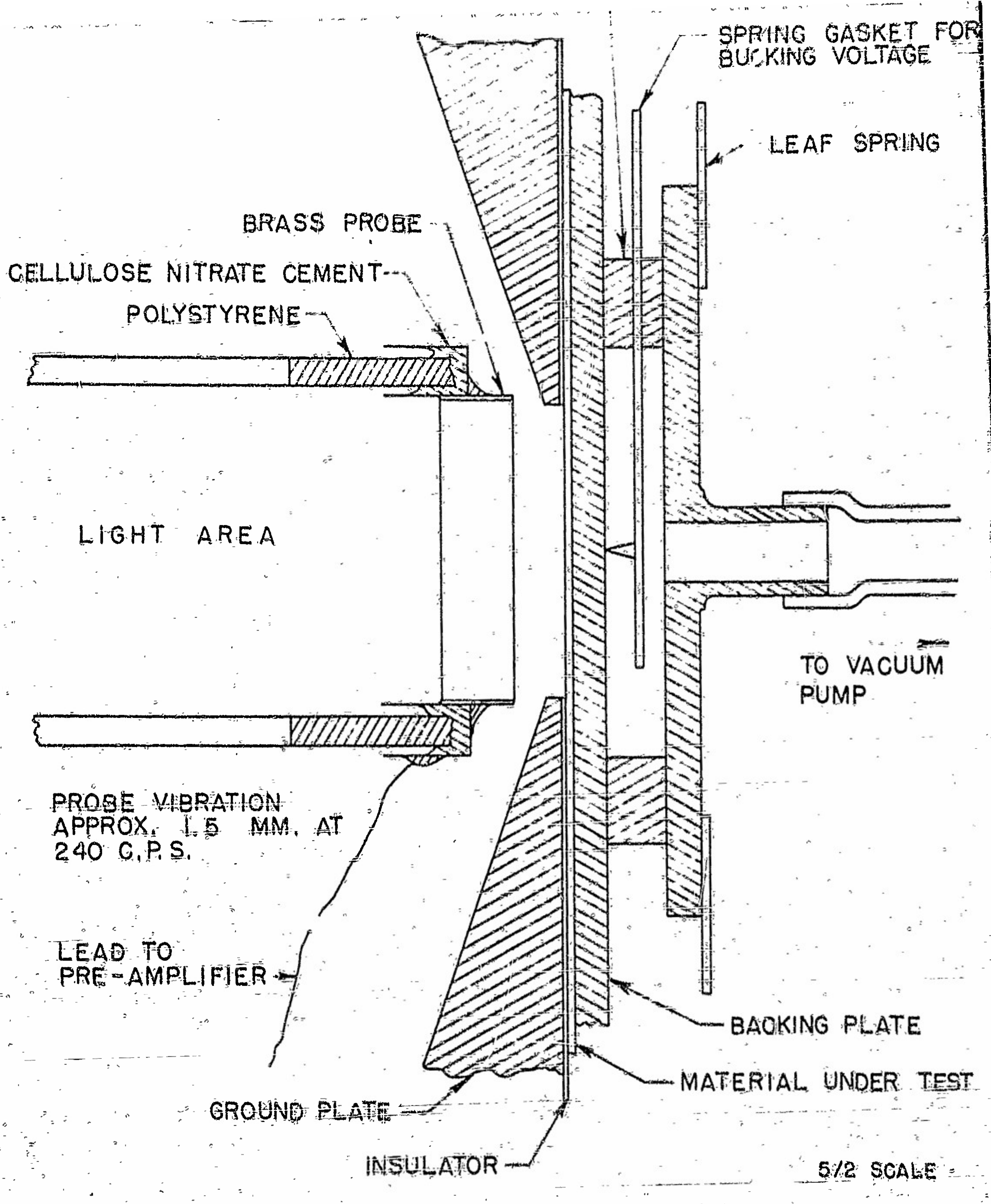
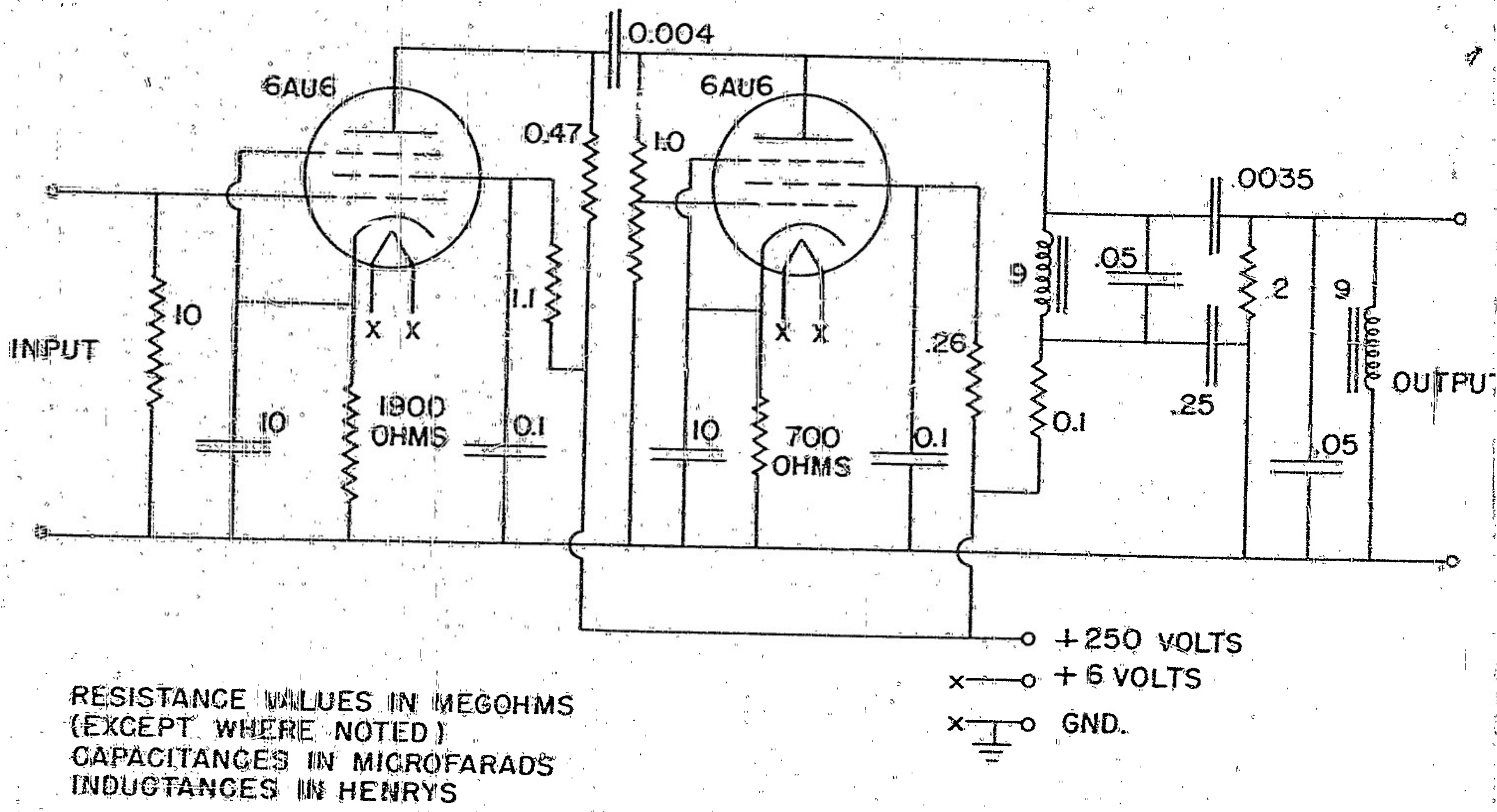


FIGURE 53. VERTICAL SECTION OF TEST AREA

shielded by a box constructed of 1/16-inch soft iron. The polystyrene Y's of the probe pass through [illegible] in the box, [illegible] light beam passes through a hole on the axis of the probe and the test area. The plate holder is a spring-mounted suction cup with an insulated needle contact connected to a potential supply. The suction cup can be swung down horizontally so that the plate may be charged. The charging apparatus is a single corona needle which can be swung into charging position above the plate, or to one side so that the plate may be raised into the measuring position.

The electronic portion of the electrometer is as shown in Figure 54. The probe is connected to the grid of the voltage amplifier through a phosphor bronze spring which is shunted to ground by a ten-megohm resistor. The amplifier circuit is a standard voltage amplifier with a band pass filter (narrow pass band at 240 c.p.s.) attached. The output of the filter is fed to an oscilloscope.

The electrometer is operated as follows: A plate is placed on the plate holder and charged at the voltage and time desired. It is then swung up against the ground plate. If a charge has remained on the plate, an AC wave form will appear on the oscilloscope. This pattern may be eliminated by either raising the voltage of the shielding until the voltage is the same as that of the charged surface, or by lowering the voltage on the backing plate until the voltage is the negative of that on the plate. A voltmeter or potentiometer may then be used to measure the voltage applied to the shielding or plate backing. Using this method, an accuracy of greater than one volt can easily be obtained.



RESISTANCE VALUES IN MEGOHMS
(EXCEPT WHERE NOTED)
CAPACITANCES IN MICROFARADS
INDUCTANCES IN HENRYS

FIGURE 54. PRE-AMPLIFIER AND BAND-PASS FILTER

0-10080

When operated as above, it is observed that a small signal persists even when all shielding and the plate surface is grounded. The signal is somewhat out of phase with the signal resulting from potentials on the plate being tested, but it can be brought to an unobjectionable minimum by the application of a zeroing voltage to the plate backing of the order of 2 volts.

APPENDIX VII.

Light Sources for Use With Vibrating Probe Electrometer

APPENDIX VII.

Light Sources for Use With Vibrating Probe Electrometer

Monochromatic

Description and Arrangement of Apparatus. The Beckman Model DU Photoelectric Quartz Spectrophotometer is used as the light source in the measurement of spectral characteristics of xerographic plates. Its useful range is in the region 220 - 1000 millimicrons.

As adapted for our purpose, the phototube housing of the monochromator is removed thus permitting direct utilization of the monochromatized beam as it emerges from the exit slit. The tungsten and hydrogen tubes which are conventionally used with the equipment are, however, retained as the primary light sources. They can be interchanged according to the spectral range desired.

In all experiments to date, the monochromator has been placed at a distance of about 20 inches from the plate under study. This arrangement conforms to the requirement that the light beam entirely cover the circular test area of the plate for any practical slit width setting and that the intensity of the beam be reasonably constant over this area. The beam is incident normally to the plate and is directed in such a manner that the center of the beam strikes the center of the circular test area.

Calibration. In order to determine the uniformity of the beam at a distance of 20 inches from the exit slit of the monochromator an Eppley thermopile used in conjunction with a sensitive (0.00004 micro-amps./mm.) moving coil galvanometer was moved across the beam and the galvanometer deflections corresponding to fixed positions of the thermopile noted. Inasmuch as the present test was exploratory in nature, the controllable variables (slit width, wave length, etc.) were adjusted to provide the most favorable conditions for test. For this reason, the monochromator slit was opened to maximum width (2 mm.) and the wave length set at an energy-rich portion of the spectrum (1550 millimicrons). The slit opening of the thermopile was set at 4 mm.

The registered intensity (as galvanometer deflection) versus displacement of the thermopile normal to the beam direction is shown in Figure 55. Since the test area is 2.0 cm. in diameter, it is seen that the intensity will be reasonably uniform over this area. Undoubtedly, the intensity distribution over the area will vary with monochromator slit width and wave length setting. Further tests will be conducted to establish intensity variations with slit width and wave length settings at values determined by future work.

Using the tungsten light source, the intensity of the beam at the test point was plotted against the wave-length setting. Since the intensity is a function of slit width, as well as a wave length, it was decided to fix the slit width at such a value that the spectral band width remained constant for each wave length setting. A spectral band width of 27 millimicrons was chosen because at 350 millimicrons (an energy-poor portion of the spectrum) this allowed a full slit opening of 2 mm.

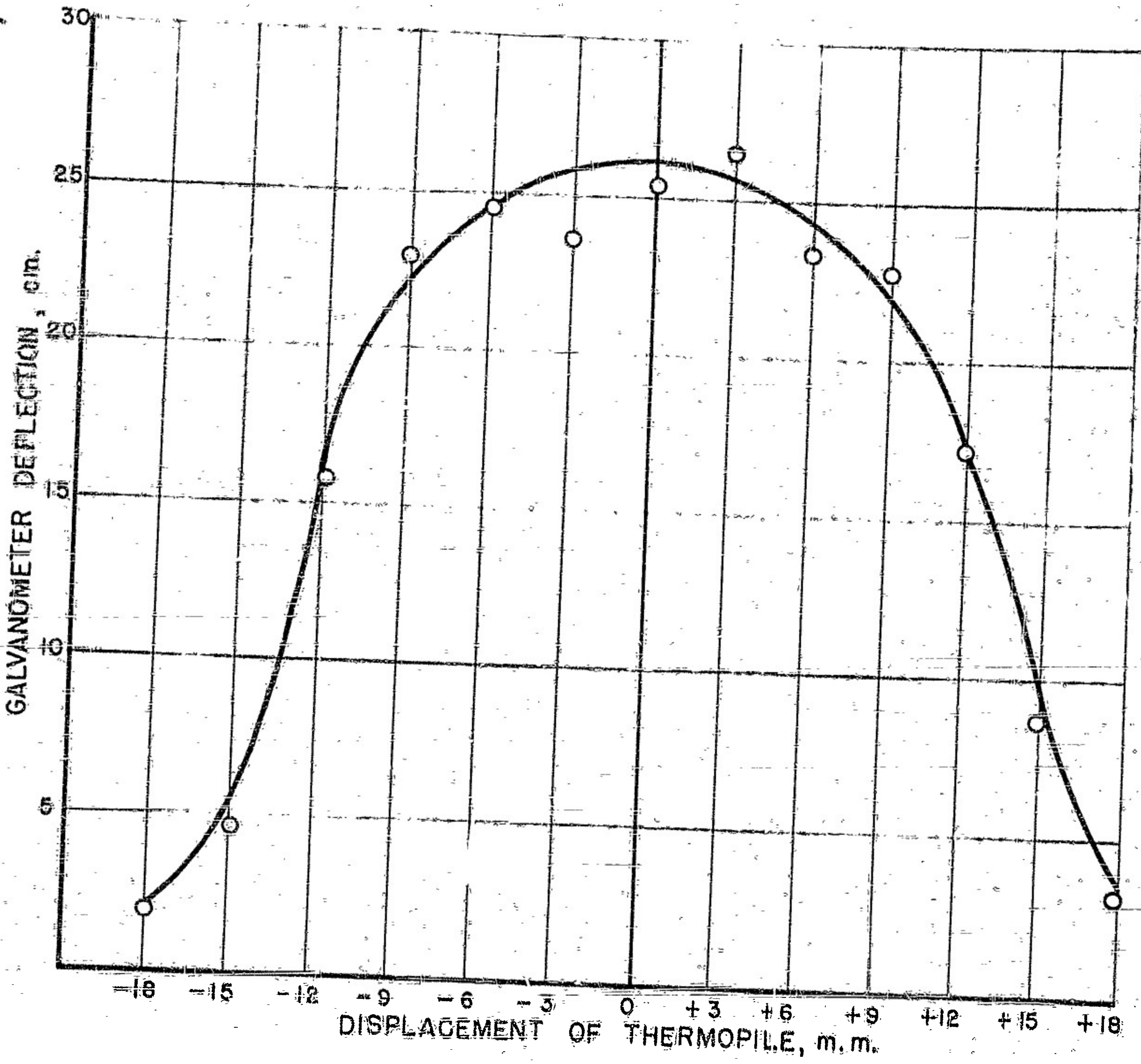


FIGURE 55. CALIBRATION OF UNIFORMITY OF INTENSITY OF LIGHT BEAM AT TEST AREA

In order to avoid the prolonged wait for the thermopile to come to equilibrium with the weak radiation at the test point and the consequent increased error in galvanometer readings due to small deflections and pronounced drift, the thermopile was placed at a point midway between the slit and the test point and the intensity readings extrapolated to the test point.

The results of these measurements are shown in Figure 56.

Similar experiments using the hydrogen discharge light source are planned.

Variable Intensity for Use With Filters

A light source was constructed for use in measuring the electrical and optical characteristics of xerographic plates. The source provides a variable-intensity beam of white or monochromatic light which (1) can be made parallel (1-3/4 inches in diameter), (2) can be made to converge to a point, or (3) can be made to diverge from a point.

A pictorial sketch of the light source is shown in Figure 57; a wiring diagram is shown in Figure 58.

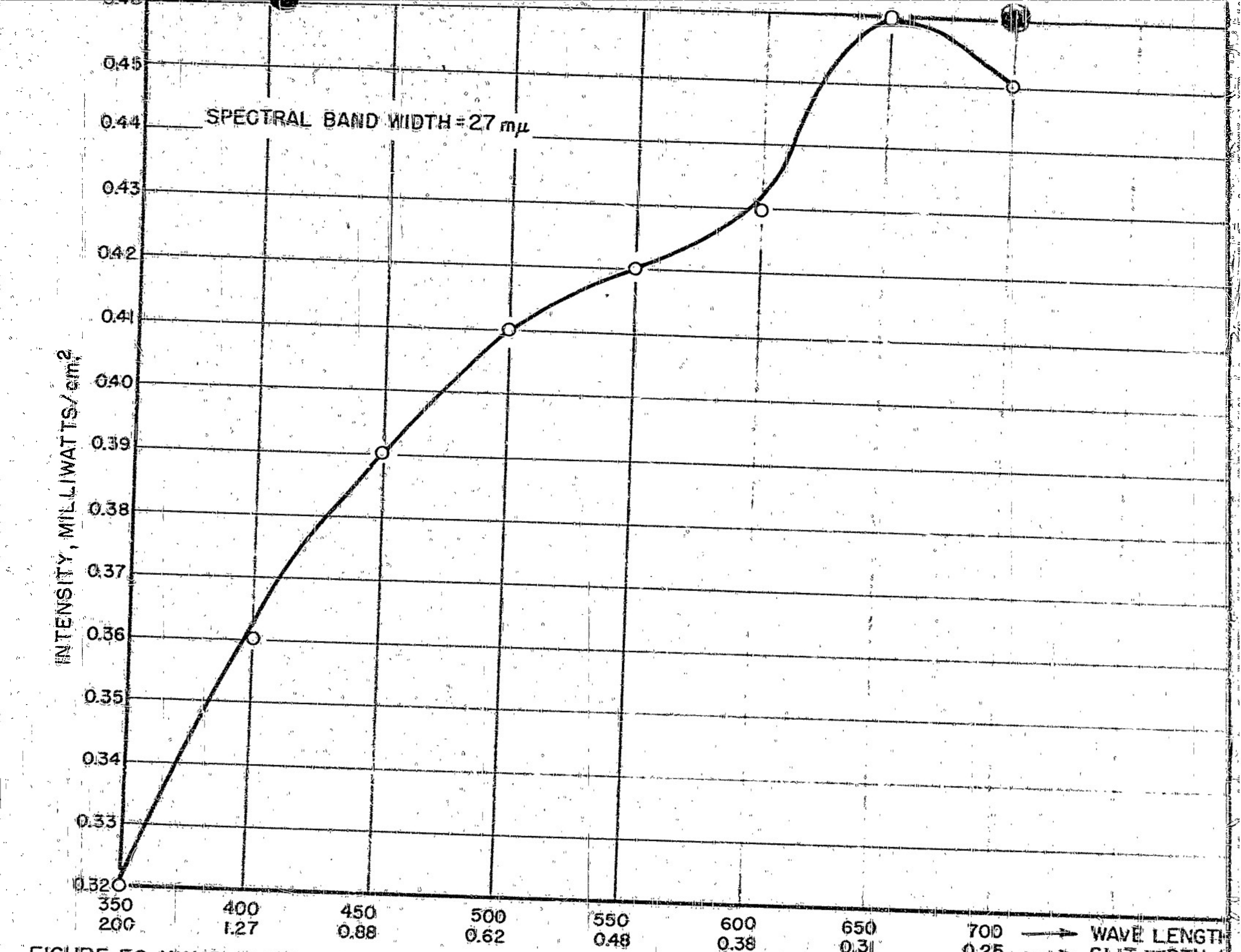


FIGURE 56. WAVELENGTH VS. INTENSITY OF LIGHT AT DISTANCE OF APPROX. 20.5 IN. FROM
BECKMAN

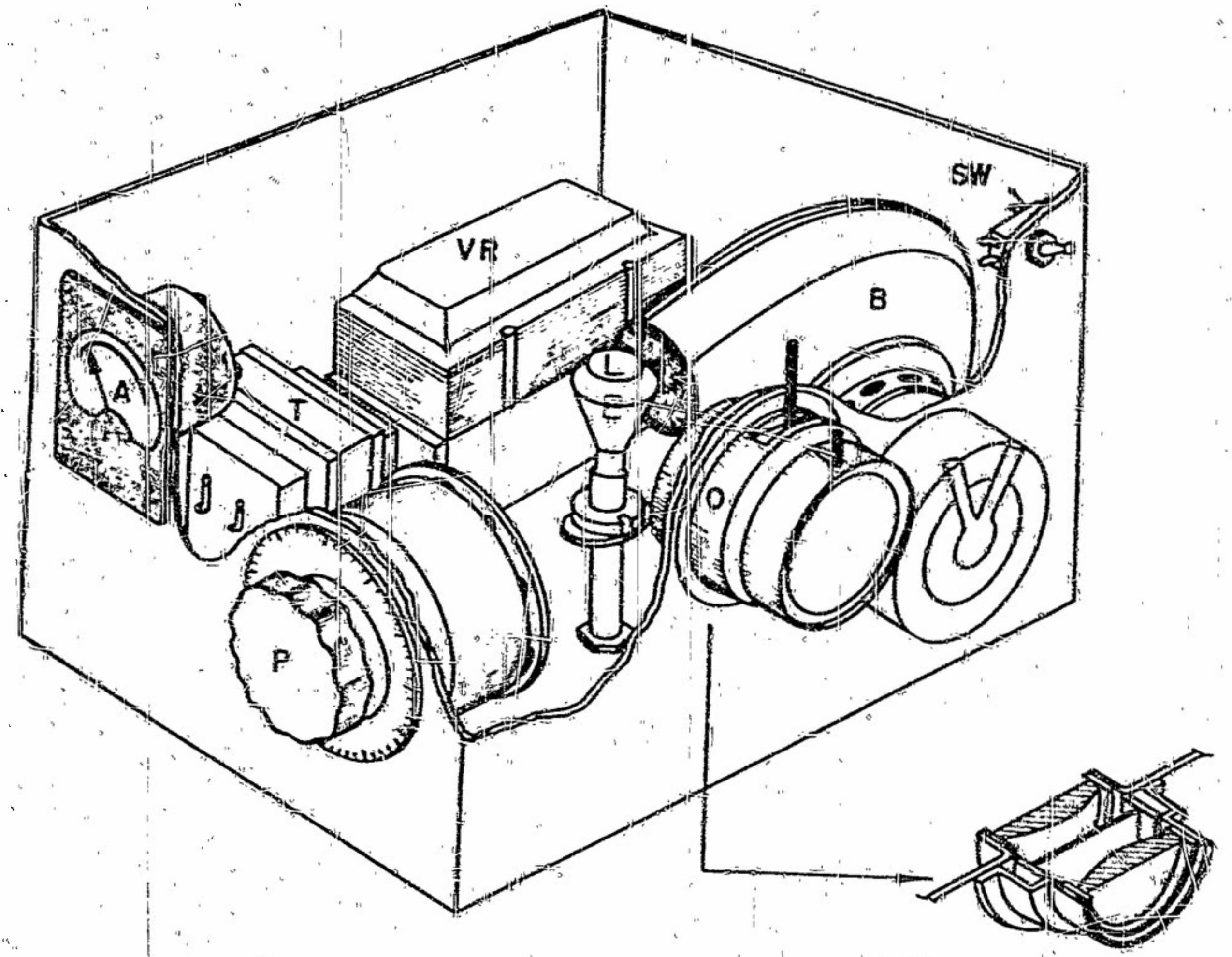
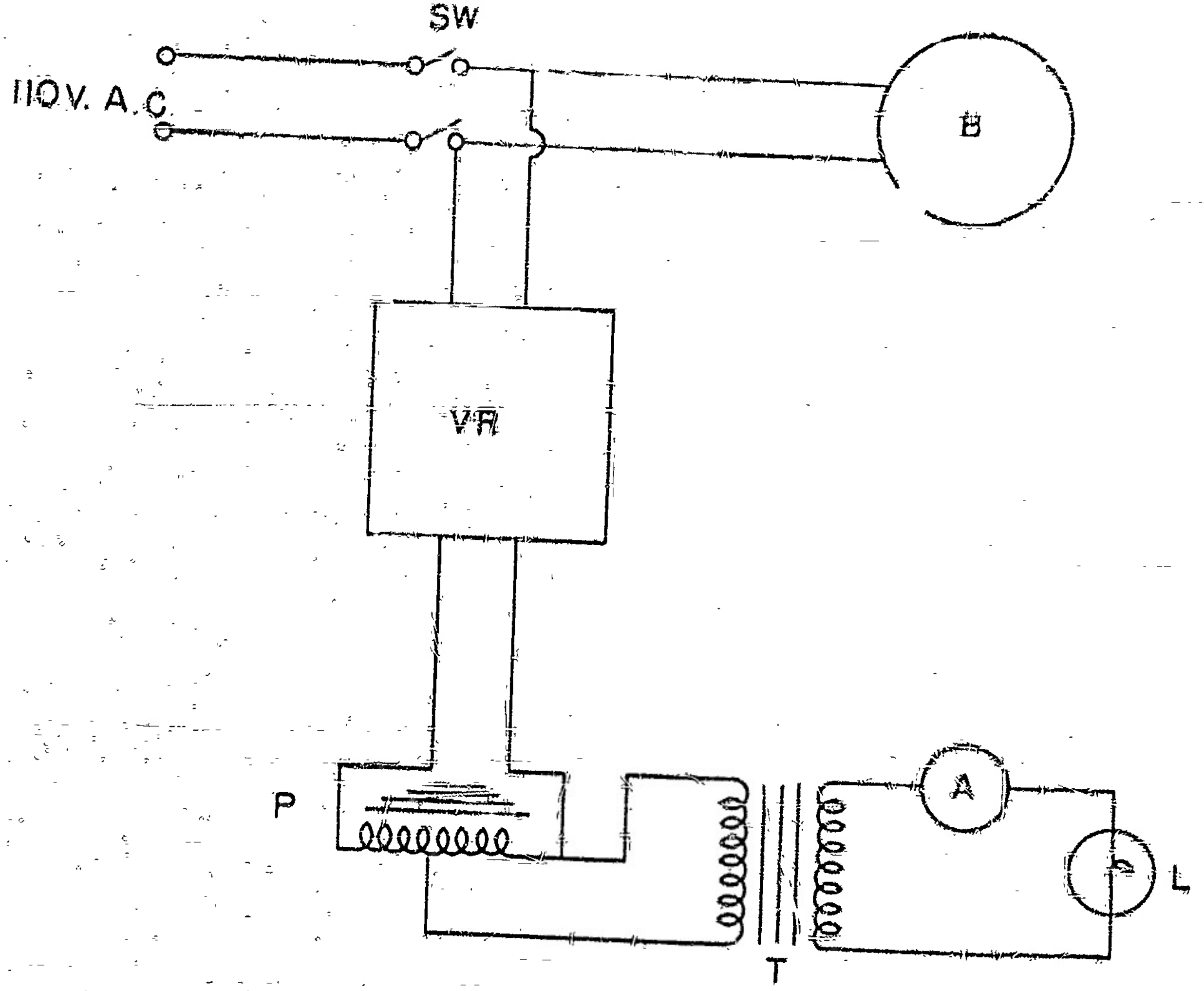


FIGURE 57. SKETCH OF BATTELLE LIGHT SOURCE

0-10084



SW - D.P.S.T. SWITCH
B - BLOWER, AMERICAN INSTRUMENT CO., MODEL 4-690
VR - VOLTAGE REGULATOR, RAYTHEON VR 6112
P - POWERSTAT, SUPERIOR ELECTRIC TYPE 20
T - FILAMENT TRANSFORMER, THORDARSON T92F20
A - A.C. AMMETER, 0-10 AMPERES
L - AUTOMOBILE HEADLIGHT, 50cp., 6-8 VOLTS

FIGURE 58. WIRING DIAGRAM FOR BATTELLE LIGHT SOURCE I

0-10083