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HORIZONS INCORPORATED
2891 EAST 79th STREET, CLEVELAND 4, OHIO

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REPORT NO. 9

THIRD QUARTERLY PROGRESS REPORT
(January 1, 1951 to March 31, 1951)

APPLICATION OF PHOSPHOR TYPE MATERIALS TO ELECTROSTATIC ELECTROPHOTOGRAPHY

Prepared for:

Signal Corps Engineering Laboratories
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By:

Horizons Incorporated
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Report Written by:	Dr. Eugene Wainer Director of Research

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APPLICATION OF PHOSPHOR TYPE MATERIALS TO ELECTROSTATIC
ELECTROPHOTOGRAPHY - AND APPENDIXES I AND II - THIRD
QUARTERLY PROGRESS REPORT - JAN 1 TO MARCH 31, 1951

EUGENE WAINER 20 APRIL '51 97PP TABLES, DIAGRS, GRAPHS

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GENERAL SUMMARY

Despite broad variations in technique, method of preparation, and material, the overall photographic speed of electrographic plates made from the best of commercially obtainable photoconductive phosphors is extremely low, being of the order of 1ASA or less. These low speeds are evident where the Carlson or Kalmann method of exposure is used. Such results have been confirmed by a variety of electrographic, sensitometric, and electrical measurements. More important is the fact that theoretical examination of the electrographic process using such photoconductive phosphors indicates that only low speeds may be expected.

The usual methods of electric treatments initiated by infra-red quenching was used in attaining such speed figures. The evidence indicates that the most important requirements for solution in order to meet the specifications of this project are:

1. A major modification in the sensitive materials.
2. A major modification in lighting techniques other than those identified by the names Carlson or Kalmann.
3. A major modification in the method of preparing the photographic plates.

Of these, the basic change in sensitive materials is considered the most important.

The photoconductive activity of zinc sulfide-cadmium sulfide phosphors appears to be greater the greater the cadmium sulfide content, and the indication is sharp that phosphor-like photoconductors consisting entirely of properly doped cadmium sulfide will be more effective than commercially available phosphors for photographic purposes by factors which may be in order of magnitude. The experimental evidence further indicates that a phosphor which has been made luminescent by use of a substitutional impurity is not photoconductive whereas a sulfide phosphor made luminescent by an interstitial impurity is photoconductive. For the present, copper seems to be the most important interstitial impurity of this type. The amounts of interstitial impurity needed to yield the best results for photoconductive purposes is not necessarily the same as that required for best luminescent properties.

Past work has indicated correlations between photographic properties and various pieces of electrical data. Of these, it is now clear that the agreement between dielectric constant changes and photographic results is fortuitous while the agreement shown between photoconductive results and the photographic results is probably proper. As a matter of fact, the theory indicates that the increase in dielectric constant exhibited on illumination of an electrographic plate made of commercially available phosphors is an adverse phenomenon with respect to photographic speed and that changes in dielectric constant of zero or in the negative direction would be more desirable if possible.

The normal method of rotation of illumination prior to exposure has always been approached in the past from the point of view of emptied electron traps, that is, infra-red quenching. If the method of illumination is reversed so that the sample is flooded with light while in a potential field, then placed in the dark, the current reversed, and the plate then exposed, a sharp pulse of photoconductive current is obtained from commercially available phosphors which is 10 to 100 times greater than the photoconductive current obtained with the normal method. This phenomenon has been termed "reversal" and may be repeated indefinitely. It involves initiation from completely filled traps.

Through use of triggered sweep oscillographic techniques, the shape of the charging curves when used as a photoconductor under photographic exposure conditions has been traced under both normal and reversal conditions. While these data indicate the possibility for marked improvement in speed by using the rise side of the pulse current, such data also show that the rate of light decay is very large and a highly specialized type of exposure will probably be necessary in order to take care of these short time pulses of current.

Initial investigations of the theoretical aspects of electrographic properties of phosphors and phosphor-like photoconductors have been completed and two reports on this subject are presented as a supplement to the present report. This theoretical approach indicates that a highly complex situation is in process during exposure. Further, the theoretical approach indicates that the increase in dielectric constant exhibited by phosphors is an adverse phenomenon as far as photographic work is concerned and that only photoconductive and electrometric changes are important for evaluating the photographic process. The photoconductive and dielectric processes appear to act separately. In those cases where large dielectric changes are accompanied by large photoconductive changes, the overall speed of the phosphor is high and it appears that the magnitude of the photoconductive changes are sufficiently large in such cases to mask the dielectric changes which are evident.

Electrometric measurements have been carried out on a variety of photographic systems using commercially available phosphors in measurement of light and dark decay rates. These results have substantiated some of the conclusions which have been reached in the experimental endeavor of the early portions of this work. Such conclusions deal with the variation in photographic speed with thickness, amount of binder, and type of phosphor relative to the cadmium sulfide content. Using such decay rate data, comparisons were made between the phosphor type plates and the selenium type plates with the result that the selenium type plates are roughly 30 times faster than the best of the phosphor plates we have made thus far. These results have been checked sensitometrically. A further sharp difference exists between phosphor and selenium type plates. In the case of selenium, the charge on the surface of the plate decays rapidly to zero on exposure to light, whereas in the case of the phosphor plates, the charge decays fairly rapidly to some high level above ground on exposure to light and appears to remain indefinitely at this high level. The theoretical approach indicates that such a result should exist in view of the increase in dielectric constant of the phosphor systems on exposure to light which in effect increase the ability of the system to retain a charge.

Preliminary tests have been carried out with respect to preparation of photoconductive films of lead sulfide, germanium, and silicon from the point of view of obtaining high resistance. Further attempts to prepare thin films of phosphors by ceramic techniques at elevated temperatures have continued. In view of other findings from a material standpoint dealing chiefly with CdS, these excursions into the field of other types of photoconductive systems have been dropped.

Probably the most important finding in connection with the work done during this quarter is the relation between cadmium sulfide content of the phosphor and photographic speed, in which the higher the cadmium sulfide content the higher the speed. Since the compositions of most phosphors are not available to the public, this information has been obtained by chemical analysis. As a result, a gross emphasis was laid on the study of pure cadmium sulfide. Cadmium sulfide of unknown purity was obtained from a variety of sources and toward the end of the present quarter, samples of luminescent free cadmium sulfide was obtained from two sources, namely Sylvania and RCA. At the same time, luminescent free zinc selenide has been included in the program. Using such materials, photoconductors having light-dark ratios of as high as 1000 to 1 have been made, but up to the present, the dark resistance of such photoconductive systems is still too high by a factor of 10 to make them useful for photographic purposes. The primary effort in this connection is the reduction of the dark resistance to a suitable level.

A new phosphorescent system has been included in the investigation which is entirely outside of the field of the type emphasized so far. This system is fluorescent glass which has been chosen chiefly because of the extremely high dark resistance it exhibits. It involves the preparation of fluorescent glass by electrolytic transfer of silver ions into the glass structure. When properly prepared, such a phosphor glows bright yellow under ultra-violet light.

Recapitulating, the various divisions of experimental endeavor which have been engaged in during the present report period may be listed as follows:

1. Development of a highly sensitive photoconductive cell for measurement purposes.

2. Determination of the effect of plate thickness and amount of binder on photographic speed.

3. The determination of variations in degree of photoconductivity as a result in variation of the spectral range of the light used for illumination purposes.

4. The laboratory synthesis of photoconductors, photoconductive phosphors, and photoconductive phosphor-like systems.

5. Modification of the base phosphor to improve the degree of photoconductivity.

6. Preparation of incomplete phosphors.

7. Initiation of exposure from the point of view of filled electron traps rather than empty traps, the process being termed "reversal" in this report.

8. The determination of the shape of the charging curves of the photoconductive phosphor under a variety of light conditions using triggered sweep oscillographic techniques.

9. Development of techniques for preparing plates by high speed spinning.

10. The analytical determination that the photographic speed of a phosphor was proportional to the cadmium sulfide content.

11. The finding that interstitial impurities such as copper are more important for developing photoconductivity than substitutional impurities.

12. Electrometric measurement: identify inherent defects present in the light and dark decay curves when compared with selenium plates.

13. Sensitometric data further substantiate the low speed of phosphor type plates.

14. Cadmium sulfide photoconductive systems and modifications.

15. An exhaustive theoretical investigation for defining many of the findings of experimental endeavor. The theoretical investigation contains some hints with respect to improvement of the photographic properties of the phosphor-like systems.

EXPERIMENTAL

A. TECHNIQUES

Photoconductive Cell Design: After considerable experimentation, a cell design of high sensitivity was evolved. The front surface of the metal backed phosphor plate was fitted with a silver screen having roughly 10 meshes to the inch and the conducting lines were about one millimeter in width. The total exposed cell area is 3 sq. in. The silver electrodes were made through use of a DuPont squeegee silver applied as a paint to a silk screen. This method of cell preparation has the advantage that the resin bonded silver is viscous and consequently, does not penetrate a minute hole. In this way, the shorting defect encountered in other methods of preparation such as evaporation is generally bypassed.

Considerably larger changes in capacity and photoconductivity were available from this design indicating that the cell was roughly 20 times as sensitive as the design described for the same device in the Second Quarterly Report.

Technique of Measurement and Illumination: Two general methods of measurement and illumination were used. The first is the same as that previously established, namely, the specimen was first quenched in infra-red, then placed in darkness, and finally exposed to light. Capacitative and photoconductive data were taken in each case. Under these conditions, a value of photoconductive current of the order of 1 to 10 x 10^{-9} amperes is obtained on steady illumination. In the second method of measurement, the voltage is maintained across the photoconductor and while in this condition, the photoconductor is flooded with bright light and while the current is still on, the light is shut off and the specimen kept in darkness. After this, the current is reversed and the surface again exposed to light. Under these conditions, a sharp pulse of photoconductive current is exhibited by the device in a reverse direction to that originally shown, but of a value 10 to 100 times greater than the current first obtained. This behavior can be repeated indefinitely if the same rotation of treatment is observed, and operates from the point of view of initiating exposure with filled electron traps rather than empty. The photocurrent is in the form of a sharp time pulse of duration such that it is obvious that ordinary meters cannot follow the cycle.

Amount of Binder: The amount of silicone bonding resin was varied from 50% by volume to 5% by volume. The thickness of a particular phosphor was varied through the use of doctor knives at a binder content of 25%.

Plate Preparation Using Spin-on Technique: The early plates were made by flooding on a suspension of phosphor in a Dow Corning No. 996 resin dissolved in Solvesso 150. With such techniques, it was difficult to control the thickness of the plate from specimen to specimen and only relatively thick plates could be made. In the spin-on technique, the brass plate used as the backing was fastened to a rotating table such that the geometrical center of the plate was coincident with the center of the rotating table. A measured amount of phosphor dispersion was heaped on this geometrical center and the table started spinning. The speed was gradually increased until the phosphor had spread uniformly over the surface of the plate after which the speed was increased to a maximum of roughly 1000 revolutions per minute. With this technique, plates having a uniform thickness of sensitive surface of 0.001" or less could be made readily in duplicable fashion.

Spectral Sensitivity: Using the cell described in this quarterly report, information as to spectral sensitivity and range was obtained and recorded for most of the phosphors using a Beckman Model B spectrophotometer. In discussing the data on spectral sensitivity, it should be remembered that the light sources from the Beckman sensitometer produces more energy in the longer wavelengths than in the shorter wavelengths so that if a particular phosphor peaks in the violet, an inherently high value of response may be expected from a photographic point of view.

Electrometric Measurements: The rate of decay of charge under a variety of electrical conditions and using various types of plates was measured using a Linderman-Ryerson Electrometer. Data covering both the normal and reversal types of illumination and under different charging conditions were taken.

In the case of regular curves designated as normal exposure, the plates were first exposed to the infra-red lamp for 30 seconds. They were then charged and allowed to decay in the light or in the dark as the case might be. In all experiments involving light decay, the light source was the sensitometric lamp burning at a color temperature of 2360° Kelvin and an approximate intensity of 4.5 meter candles.

The reverse charging technique was as follows:

1. Infra-red for 30 seconds.
2. Place plate under charging grid in the dark and apply the charging voltage.
3. Illuminate with white light (these are fluorescent lamps of about 15 foot candles intensity) for 30 seconds. Turn off lights.
4. Charge plate with reverse polarity in normal fashion.
5. Allow the plate to decay in light or dark.

Sensitometry: The speed of various plates was measured with a step sector type of sensitometer. Phosphor, silver halide, and selenium plates were measured in this way and compared.

Triggered Oscillographic Techniques: A DC amplifier comparable to the type normally available in a microammeter was constructed and built up into a circuit involving the photoconductive cell and an oscilloscope having a frequency of response in the range of 300,000 inverse seconds. The oscilloscope was placed in the circuit in such a way that the triggered sweep would operate and be initiated by the onset of the illumination of the photoconductor. A long persistence screen having a persistence value of 100 seconds was used in the scope so that the current-time curves could be traced directly from the face of the cathode ray tube.

The major difficulty in use of this technique was the devising of a proper lighting system of nature such that the rise time of the illumination may be considered minor relative to the rise time of the photoconductive effect in the phosphor systems. The solution finally arrived at was the use of a high speed camera and lens system. The camera used was a Zeis-Ikon, Maximar Model having a Compur shutter with an indicated speed of 250 inverse seconds. For the types of measurements taken, the open time of the shutter is not important, but the rise and close time of the shutter is. The illumination arrangement used involved placing the camera over a shielded box containing the photoconductive cell with the shutter closed, then turning on a strong light so that the light was focused on a portion of the photoconductive cell by the camera lens when the shutter was opened. The entire electrical system was thoroughly shielded to prevent AC pickup, the shielding being copper screening. The cathode ray tube was calibrated so that each horizontal 0.1" was equivalent to 120 inverse seconds and the vertical scales calibrated so that each 2" on the maximum amplification range of the oscilloscope was equivalent to 1 x 10^{-9} amperes. Current sweeps of several hundred inches were possible.

The action of the shutter was checked through use of a gas filled photocell having a frequency of response greater than 100 inverse seconds.

The method of procedure in measuring current versus time curves of the various phosphors is as follows: The camera is removed from the face of the shielded box containing the photoconductor and the photoconductor was quenched in the infra-red without the application of voltage. While still exposed to infra-red, the photoconductor was placed in the holder and the camera positioned in proper place over the cell. Forty-five volts are then applied to the photocell in a direction through the film. The light is turned on and after a period of 10 to 15 seconds, the shutter is then actuated on a fixed time period. Triggering is accomplished by simultaneous connections to the shutter and scope. The synchronization obtained was better than 1 millisecond. The curve traced on the scope obtained in this manner is designated as the "normal curve". After this normal curve was traced, the camera is again removed from on top the photocell and the voltage is still maintained in the original direction. The cell is flooded with strong light for about a minute. The light is turned off and the battery leads are reversed. The camera is placed in position and the cell is again illuminated as before. In this case, a sharp pulse of current is obtained in the opposite direction which is considerably greater in magnitude than the original normal current. This sharp pulse obtained after flooding with white light is termed the "reversed current".

It should be emphasized that the procedure just described must be designated as qualitative since the light sources used did not fill the aperture of the lens with the result that less than 1/5th of the available surface of the photoconductor was illuminated. Time was not available for building a rigid system including illumination such that the entire surface of the photocell could be treated with light in a perfectly uniform manner over the entire surface. It is important to note, however, that even though qualitative, the procedure provided useful information.

The results indicate the rise time of charge of the phosphor, the nature of the behavior of the charge on illumination, and also provide some idea of speed by determination of area under the charge-time curves. Two shutter openings were used during the course of the work, the first being 200 inverse seconds and the second being 5 inverse seconds. The full rise time to saturation of all the phosphors seldom exceeds a value of 120 to 150 inverse seconds and for the most part is of the order of 15 to 60. For this reason, the data obtained with a shutter speed of 5 inverse seconds is of more value than that developed with a shutter speed of 200 inverse seconds.

B. PREPARATION OF MATERIAL

In spite of broad variations of experimental technique, speed measurements have shown that even the best of the commercially available phosphors are very slow devices from a photographic point of view when used in electrography. For this reason, it was recognized that phosphor type materials and other photoconductive systems would have to be synthesized in the laboratory or presently available phosphors would have to be so modified as to improve their photoconductive properties. Experiments were thus initiated in synthesis and modification of phosphors.

The phosphor manufacturing process is known to be a highly delicate process which normally can be carried out only in exceptionally clean laboratories. Preliminary tests on the doping of chemically pure zinc sulfide establish the fact that a good grade of luminescent phosphors could be made in our laboratories and that doping results could be counted on.

Synthesis thus proceeded in these directions:

1. Analysis of existing phosphor type photoconductive systems for purposes of correlation of composition with photographic properties.

2. Modification of commercially available phosphors and phosphor base materials through doping procedures.

3. Preparation of incomplete phosphors or photoconductive systems in which the luminescent properties are ignored.

4. Treatment of cadmium sulfide in order to provide the best photoconductive properties.

The work was initiated by subjecting luminescent free grades of zinc oxide and zinc sulfide to various treatments at various temperatures and in various atmospheres. The purpose of this work was to develop techniques in preparation for improvement of photoconductive properties. Zinc oxide was calcined in air, in a slightly reducing atmosphere, and in hydrogen at temperatures varying from 1800°F up to 2600°F. Zinc sulfide was calcined in nitrogen and in hydrogen sulfide at temperatures varying from 1800° to 2600°F. These calcinations were carried out in electrically heated tube furnaces using zircon trays as the carrying medium. In the case of zinc oxide calcined in air, these were quenched from the top calcination temperature. In the case of zinc sulfide fired in specialized atmospheres, these were cooled to room temperature after calcination while still maintaining the specialized atmospheres.

The products resulting from these various calcinations were baked onto brass plates and the photoconductive properties measured.

The base materials used in the doping experiments were of three general types: (a) luminescent free pure zinc sulfide
(b) commercial cadmium sulfide of indeterminate composition
(c) phosphor No. 2225.

In the first group of doping experiments, copper chloride was used as the purity agent; and in the second group, silver nitrate was the activating impurity. Two solutions were prepared in distilled water, one solution having a concentration of either one milligram of copper chloride per cc of water or one milligram of silver nitrate per cc of water and the second having a concentration of 0.1 milligrams of the respective reagent per cc of water. Adequate mixing of this amount of doping agent was assured by first preparing a fairly thick but easily stirable slurry of the base sulfide ingredient in water. The water was first placed in a porcelain evaporating dish and the designated amount of doping agent added and stirred in. To this extremely dilute solution of doping agent, a designated amount of the various sulfide materials was added and the slurry obtained was stirred thoroughly. The slurry was then evaporated rapidly to dryness in a clean drier. The dried cake was removed from the evaporating dish and ground gently in the glass mortar to further insure complete mixing. The batch was then placed in a clean porcelain crucible and a cover placed on.

In the first group of doping experiments, the crucible and contents were heated at a temperature of 500°C for one hour. In the second group of doping experiments, six grams of sodium chloride was added per 100 grams of base mix and the batch was then heated for one hour at 980°C in an atmosphere of nitrogen. After the heat treatment, the furnace was cooled as rapidly as possible to 600°C and the prepared material was removed from the furnace and quenched in air. The contents of the crucible were leached with distilled water and washed thoroughly on the filter to remove all sodium chloride. The filter cake was dried and the powder resulting was presented to the Physics Laboratory for preparation of photoconductive plates. These doping experiments were effective in that in some cases an improvement in the photoconductive activity of the original material was obtained.

The inferences from the experimental data are that in all probability relatively pure cadmium sulfide is the best material thus far found for the purposes of this project. Samples of allegedly pure cadmium sulfide have been obtained from the Baker Chemical Co., the Ferro Enamel Corp., the Harshaw Chemical Co., and Fisher Scientific. In addition, by special arrangement, substantial quantities of luminescence pure cadmium sulfide of unactivated type has been obtained from the RCA Manufacturing Co. and from the Sylvania Electric Products, Inc. Further, a sample of silver activated cadmium sulfide has also been investigated. Ultra-pure zinc selenide has been included in the program.

Considerable difficulty had been experienced in obtaining the proper purity cadmium sulfide for the purposes of this project and it is only recently that this grade of chemical has been placed in experimental treatment. In view of the delay that was anticipated, work was initiated in preparation of luminescence pure cadmium sulfide through use of the Leverenz "acid" process. Since the luminescence free cadmium sulfide is now available to us, these attempts at synthesizing chemically pure cadmium sulfide have ceased.

Modification of the cadmium sulfide for photoconductive purposes has followed many lines. In those cases where cadmium sulfide of purportedly pure grade was used as the base material, this grade was always the Harshaw type material. We have found recently by spectrographic analysis that this type of cadmium sulfide is anything but pure for the purposes of this project. The cadmium sulfide was treated as described previously by doping with copper and silver. In addition, cadmium metal coated brass plates were dipped and soaked in molten sulfur for periods up to two hours. Any excess sulfur remaining on the film was dissolved off with carbon disulfide. In another group of experiments, 10% sodium sulfide was added to molten sulfur and the dipping experiments just described were repeated. Further, a 50% solution of sodium sulfide was made up. Plates of cadmium coated brass were boiled in the solution for periods of 30 minutes up to six hours. Next plates consisting of cadmium coated brass were heated in hydrogen sulfide. Since cadmium melts at 320°C, it was found necessary to keep the temperature below this and a temperature of 250°C was found to be the best range for formation of a film of cadmium sulfide. Since brass was sharply affected by the hydrogen sulfide, cadmium coated stainless steel plates made by evaporative techniques were used. Cadmium sulfide was formed but a completely satisfactory film was not obtained, in that pinholes always showed up. The amount of the deposited cadmium sulfide is determined by the thickness of the evaporated coat of cadmium on the base material. The best film was obtained by treatment at 250°C for four hours using a hydrogen sulfide gas flow of 150 cc per minute.

Cadmium sulfide plates were made by evaporation of cadmium sulfide onto brass. Though clear transparent films were obtained by this technique, the resistance was too low for such films to take a charge.

In view of the present availability of luminescence free cadmium sulfide, the major effort is being based on such material and some of the earlier experiments will be repeated. In addition, a method for forming cadmium sulfide involving electrolysis is being examined.

Other Photoconductors: Lead sulfide is known to be a powerful photoconductor and in earlier reports a method was described for chemical deposition of lead sulfide through the medium of mixing lead salts, thiourea, and caustic. The deposited mirrors were found not to be effective for electrography purposes since their resistance was too low. Consequently, such lead sulfides surfaces were subjected to a variety of heat treatments in an attempt to raise the resistance to a suitable value. The end to end resistance of an untreated lead sulfide film deposited for a period of 16 minutes using the concentration of ingredients listed in previous reports was of the order of 0.3×10^6 ohms. The various treatments to which lead sulfide was subjected were the following: heating in air at temperatures up to 500°C for periods of half an hour, heating in hydrogen up to temperatures of 500°C for periods of one hour, in nitrogen up to 500°C for periods of one hour, in hydrogen sulfide up to 750°C for one hour, in carbon dioxide up to 750°C for one hour, in combinations of carbon bisulfide and sulfur, in combinations of carbon bisulfide and CO_2. Of all these treatments, treatment of nitrogen at 300°C and hydrogen at the same temperature for periods of about one hour was the most effective, values of the order of 3 to 9×10^7 ohms being obtained. This value of resistance is still not sufficient for electrographic purposes and in view of the importance of other photoconductive systems, these experiments have now been abandoned.

Germanium and silicon were evaporated on brass using vacuum evaporation techniques. The purpose in using these materials is the fact that both substances are known to be photoconductors and when applied by evaporation techniques, they are resistors. However, even when applied relatively thickly, the resistance was found to be too low for electrographic purposes. Again in view of the promise exhibited by cadmium sulfide, this experimental approach is being abandoned.

An intriguing phosphor system is now being investigated. This involves the insertion of colloidal silver into a glass system. The method is as follows: A soft glass thin walled receptacle is provided as a diaphragm in a two part electrolytic cell using fused salt electrolytes. The cathode compartment consists of a nickel cathode and a fused bath comprised of 56 parts of potassium nitrate and 44 parts of sodium nitrite. The anode compartment consists of silver nitrate using graphite as the unattackable electrode. Electrolysis is carried out at 350°C at which all of the salts are thin liquids. Currents of the order of 20 to 40 volts are used and the electrolysis is continued for periods of one to three hours. Currents of the order of magnitude of 2 to 10 milliamperes are developed. Under these conditions, small amounts of colloidal silver are deposited in the glass structure itself and after cooling and washing, the areas of silver deposition are found to fluoresce strongly when exposed to ultra-violet light. The purpose of examination of this system is the fact that its dark resistance is exceptionally high.

C. CHEMICAL ANALYSIS

The exact makeup of the various phosphors used in this project and as obtained from commercial suppliers is not available. In view of the importance of the nature and type of impurity in the phosphor with respect to its photoconductive properties, and the desire to determine the effect of variation in base composition, some of the phosphors were analyzed chemically to determine at least qualitatively the nature of the impurities and some indication of their amount. While the information obtained may be used only for hypothesis purposes since systematic variations are not expected in these phosphors, at least trends may be shown and these trends may be checked by synthesis. The general procedure used was to dissolve the sulfide phosphor in dilute nitric acid and boil until all odor of hydrogen sulfide was eliminated. The presence of silver was determined after the dilution through the addition of hydrochloric acid. The presence of copper was determined by the addition of an excess of ammonia, filtering, and examining the depth of blue color which developed. The presence of manganese was determined by evaporating a portion of the nitrate solution of phosphor to dryness, then adding sodium bismuthate and nitric acid and heating in order to develop the permanganate color. The relative amount of cadmium was determined by inspection since this additive deposited a distinct yellow color to the phosphor. Spectrographic analysis of the various materials used in this project is now in progress and some of the preliminary data represent a verification of the wet method of chemical analysis.

RESULTS AND DISCUSSION

The experimental data obtained are summarized in the tables and figures attached.

The most important result is the finding that the overall speed of an electrophotographic plate made from photoconductive phosphors is extremely low in spite of broad variations in plate preparation technique, type, and nature of illumination. These low speeds have been checked by electrical measurements, sensitometrically, by comparison with selenium plates of known speed, and substantiated by measurement of decay curves in both light and dark. The speed factor obtained is in the neighborhood of 1ASA or less and is roughly 1/30th of a properly made selenium plate. The charge decay curves indicate a phenomenological reason for this broad disparity in speeds. Under illumination conditions, the charge on a selenium plate decays rapidly to zero whereas in the case of the phosphor plate, the charge decays fairly rapidly but to a value considerably above ground and maintains this partially charged condition indefinitely even on continued illumination. The theoretical treatment provides at least a portion of the reason for the differences shown. The majority of the phosphors exhibit a rather sharp increase in dielectric constant on illumination which may or may not be a long time phenomenon. Thus the ability of the system to hold a charge is actually increased under such conditions. If any device is placed in the mechanism which provides for leakage of the charge into the base plate, the theory indicates that those phosphors which have the largest photoconductive change accompanied by the smallest capacitative change will be the most rapid from a photographic point of view. Though complete photographic measurements on this type of system have not been included as yet in this report, some of the doping experiments have been successful in approaching this sort of system.

An adverse effect of increase of dielectric constant is shown very clearly in Figure 2 in which current versus time characteristics of phosphor No. 2225 is measured oscillographically. On illumination, the current carrying capacity of the photoconductive system increases or conversely the resistance decreases. This effect is exhibited in the very early portions of exposure. Almost immediately the reverse situation makes itself evident and the overall photoconductive activity of the system decreases. This is obviously due to an increase in the dielectric constant of the phosphor and it is evident that, either means will have to be established for elimination of this dielectric constant change, or, a type of illumination and exposure will have to be used which bypasses this effect. Examination of such possibilities are now in progress.

The thinner the phosphor type of electrographic plate and the less the amount of binder, the greater the speed. These indications have been obtained previously from both sensitometric and electrical data and have now been checked by measurement of light and dark decay rates, in which the differences between these two rates are in accord with the conclusions previously drawn.

It is significant that the dark decay rates are not much affected by either thickness or variation in binder content and the major effect takes place on the nature of the light decay curves. At first glance, the effect appears to be due to the increase in potential difference which may be expected as the result of the reduction in thickness. This does not, however, appear to be the entire story for the reason that apparent trap depth, apparent light-dark ratios, and overall improvement of the values from light to dark develop as the result of the reduction in thickness. There are several possibilities which might explain the effects obtained. One logical conclusion is the assumption that the thinner the plate, the more effectively is the incident light used and in the last analysis, the increase in photographic effectiveness is the result of the increase in the use of the light rather than the increase in potential difference or other electrical factors. In addition, the possibility also exists that the thicker the plate the more probable is the existence of a retrapping phenomenon which in effect nullifies the leakage of electrons into the base plate. Under normal conditions of exposure, the traps are first completely emptied by exposure to infra-red light. Thereafter on illumination, the traps in the first layer of phosphors become filled. However, if this first layer of phosphor is a considerable distance away from the base plate, the possibility exists that successive layers of phosphors may have their traps filled by robbing the trapped electrons from the first layer and under such conditions, the light decay rate would be a slow process. Finally, layers of potential barriers would be set up and the overall effect would be roughly the same as that predicted by the experimental portions of this report, namely, that a high residual charge would remain in the body of the phosphor film which had no means for leaking off through the base plate.

In any event, it is definite that the major item in technique with respect to preparation of plates useful for increasing the speed may be obtained through reducing the thickness to the least practical value.

The spectral sensitivity data indicate that the region of maximum sensitivity or peak value of change in electric characteristics is on the short wavelength side of the spectral region in which the particular phosphor exhibits visible luminescence. It appears that the region of maximum sensitivity of most of the commercially available phosphors is in the violet or in the ultra-violet and if light conditions of this type are used, phosphors normally rated as poor from the point of view of speed show to better advantage. It is understood that the use of ultra-violet sources of illumination are not desirable for the purposes of this project but it is equally important to realize that most of the phosphors being examined have been used in spectral ranges at a considerable distance away from their region of maximum sensitivity from the point of view of wavelength of illumination. A case in point is the following example: Using previously described white light sources, phosphor No. 1504 was found to be less sensitive and slower than phosphor No. 2225. Using an ultra-violet light source, phosphor No. 1504 was found to be several times faster than phosphor No. 2225. It should be noted here that methods for shifting the spectral sensitivity of phosphors are known and once a system having a speed at least comparable to that of selenium is found, then the means for shifting such sensitivity ranges will be investigated.

The various electrical data have established the significance and need for infra-red quenching or trap emptying. Generally speaking most of the phosphors reached equilibrium under exposure to strong infra-red lamp in a few seconds, but in isolated cases times extending up to several hours were required. The various measurements have shown distinctly that if the phosphor is not previously quenched in infra-red, the trap emptying takes place with extreme slowness in darkness and a loss of speed results. For example, a plate carrying phosphor No. 1304 as the sensitive surface was exposed to a strong light and then placed in a dark box suitably connected to the capacitance bridge. The capacitance had not reached equilibrium 24 hours later and was still falling asymptotically to a minimum value. This is generally true of all of the phosphors, that is, once it is exposed to light and not subsequently quenched in infra-red light, the time required to reach electrical equilibrium in darkness is extremely lengthy--the deeper the traps the longer the time. However, even if the infra-red quenching equilibrium is reached very slowly, if the phosphor is first quenched in infra-red, the time required for the phosphor to reach equilibrium from an electrical point of view after being placed in the dark box never exceeds a few minutes.

The nature of the pulse measurements obtained through use of the triggered sweep oscillographic techniques are shown in Figures 1 to 3 inclusive. In both the normal and reverse methods of elimination, the initial effect is in the form of a pulse of current whose magnitude almost immediately starts to decay from its initial high value. As has been indicated before, this decay is believed to be due to the increase in dielectric constant. In view of the intensity of the light being used, the effect must be of saturation order. The higher this initial pulse the more rapid the decay for phosphors such as 2225 and to a lesser extent the same is true of phosphor No. 1504. From the peak of the curve, the current flow decays for about 1/10th to 1/20th of a second and then starts to rise. It is believed that this rise is not due to the phosphor itself at all, but is more probably due to the closing action of the camera shutter, that is, with the wide opening of the shutter, the shutter bounces on closing so that the effect is to reilluminate the phosphor for a very brief period giving rise to the secondary pip shown on the curves.

As has been explained previously, the normal curve is accomplished by illumination proceedings which are initiated by electron trap emptying while the reverse curve is accomplished by illumination proceedings which is initiated by electron trap filling before exposure. In every case where extreme care was taken so that positioning from normal to reverse of the illumination system was exact, the initial pulse on reversal is of the order of 10 to 100 times greater than that obtained through the normal method of trap emptying illumination.

The triggered sweep technique also gives some indication of the rise time of the photoconductive system. If the hypthesis of adverse effect of dielectric constant change is warranted, an indication is also given of the rise time of the increase of dielectric constant. Of all the various phosphors tested, and under the various conditions indicated, the rise times are of the same general order of magnitude and are in the range of 10 to about 100 inverse seconds. At most the variation from phosphor to phosphor is not greater than a factor of 2 to 3. This indicates that the mechanism initiating photoconduction in these types of phosphors is probably substantially the same from one type of phosphor to the other.

It is interesting to note that the results obtained in such experiments have been substantiated in a recent publication of the February 15, 1951 issue of Physical Review on the photoconductive characteristics of thallium sulfide by A. W. Ewald. Ewald used AC methods of examination and found rise times of the order of 10 to 20 milliseconds and it may be pointed out that his thallium sulfide films are extremely thin in comparison to the relative thick phosphor films used in this case.

A significant comparison may be drawn between the current-time curves measured oscillographically and the charge-time curves measured electrometrically. In the first case, the phosphor continues to be subjected to a steady voltage during illumination and the photoconductive properties decrease after the development of the first pulse in spite of the steady potential. In the second case, the surface of the insulator is sprayed with electrons. On illumination, the charge decreases to some value above ground. It is obvious that the same mechanism which prevents the maintenance of the high initial charge in the pulse experiments is operating in the second case. This prevents the charge from decaying to zero and it appears reasonably evident that this mechanism is the increase in dielectric constant which takes place on illumination. The same general results are obtained from the light decay curves and from the pulse currents on steady illumination as modified by the decrease of the amount of binder and the thickness of the film. This again leads to the inevitable conclusion that in order to make phosphor type systems effective for photographic purposes, either better photoconductive mechanisms are required than are available in commercial phosphors or methods of illumination and charging will have to be sharply modified.

At first glance, it would appear that the reversal method of illumination may be expected to be more suitable from an electrographic point of view than the normal method and it has been suggested previously that this reversal or trap filling will be effective only if light flooding takes place while the plate is being charged. However, investigation of the charge decay properties in both light and dark using the reversal method of illumination show that at least for the present, not too much can be expected from this finding. The light decay ratesare considerably improved or that is light decay takes place at a faster rate and to a greater extent using the reversal method of illumination, but unfortunately the dark decay rates also increase so that the overall increase in speed obtained is not significant.

Detailed study of the pulse current curves and the light decay curves provide certain hints as to possible means of illumination which may provide an overall increase in speed. Some further experimentation is needed to determine whether these hints are possible or not and there is a probability that a direct approach may be the most suitable. The first of these would serve to indicate (and this is a finding which has been suggested in the theoretical portions of this report) that if the reversal method is used and illumination and charging are carried on simultaneously and then immediately after this first stage, the plate is developed, then the peak effectiveness of the photoconductive system might be available. This development would have to take place in time intervals of milliseconds and for this reason might be academic for the purposes of this project. A second possibility also exists which may be derived from study of the pulse current curves. It has been indicated that the rise times on these curves for all phosphors are of the same general order of magnitude and are in the range of 10 to about 100 inverse seconds. The current rises to peak and then starts to decay even under conditions of steady charging and illumination. It has been hypothesized that this decrease in photoconductive current is due to the development of increase of dielectric constant. If this hypothesis is correct and if the same conditions are not obtained under like conditions of charging in the dark and if the increase in dielectric constant takes place at a time later than the phenomenon associated with photoconductivity, then a means of illumination presents itself which might make these systems extremely fast from the point of view of speed. Naturally all the "if's" in the foregoing hypothesis will have to be checked before the suggestion about to be given can be shown to have any real value. The illuminative possibility is the following: It is altogether possible that if the exposure of the phosphor type plate is accomplished in units of time less than that represented by the rise time of the pulse current, then the adverse dielectric constant effect will not have time to make itself available. Two means of checking this hypothesis present themselves. The first is to use a single exposure of extremely short time duration, that is, considerably less than 0.1 second, and in accordance with the curve on Figure 2, exposure time should be of the order of 0.01 seconds or less. Another possibility is the use of illumination through a rotating shutter in which the open time of the shutter never exceeds a unit of 0.01 seconds or less. Thus, if the hypothesis that the adverse dielectric constant changes operate in an opposing direction to that of the current changes is a correct one and if such dielectric constant changes take place at an interval of time later than the current changes, then the possibility should be a good one that this method of illumination may be a valuable technique. This idea will be checked during the coming report period.

The possibilities with respect to decrease in dielectric constant changes while increasing photoconductive changes will be discussed in further detail in connection with actual data reported in the tables.

The qualitative chemical analysis has brought to light several interesting points and in view of the fact that the general class of commercial phosphors available for study does not represent systematic changes, only qualitative conclusions may be drawn. The conclusions are these: Other things being equal, only phosphors which contain interstitial impurities, such as copper or silver or both, are photoconductors in the zinc sulfide type system. This conclusion is complicated by the presnece of other impurities; an analysis of phosphor CE5109 showed only copper as an impurity and yet it is not a good photoconductor and is extremely slow or practically negative as far as photographic properties are concerned. The solutions were reexamined and a trace of cobalt was found. Cobalt is known to be a powerful poisoner of photoconduction and in amounts larger than traces will also kill luminescence. Phosphors such as 2703 which contains only manganese, a substitutional type of impurity, are shown by the electrical measurements not to be a good photoconductor and has practically negligible speed for electrographic purposes. In addition, generally, the more brightly yellow the phosphor, the higher the photoconductive value and the higher the electrographic speed, leading to the hypothesis that cadmium sulfide based phosphors will be more effective photoconductively and photographically than zinc sulfide based. It is further evident that the conclusions with respect to impurities and with respect to cadmium content must be treated separately since phosphor No. 1304 which is relatively fast contains no cadmium, but does contain both copper and silver. (In connection with the hypothesis that the increased content of cadmium will increase the speed, it is interesting to note that the last report prepared by Battelle on the subject points out that phosphor RCA No. F2903 is roughly 10 times faster than phosphor No. 2225. We have been able to obtain the general chemical analysis of phosphor F2903 and find that it is one of the highest cadmium content phosphors available commercially, containing roughly 90 parts of cadmium sulfide, 10 parts of zinc sulfide, and activated by silver.)

In any case, the hypothesis may be presented that photoconductivity in a phosphor is the result of the presence of an interstitial impurity, that certain impurities such as cobalt will quench photoconductivity, and that substitutional impurities such as manganese which are useful for luminescence purposes do not provide photoconductivity, and that the photoconductive and in all probability the electrographic properties of a sulfide phosphor will be proportional to the cadmium content. On this basis, it appears advisable to emphasize pure cadmium sulfide systems rather than those which contain any amounts of zinc sulfide.

It was the result of these analytical findings that doping experiments were initiated based on zinc sulfide phosphor No. 2225 and cadmium sulfide. The data obtained are reported in Tables 4, 5, and 6. The cadmium sulfide used for the purpose of these experiments was the Harshaw grade and in all cases, the end product had too low a resistance to be effective for the purposes of the project and are therefore not reported. These experiments are now being repeated with the luminescence free type of cadmium sulfide which we have been fortunate in obtaining recently. The general data with respect to cadmium sulfide will be reported as a unit later. Referring again to Tables 4, 5, and 6, the results of these synthesis experiments and of the qualitative analysis indicate that doping for photoconductive purposes may extend beyond or in a different direction than that considered maximum for luminescence efficiency. In the case of luminescence free zinc sulfide, photoconductive properties could be imparted through suitable additions of either copper or silver, but the maximum photoconductive current obtained in any case is not sufficiently high to be useful. This is simply another way of saying that zinc sulfide systems are not as effective as systems containing cadmium sulfide. Another significant point is that copper seems to be more generally effective than silver and that doping of No. 2225 results in much more desirable changes than the doping of zinc sulfide. In the case of No. 2225, when the conditions of preparation are proper, the photoconductive values continue to increase with increase in copper content up to about 0.01 grams of copper chloride per 100 grams of No. 2225. Both the steady state photoconductive values and the pulse current values were measured for the purposes of these tables with care. So far, the best results have been obtained by flux treatment at 980°C. Most significant is the experimental finding, however, that the activity of the phosphor rises rather steadily with increase in copper content as far as photoconductive properties are concerned. If at the same time, the capacitative differences in the hypothetical figure, designated as trap depth, appear to decrease and if the hypothesis developed in the theoretical supplement with respect to the adverse effect of increase of dielectric constant are shown to have a basis in fact, then it is certain that the dielectric constant and photoconductive changes are separately operating mechanisms. A means for changing one without affecting the other is available through doping procedures and a much greater increase in speed should be expected than would be indicated by the figures given in Table 4.

Referring specifically now to Table 4, the capacitative differences of phosphor No. 2225 without added copper are 63% and the photoconductive current in light is 1.8 millimicroamperes. The capacitative differences of the phosphor doped with 0.0100 grams of copper chloride per 100 grams of No. 2225 is roughly 11% and the photoconductive current under illumination conditions is 8.6 millimicroamperes. If the hypotheses given in the theoretical portions are correct, then the speed of the sample represented by plate No. 284 should be several times faster than the speed of the sample represented by plate No. 282. In order to determine whether these suggestions are correct, the rate of decay of light and dark currents under normal methods of charging are now being measured.

In summary of this section of the discussion, it would appear that the results of chemical analysis and experimental data indicate that copper is an effective impurity in sulfide type phosphors for photoconductive purposes.

In view of the effectiveness of certain titanates from the point of view of infra-red, combinations of these materials and phosphor No. 2225 were examined. No unusual results were found.

The major emphasis has been placed on cadmium sulfide in the latter sections of this report period. The work has been handicapped by the lack of availability of suitable raw material of sufficiently pure grade and work was initiated with the types of cadmium sulfide available commercially. Fortunately, recently we have obtained substantial quantities of luminescence free cadmium sulfide from both RCA and Sylvania, and these materials have now been placed in experimental evaluation. Prior to the stocking of such materials, a variety of experiments were carried out in the general field of cadmium sulfide. The doping experiments as described before on Harshaw cadmium sulfide were failures in that the product had too low a resistance to be effective for the purpose of the project. All experiments dealing with the heating of cadmium oxide in oxygen and the attempts to develop a cadmium sulfide film on brass, stainless steel, or other metals, resulted in failure either because the properties of the film were physically poor, or large pinholes existed, or the resistance was too low for the purposes of the project.

Cadmium sulfide from the different sources was examined for investigation of their photoconductive properties. Light and dark decay curves could not be obtained from these cadmium sulfides since their dark resistance in all cases was too low to permit the material to hold a charge. The dark resistance for photographic purposes should be of the order of 0.1×10^{-9} amperes or less and all of the cadmium sulfides are higher than this value. One of the intriguing findings with respect to the various cadmium sulfides is the relatively high order of current which passes or is developed in these materials when exposed to light. A silver doped cadmium sulfide supplied by the Signal Corps exhibits unusually large amounts of current on illumination, but the dark current was also quite high resulting in a light-dark ratio of 4 to 1.

Mixtures of phosphor No. 2225 and the Harshaw type cadmium sulfide were prepared covering a broad range of binaries and some of the adverse dark current conditions exhibited by cadmium sulfide were suppressed in this manner although they still remained in a range too high to make them useful for photographic purposes. It is significant to note, however, that at least a method for making a very effective photoconductive cell was provided in this way. As a matter of fact, using cell No. 325 in an intense illumination, a light-dark ratio of over 1000 to 1 is readily exhibited. The continuing endeavor on cadmium sulfide is for the purposes of emphasizing means for reducing the dark current to values below 1×10^{-10} amperes.

The light and dark decay rates, measured electrometrically, of this combination of cadmium sulfide and 2225 plus results on phosphor No. 2225 alone, No. 1504, and No. 2200 are exhibited in Figures 4 and following. In general, these data substantiate conclusions obtained earlier by photographic procedures. Phosphor No. 2225 has a faster light decay rate than a No. 1504 whereas No. 2200 is by comparison very slow. The effect of thickness of binder is clearly exhibited, light decay rates being greater with thin films rather than with thick. The reverse charging techniques gives faster light decay rates, but also faster dark decay rates. The net result appears to be a net gain in photographic speed of approximately a factor of 2. As has been indicated, this might be improved by automatic charging and developing devices which would charge the plate during exposure and develop it immediately afterwards. This suggestion remains to be checked experimentally. Other methods of reverse charging might be possible and have been suggested in previous sections of this report. The results on the addition of cadmium sulfide to 2225 indicate a decrease in the rate of light decay and it is to be noted that as the amount of cadmium sulfide increases, the effect of reverse charging also decreases up to the point where with 20% cadmium sulfide, normal and reverse charging curves are substantially identical.

At first glance, it would appear that this result is contrary to what might be expected or may be anomalous. However, when it is remembered that the cadmium sulfide used in this case was the Harshaw type which shows an extremely high dark conductivity, then the effect is substantially as expected and it is exactly the same as though conducting particles were placed in the film. Under these conditions, it would be difficult to charge the plate to the same potential as when these conducting particles were absent and the data clearly indicate this adverse condition. Thus it does not appear safe to draw any conclusions with respect to the role of cadmium sulfide with respect to the light decay rates until assurance is had that the photoconductive dark current is sufficiently low.

Light decays were tried on two selenium plates furnished by the Signal Corps. These were charged plus 7500 volts on the corona wires, plus 480 volts on the grid resulting in a plate voltage of 180. The plates decayed in the light to 30 volts in less than 5 seconds, which was too fast to plot the curves. However, these data indicate that the selenium plates are about 30 times faster than phosphor No. 2225.

In Table 9, the effect of light intensity was examined using a single plate for all the measurements. The light intensity was measured with a meter and as indicated in the note attached to this table, the figures may be considered only relative in view of the small area of the plate which was illuminated. Light intensity used for all measurements in all other tables was equivalent to the 700 value given in Table 4. The results indicate reasonably conclusively that the pulse current increases with light intensity, particularly on reversal, and the evidence is that saturation effects become noticeable at high values of intensity. To a limited extent, it appears that the rise time of the photoconductive current is higher at high values of light intensity than at low, though this factor appears to level off at lower light intensity values than indicated by saturation of photocurrent. These results are substantially as expected.

CONCLUSIONS

Some of the conclusions and hypothesis which may be drawn may be listed as follows:

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2. The speed is proportional to the cadmium sulfide content and the evidence indicates that phosphors based on cadmium sulfide should be

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very much faster than those which contain more or less zinc sulfide.

3. Interstitial impurities such as copper appear to be more important for photoconductive purposes than substitutional impurities.

4. Cobalt appears to be a poisoner for photoconduction.

5. In order to obtain the speeds presented as the specification for this project, major modifications in lighting techniques, in sensitive materials, and in plate making techniques, or in all three, are required in order to meet such specifications.

6. Leads as to the nature of these modifications have been presented both experimentally and theoretically.

Eugene Wainer
Eugene Wainer
Director of Research

David A. Bennett, Jr.
per ess
David A. Bennett, Jr.
Research Physicist Supervisor

Paul S. Maybaum Jr.
Paul S. Maybaum, Jr.
Research Ceramist

Marie Rose
Marie Rose
Research Associate

Paul Pavliska
Paul Pavliska
Research Assistant

N. Lucille Campbell
N. Lucille Campbell
Laboratory Assistant

Donald Gollwitzer
Donald Gollwitzer
Laboratory Assistant

James G. Tabler
James G. Tabler
Research Physicist

HORIZONS INCORPORATED
Cleveland, Ohio
April 20, 1951

TABLE I

ELECTRICAL AND SPECTRAL DATA

Phosphor	$\frac{C_L - C_D}{C_D}$	$P_L - P_D$	Visual Speed Order	Trap Depth $\frac{C_I - C_D}{C_D}$	Spectral Range Response A°	Spectral Peak Response A°
1304	118.0	0.041	1304	20.0	3750 - 4750	4250 - 4500
2225	88.5	0.038	2225	9.4	4750 - 6000	5500 - 5800
1504	59.0	0.024	1504	4.0	3500 - 4000	3750
2330	37.7	0.023	2330	2.7	3250 - 4000	3750
2220	25.8	0.028	2220 ?	0.76	3800 - 5800	4750
2200	30.1	0.026	2200 ?	3.4	4000 - 5000	4250 - 4750
1617	26.2	0.014	1617	1.16	4250 - 6000	4250 - 4900
CE 5109	34.1	0.031	CE 5109?	1.7	4250 - 5000	4750
1409	10.0	0.015	1409	0.47	3250 - 4250	3900
2210	5.6	0.008	2210	0.44	-----	-----
2479	2.6	0.007	2479	0.21	-----	----
2703	0.64	0.006	2703	0.00+	-----	----
LM476	0.41	0.001	LM476	0.00+	----	----
2469	0.31	0.002	2469	0.02	----	----
CE 6138	0.27	0.001	CE6138	0.00+	----	-----

C = capacity (micromicrofarads) at 1000 cycles

L = light

D - dark

I - infra-red

P = dissipation factor

TABLE 2

ZnO + ZnS CALCINATIONS

Product No.	Description	Resistance	Photoconductor
H-1	ZnO at 1800°F in air	3×10^6	yes, slight
H-11	ZnO at 2200°F in air	1×10^5	yes, slight
H-9	ZnO at 2600°F in air	1×10^2	no
H-8	ZnS in N_2 at 1800°F	8×10^8	yes, good
H-2	ZnS in N_2 at 2200°F	3×10^6	yes, slight
H-10	ZnS in N_2 at 2600°F	1×10^3	no
H-3	ZnO in reducing atmosphere 1800°F	8×10^6	yes
H-11	ZnO in reducing atmosphere 2200°F	1×10^2	no
H-9	ZnO in reducing atmosphere 2600°F	6	no
H-4	ZnS in H_2S at 1800°F	1×10^{11}	yes
H-5	ZnS in H_2S at 2200°F	1×10^8	yes
H-5	ZnS in H_2S at 2600°F	volatilized	

None of these were as good photoconductors as the standard phosphors, but treatments similar to H-8 or H-4 might be suitable for thin film firing.

TABLE 3

Effect of Thickness and Binder Contents on Electrical Properties of Phosphor No. 2225

Plate No.	Phosphor Binder Ratio	Thickness Inches	$\frac{C_L-C_D}{C_D}\times100$	P_L-P_D	Trap Depth $\frac{C_1-C_D}{C_D}\times100$	i_L $\times10^{-9}$	Pulse current $\times 10^{-9}$ 250 sec^{-1} N		5 sec^{-1} N		Rise Time sec^{-1} N	
							N	R	N	R	N	R
190	8/2.5	0.0121	115.5	0.007	42.5	0.6	1.3	15	40	42	40	22
191	8/2.5	0.0112	127.6	0.028	47.7	1.0	--	--	--	--	--	--
192	8/2.5	0.0065	48.5	0.013	31.6	1.8	--	--	--	--	--	--
193	8/2.5	0.0061	89.5	0.011	30.4	1.8	35	90	45	55	17	30
196	8/1.25	0.0065	111.7	0.012	38.2	3.2	--	--	--	--	--	--
197	8/1.25	0.0078	127.5	0.005	44.8	3.6	--	--	42	70	100	30
198	8/0.625	0.0078	109.2	0.011	43.6	3.6	10	45	5	82	17	48
199	8/0.625	0.0079	113.2	0.011	41.6	3.5	--	--	63	70	80	40

L_L = photocurrent under steady and continued illumination.

Pulse current = photocurrent under short exposure conditions, rise time of shutter used > 1000 sec^{-1}

N = normal exposure (infra-red quench, dark, expose)

R = reverse exposure (after normal exposure, flood with light with current on, dark, expose.)

TABLE 4

Effect of Doping Phosphor No. 2225 with $CuCl_2$

Plate No.	g. $CuCl_2$ added per 100g. No. 2225	Thickness Inches	$\frac{C_L - C_D}{C_D} \times 100$	$P_L - P_D$	Trap Depth $\frac{C_I - C_D}{C_D} \times 100$	$I_L \times 10^{-9}$	Pulse Current $\times 10^{-9}$ 250 sec^{-1} N	250 sec^{-1} R	5 sec^{-1} N	5 sec^{-1} R	Rise Time sec^{-1} N	Rise Time sec^{-1} R
A. After heating 1 hr. at 500°C without flux												
B2	none	0.0060	63.3	0.032	4.1	1.8	8.5	102.0	30	102	15	34
215	0.0002 g.	0.0064	110.1	0.0002	38.1	5.2	--	--	34	34	60	60
253	0.0010 g.	0.0067	80.6	0.004	30.3	3.6	--	--	50	43	34	26
260	0.0020 g.	0.0084	63.8	0.021	14.2	10.0	8	125	48	90	17	40
247	0.0060 g.	0.0054	62.1	0.039	5.8	10.1	22	60	66	80	30	40
257	0.0100 g.	0.0061	25.3	0.050	0.4	6.8	--	--	50	68	120	40
B. After heating 1 hr. at 980°C with 6% NaCl												
82	none	0.0060	63.3	0.032	4.1	1.8	--	--	30	102	15	34
278	0.0002 g.	0.0072	10.2	0.049	0.46	1.3	--	--	45	50	48	10
277	0.0010 g.	0.0112	11.8	0.060	0.51	1.4	--	--	45	85	60	60
280	0.0020 g.	0.0020	6.4	0.033	0.36	3.1	--	--	55	105	34	12
282	0.0060 g.	0.0084	8.0	0.037	0.33	6.5	--	--	50	130	30	12
284	0.0100 g.	0.0077	11.4	0.051	0.32	8.6	--	--	70	150	30	12
298	0.0200 g.	0.0081	10.0	0.035	0.00	0.6	--	--	--	--	--	--
300	0.0400 g.	0.0062	5.9	0.034	0.00	1.0	--	--	--	--	--	--
328	0.0800 g.	0.0051	10.0	0.047	0.00	1.4	--	--	--	--	--	--

TABLE 5

Effect of Doping pure Zns with $CuCl_2$
by Heating 1 Hour at 980°C with 6% NaCl

Plate No.	g. $CuCl_2$ added per 100 g. Zns	Thickness Inches	$\frac{C_L - C_D}{C_D} \times 100$	$P_L - P_D$	Trap Depth $\frac{C_I - C_D}{C_D} \times 100$	I_L $\times 10^{-9}$	Pulse Current $\times 10^{-9}$ 250 sec.$^{-1}$		5 sec^{-1}		Rise Time sec^{-1}	
							N	R	N	R	N	R
CE6138	none	0.0040	0.27	0.001	0.00+	0.1	0	0	0	0	0	0
266	0.0002 g.	0.0045	14.4	0.029	1.32	0.8	--	--	2	5	20	30
270	0.0010 g.	0.0096	15.4	0.025	1.40	1.2	--	--	5	20	20	24
272	0.0020 g.	0.0072	20.2	0.022	2.10	1.5	--	--	30	35	60	60
269	0.0060 g.	0.0041	11.7	0.027	2.31	1.8	--	--	30	50	24	40
274	0.0100 g.	0.0093	25.7	0.026	1.80	1.6	--	--	35	60	50	70
292	0.0200 g.	0.0061	15.8	0.015	1.58	1.0	--	--	--	--	--	--
294	0.0400 g.	0.0065	4.6	0.010	0.00	0.5	--	--	--	--	--	--
296	0.0800 g.	0.0065	5.6	0.010	0.01	0.6	--	--	--	--	--	--

$BaTiO_3$, $BaSrTiO_3$, and Combinations with Phosphor No. 2225

Plate No.	Type	Thickness Inches	$\frac{C_L - C_D}{C_D} \times 100$	$P_L - P_D$	Trap Depth $\frac{C_I - C_D}{C_D} \times 100$	I_L $\times 10^{-9}$	250 sec.$^{-1}$ N	R	5 sec^{-1} N	R	Rise Time N	R
173	$BaTiO_3$	0.0060	0	0.0008	0	0.4	0	0	0	0	0	0
180	$BaSrTiO_3$	0.0060	0	0.0006	0	0.4	0	0	0	0	0	0
186	75 $BaSrTiO_3$ 25 No. 2225	0.0053	11.8	0.005	1.8	1.0	--	--	40	48	17	17
184	50 $BaSrTiO_3$ 50 No. 2225	0.0047	26.4	0.011	4.7	1.0	--	--	40	48	40	120
187	25 $BaSrTiO_3$ 75 No. 2225	0.0056	45.9	0.014	11.9	2.3	--	--	45	60	20	120

TABLE 6

Effect of Doping Pure ZnS with $AgNO_3$
After heating 1 hour at 980°C with 6% NaCl

Plate No.	grams $AgNO_3$ added per 100 g ZnS	Thickness Inches	$\frac{C_L - C_D}{C_D} \times 100$	$P_L - P_D$	Trap Depth $\frac{C_I - C_D}{C_D} \times 100$	Photocurrent x 10^{-9} I_I	I_D	I_L
341	0.0020 g	0.0061	14.8	0.015	1.8	0.1	0.0	0.3
343	0.0100 g	0.0032	16.3	0.016	1.4	0.2	0.0	1.4
345	0.0200 g	0.0047	11.2	0.013	1.7	0.1	0.0	0.2
347	0.0400 g	0.0062	9.3	0.013	1.9	0.1	0.0	0.4
349	0.0800 g	0.0058	5.3	0.010	0.4	0.3	0.2	0.3
			Effect of Doping Phosphor No. 2225 with $AgNO_3$ After heating 1 hour at 980°C with 6% NaCl					
331	0.0020	0.0042	6.1	0.035	0.00^{+}	0.1	0.0	0.5
332	0.0100	0.0067	5.8	0.026	0.00^{+}	0.2	0.0	0.4
334	0.0200	0.0051	10.0	0.035	0.00^{+}	0.1	0.0	0.4
337	0.0400	0.0075	19.3	0.044	0.00+	0.0	0.0	0.6
339	0.0800	0.0092	22.0	0.040	0.00^{+}	0.1	0.0	0.2

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TABLE 7

Photoconductive Properties of CdS from Various Sources

Plate No.	Source	Treatment	C_{IR}	D_{IR}	C_D	I_D	C_L	D_L	I_{IR}	I_D	I_L	$\frac{I_L}{I_D}$
285	Harshaw	Standard	670	0.122	670	0.158	1700	0.82	18000	12000	94000	8
287	Harshaw	Standard	640	0.091	610	0.080	780	0.19	800	230	520	2
308	Harshaw	Tricresyl and phosphate	718	0.088	672	0.066	770	0.11	520	60	2800	47
311	Harshaw	100°C	466	0.155	450	0.139	660	0.29	1000	580	3000	5
312	Harshaw	100°C	376	0.150	360	0.132	515	0.29	880	470	10800	23
386	Harshaw	Plasticized Silicone	406	0.109	394	0.099	492	0.192	620	120	8200	7
384	Harshaw	+ 25% S	600	0.142	578	0.115	680	0.124	15	5	100	20
385	Baker	100°C	832	0.105	830	0.104	930	0.152	80	68	2000	29
396	Fisher	Standard	766	0.051	758	0.038	846	0.115	120	34	840	25
397	Fisher	100°C	840	0.050	838	0.047	900	0.087	140	54	2000	37
395	Sylvania	Standard	500	0.05	492	0.042	532	0.087	40	14	160	11
315	Ferro F3839	100°C	593	0.022	591	0.019	600	0.026	2	0.6	5.4	9
392	Ferro F3841	Standard	583	0.014	582	0.010	599	0.026	2.2	1.6	2.2	1.5
389	Ferro F3841	100°C	315	0.025	315	0.022	321	0.037	25	22.	30	1.5
316	Ferro F3841	Tricresyl and Phosphate	683	0.008	680	0.007	690	0.13	---	---	---	---
394	Ferro F5897	Standard	339	0.053	330	0.039	376	0.087	12	1.4	360	260

(see next page for symbols)

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TABLE 7 (continued)

Photoconductive Properties of CdS from Various Sources

Plate No.	Source	Treatment	C_{IR}	D_{IR}	C_D	I_D	C_L	D_L	I_{IR}	I_D	I_L	$\frac{I_L}{I_D}$
391	Ferro F5897	100°C	280	0.078	268	0.050	300	0.094	38	34	42	1.2
388	Ferro F504	100°C	1065	0.082	1050	0.077	1650	0.105	--	--		
387	Cd S-Ag	Signal Corps	930	0.045	817	0.033	1060	0.074	40,000	20,000	80,000	4

Note: Standard Treatment is use of Dow Corning Silicone No. 996, baked 1 hour at 300°C.

Sub I_R = infrared

Sub D = dark

Sub L = light

C = capacity

D = dissipation factor

I = photocurrent (Base = 1 × 10^{-9} amperes)

TABLE 8

Photoconductive Properties of Mixtures of Phosphor No. 2225 and Harshaw CdS Prepared by Standard Technique.

Plate No.	Percent No. 2225	Percent CdS	C_{IR}	D_{IR}	C_D	D_D	C_L	D_L	i_{IR}	i_D	i_L	$\frac{i_L}{i_D}$
371	99.9	0.1	490	0.034	450	0.023	748	0.034	0.6	0.2	10	50
372	99.8	0.2	397	0.039	348	0.029	600	0.039	0.6	0.2	5	25
365	95.0	5.0	400	0.039	361	0.027	594	0.043	0.4	0.2	6	30
360	85.0	15.0	345	0.073	291	0.053	520	0.079	0.4	0.2	3	15
363	80.0	20.0	303	0.059	274	0.044	440	0.082	unstable			--
318	75.0	25.0	730	0.052	680	0.038	930	0.075	10.0	1.0	480	480
325	75.0	25.0	491	0.068	451	0.052	601	0.086	41.0	0.8	520	650
354	65.0	35.0	610	0.065	578	0.050	715	0.098	100.0	6	1200	200
356	65.0	35.0	512	0.067	481	0.053	603	0.101	70.0	2.2	680	310
321	50.0	50.0	940	0.089	882	0.062	1102	0.153	1800	100	10,600	106
322	25.0	75.0	918	0.088	870	0.055	1065	0.198	8200	540	94000	170

(see end of Table 7 for symbols.)

TABLE 9

Effect of Variation of Light Intensity on Pulse Current and Rise Time

Phosphor No. 2225 Plate No. 83

Light Intensity Foot-Candles	Pulse Current x 10^{-9} 5 sec-^{11}		Rise Time sec-^{11}	
	N	R	N	R
80	10.0	18.0	24	20
150	10.0	24.0	25	30
230	18.0	30.0	40	24
340	20.0	50.0	40	24
460	21.0	52.0	40	60
580	25.0	57.0	40	60
700	26.0	60.0	30	60

NOTE: Less than 20% of the photoconductive area is illuminated so that foot-candle values are entirely relative.

TABLE 10

Pulse Current and Rise Time For All Phosphors

Phosphor	Pulse Current × 10^{-9} 250 sec^{-1} N	R	5 sec^{-1} N	R	Rise Time sec^{-1} N	R
1304	9	19	30	30	40	24
2225	9	102	30	102	15	34
1504	4	42	3	55	24	34
2330	1	25	1	7	20	13
2220	9	68	5	51	20	60
2200	1	7	23	23	30	30
1617	1	49	14	43	30	60
CE5109	0	0	0	0	0	0
1409	1	13	5	18	30	48
2210	1	2	1	6	40	22
2479	0	0	0	0	0	0
2703	0	0	0	0	0	0
LM476	0	0	0	0	0	0
2469	0	0	0	0	0	0
CE6138	0	0	0	0	0	0

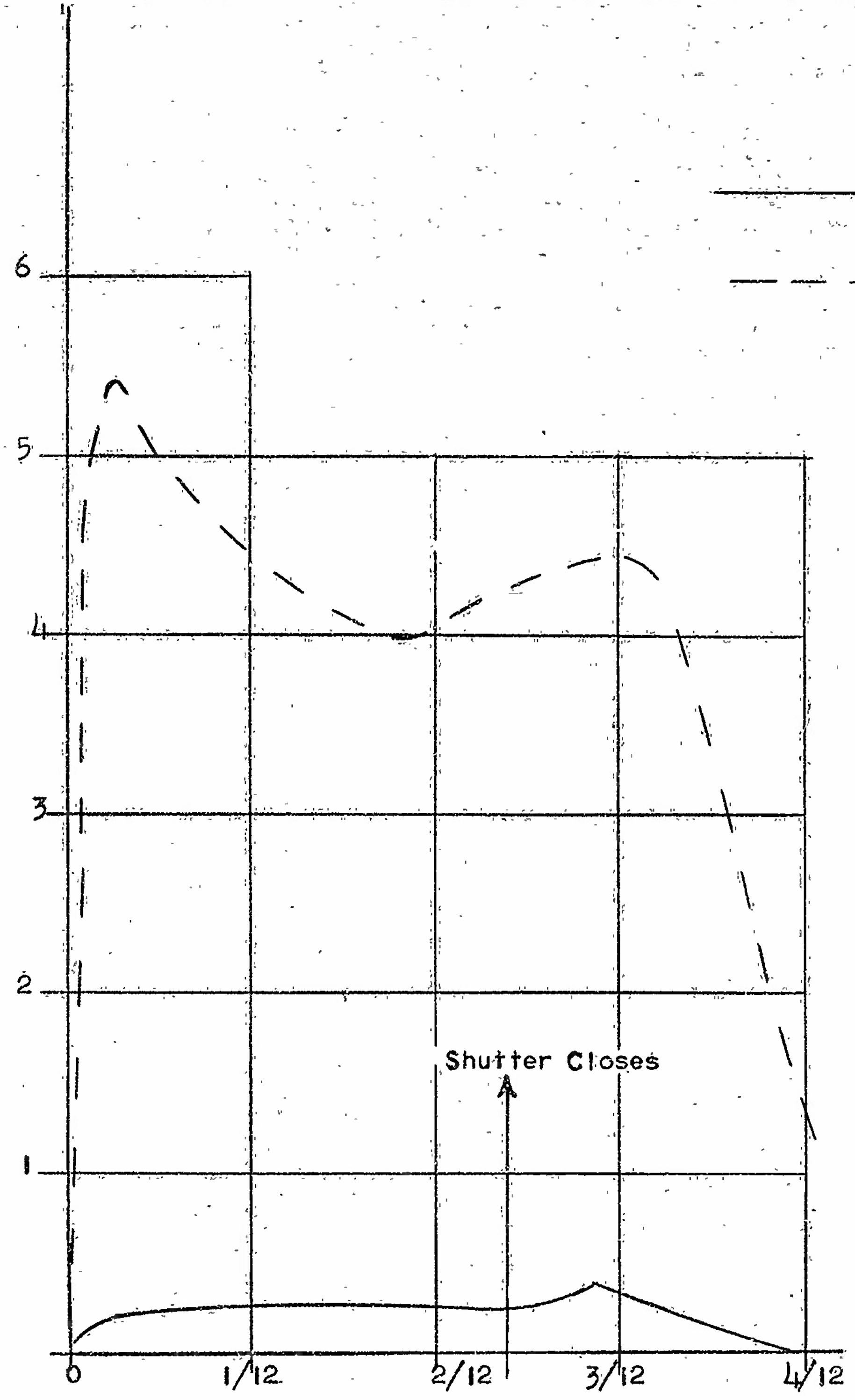
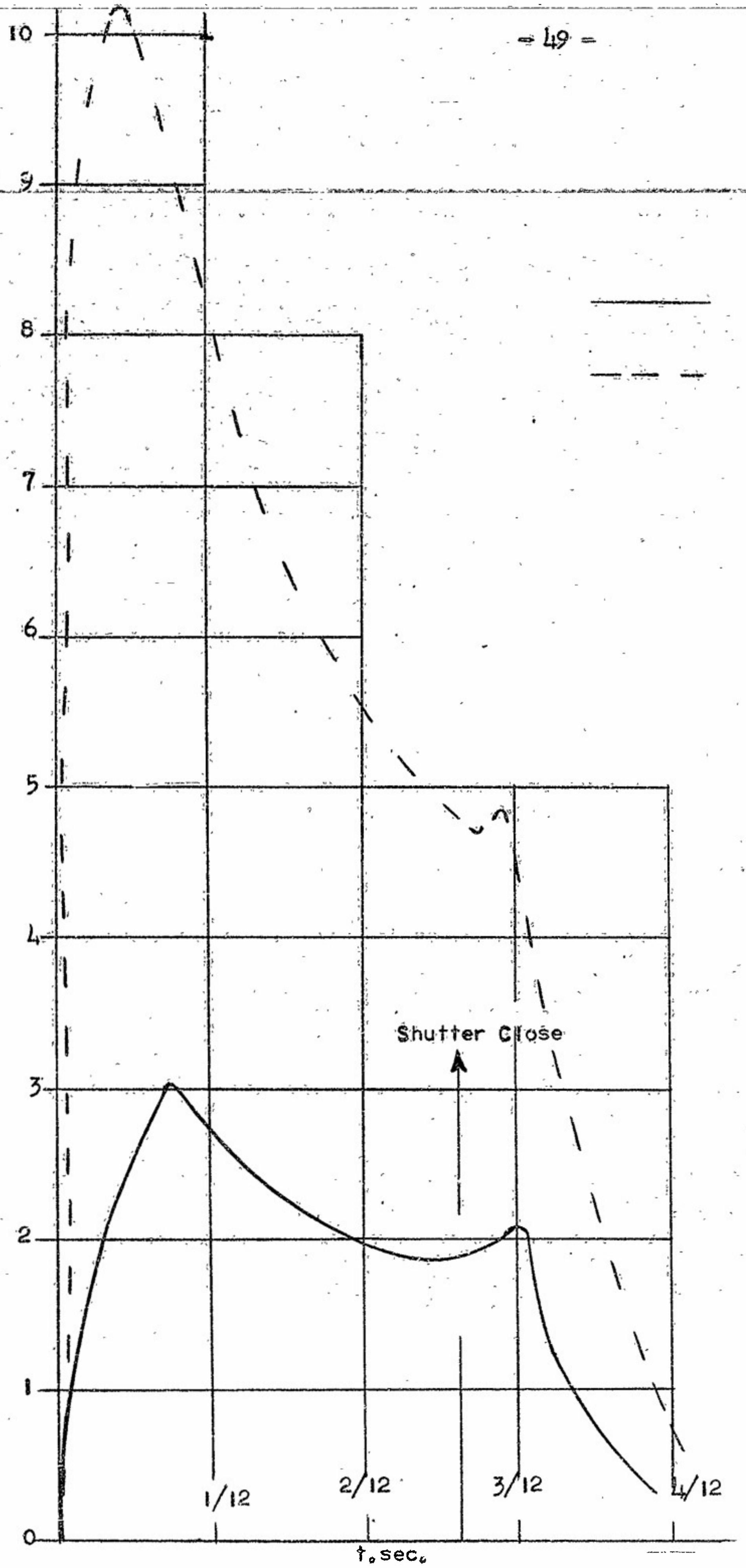


FIGURE 1

CURRENT VS. TIME
OF PHOTOCONDUCTOR
ON ILLUMINATION



Phosphor No. 2225
Plate No. 82

FIGURE 2

CURRENT VS. TIME
OF PHOTOCONDUCTOR
ON ILLUMINATION

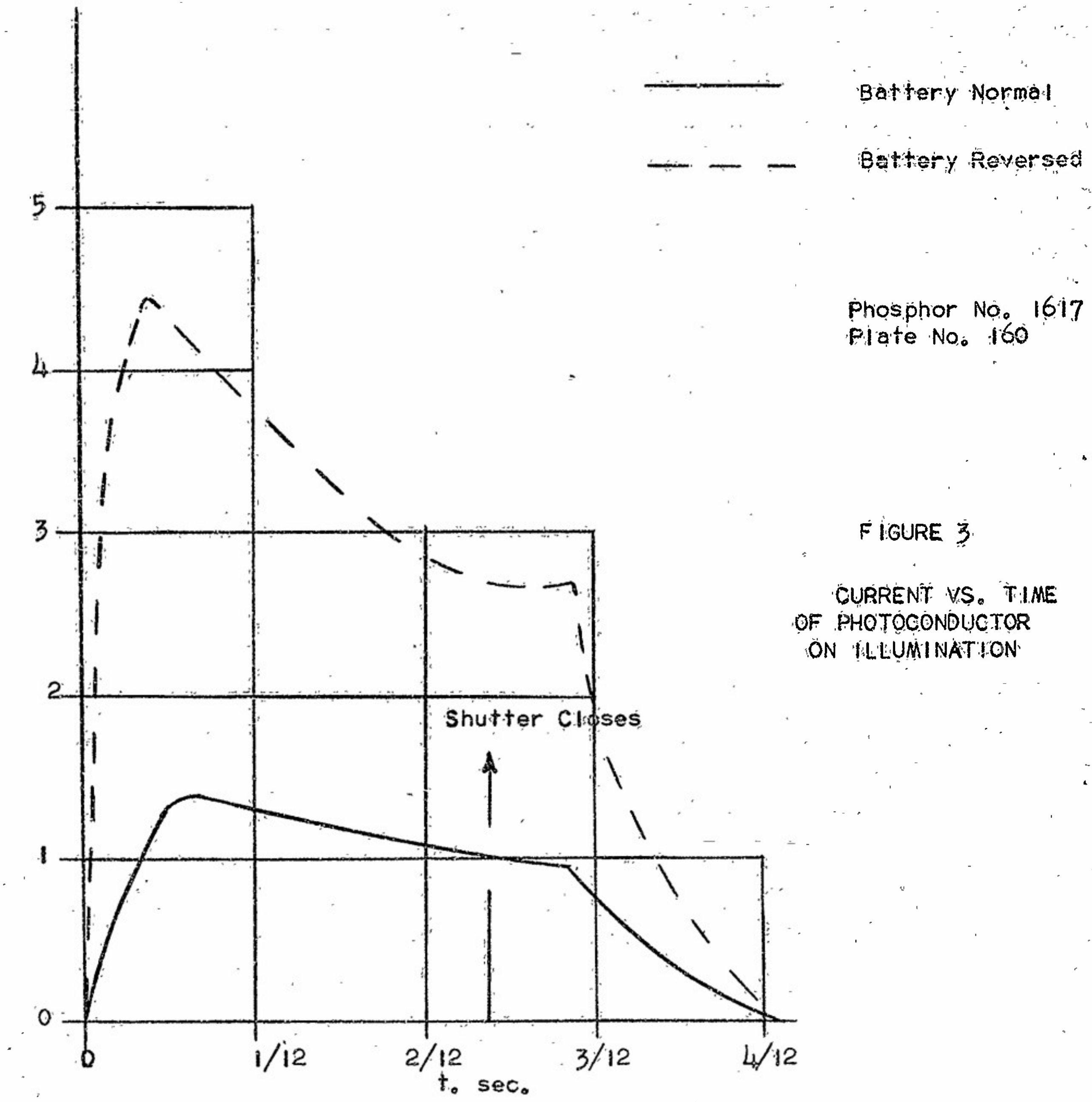


FIGURE 3

CURRENT VS. TIME
OF PHOTOCONDUCTOR
ON ILLUMINATION

FIGURE NO. 4

2225 plate 0.035"

- ° Dark Decay, time in min. $\frac{-\ 4500\ V}{0\ V}$
- × Light Decay, time in sec. $\frac{-\ 5000\ V}{+\ 675\ V}$

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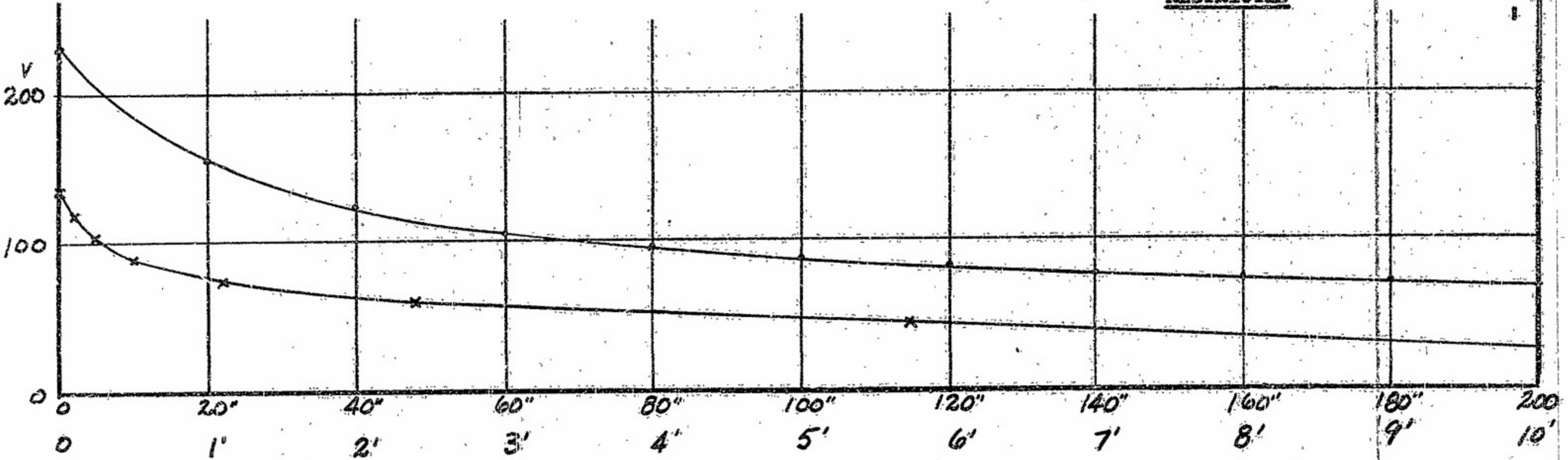

FIGURE NO. 5

2225 plate 0.001" + 7000 V
+ 480 V

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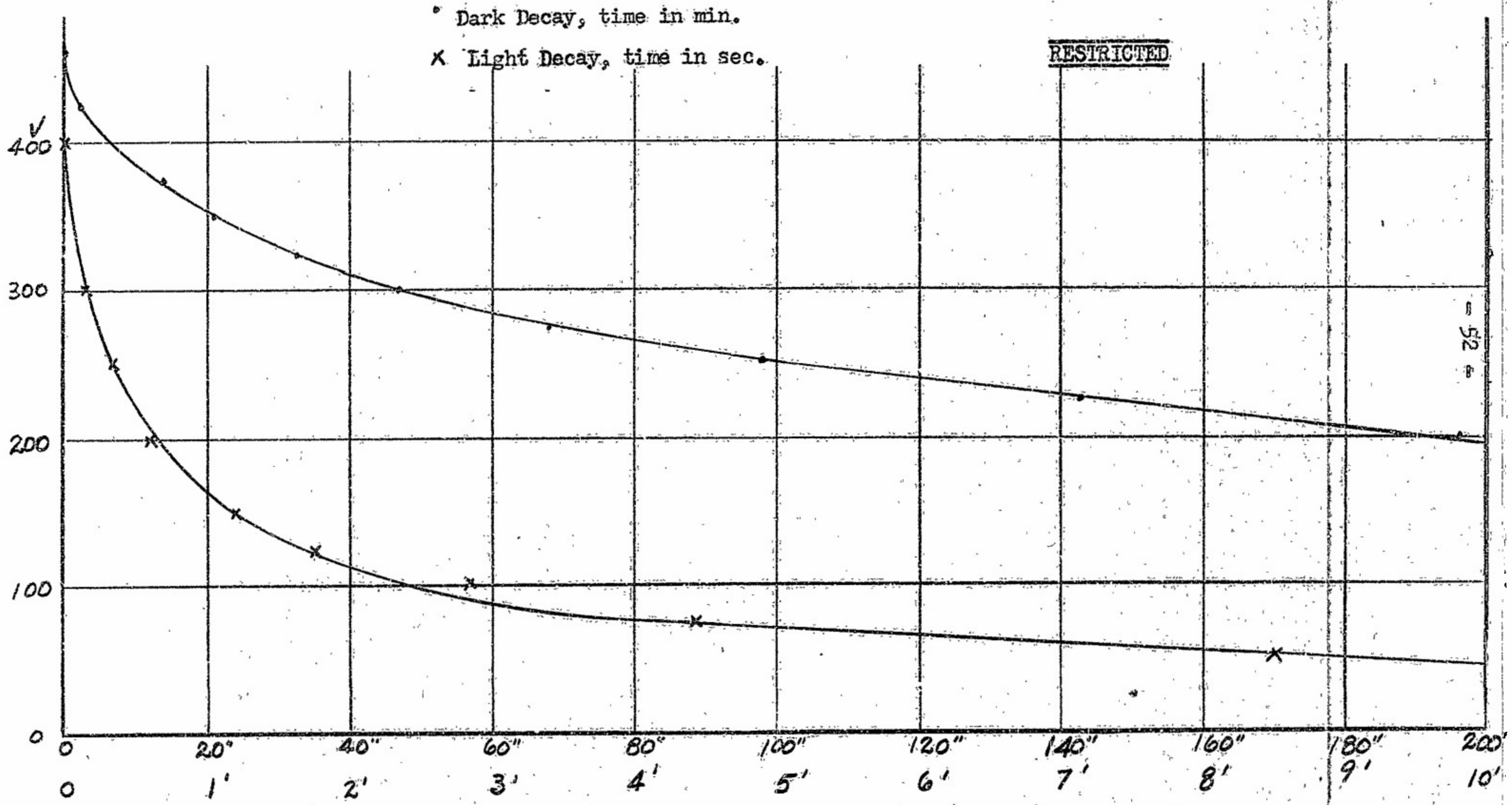

FIGURE NO. 6

2225 Plate 0.001"

• and X : Charge +, illuminate charge -

⊡ and ⊙ : Charge + during illumination, Charge -

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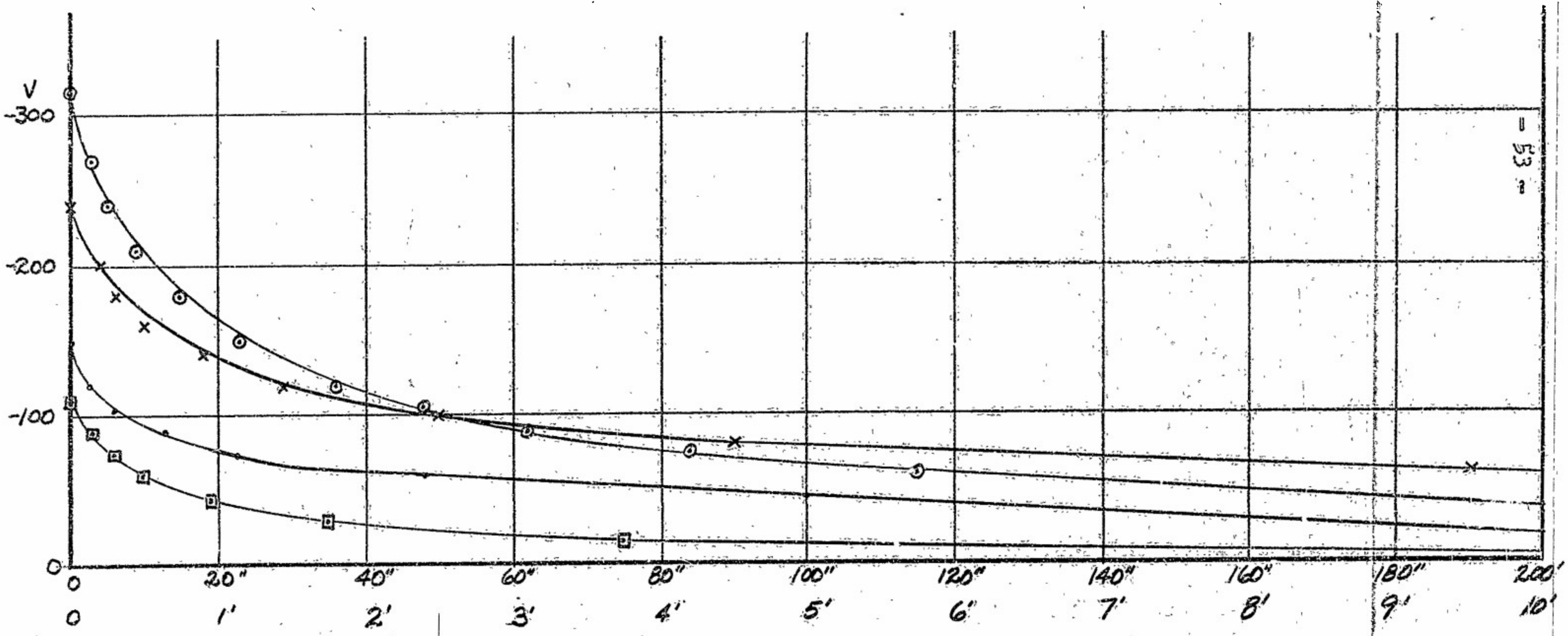

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FIGURE NO. 7

Reverse Charging

+ 5000 V
- 62.5 V } with light

- 5000 V
+ 67.5 V

• Dark Decay, 2225 plate, 0.005", time in min.

X Light Decay, 2225 plate, 0.005", time in sec.

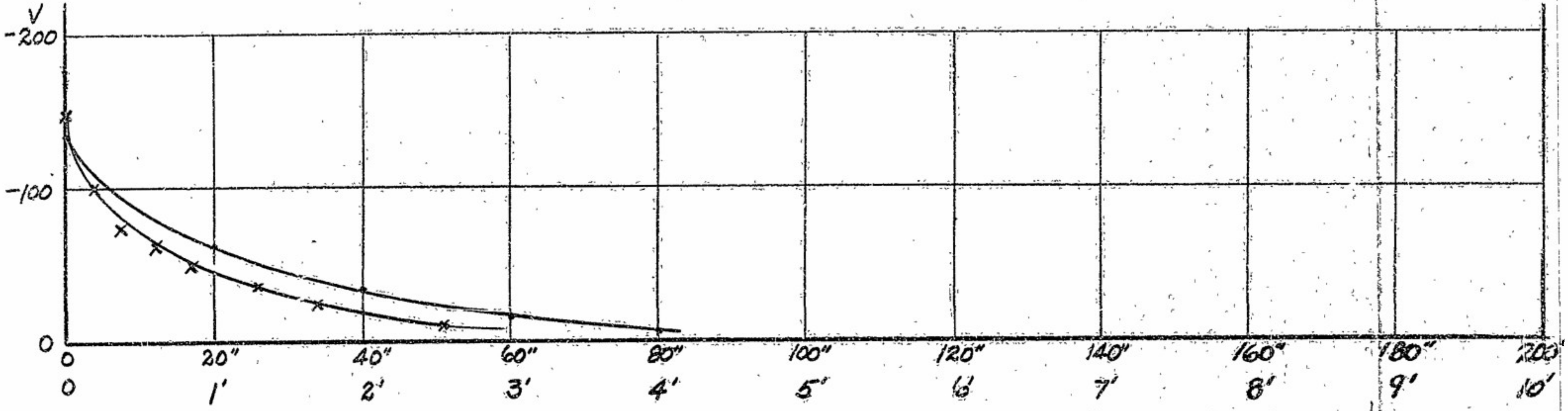

FIGURE NO. 8

Reverse Charging

+ 5000V } with light
+ 480V }

− 5000 V
− 480 V

● Dark Decay, 2225 plate, 0.0035", time in min.

X Light Decay, 2225 plate, 0.0035", time in sec.

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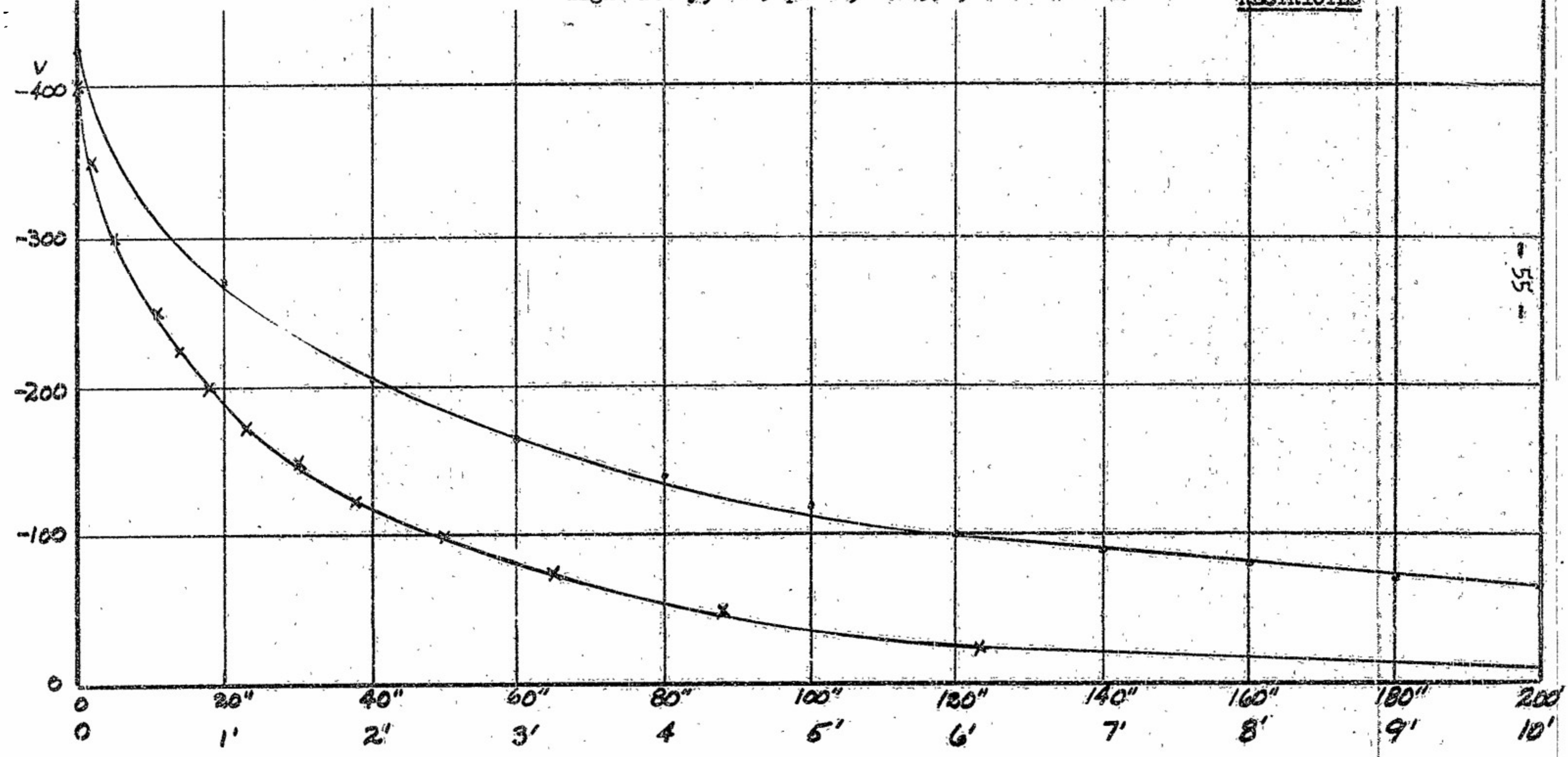

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FIGURE NO. 9

Reverse Charging

+ 5000 V} with light
+ 480 V}

- 5000 V
- 480 V

• Dark Decay, 2225 plate, 0.001, time in min.

× Light Decay, 2225 Plate, 0.001", time in sec.

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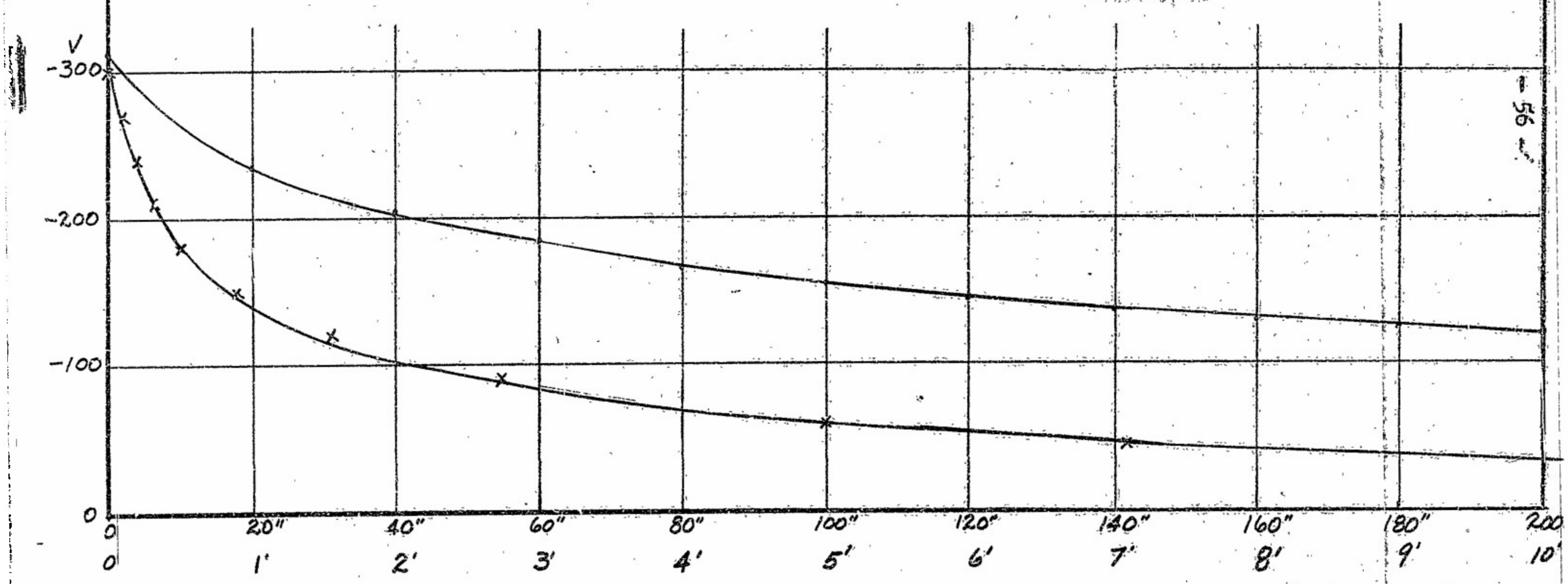

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FIGURE NO. 10

2200 Plate 0.005"　　+ 4500 V
0 V

• Dark Decay, time in min.

X Light Decay, time in sec.

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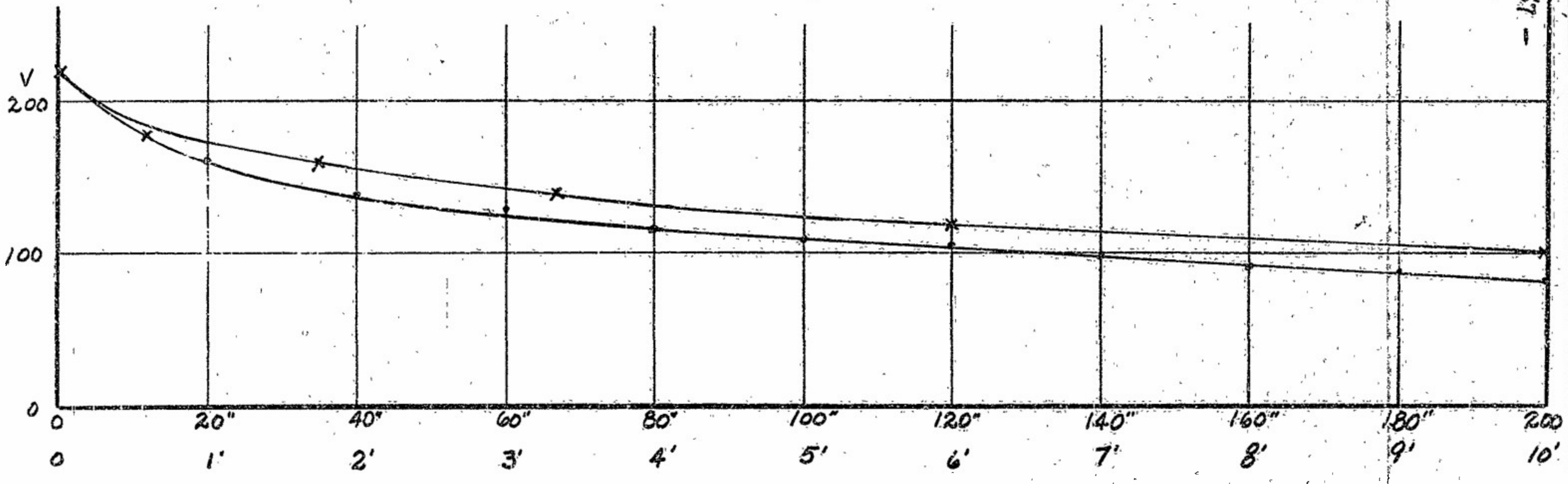

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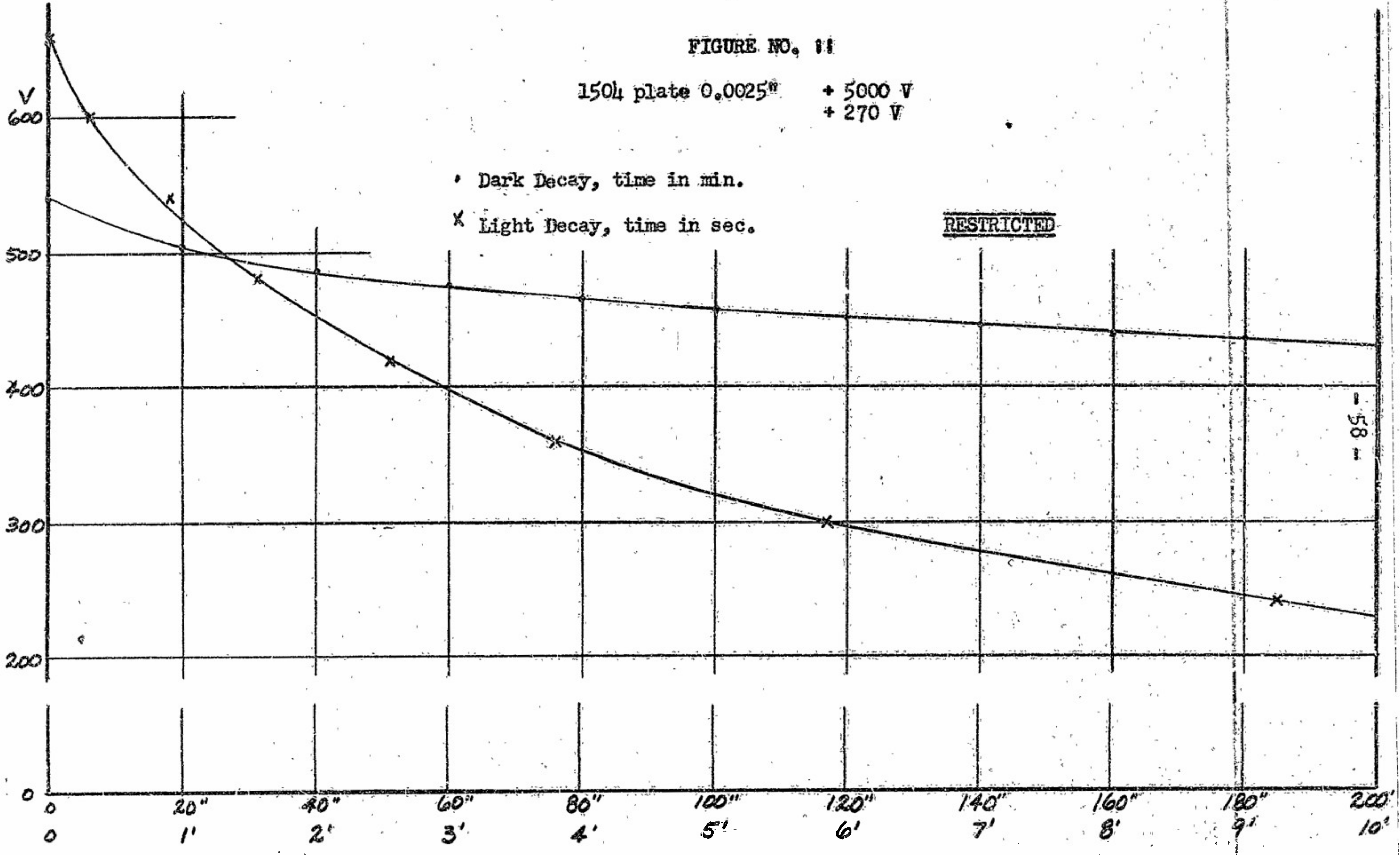

FIGURE NO. 11

1504 plate 0.0025" + 5000 V + 270 V

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FIGURE NO. 12

1504 plate 0.0025"

• Dark Decay, time in min. + 5000 V − 67.5 V

X Light Decay, time in sec. + 5000 V − 135 V

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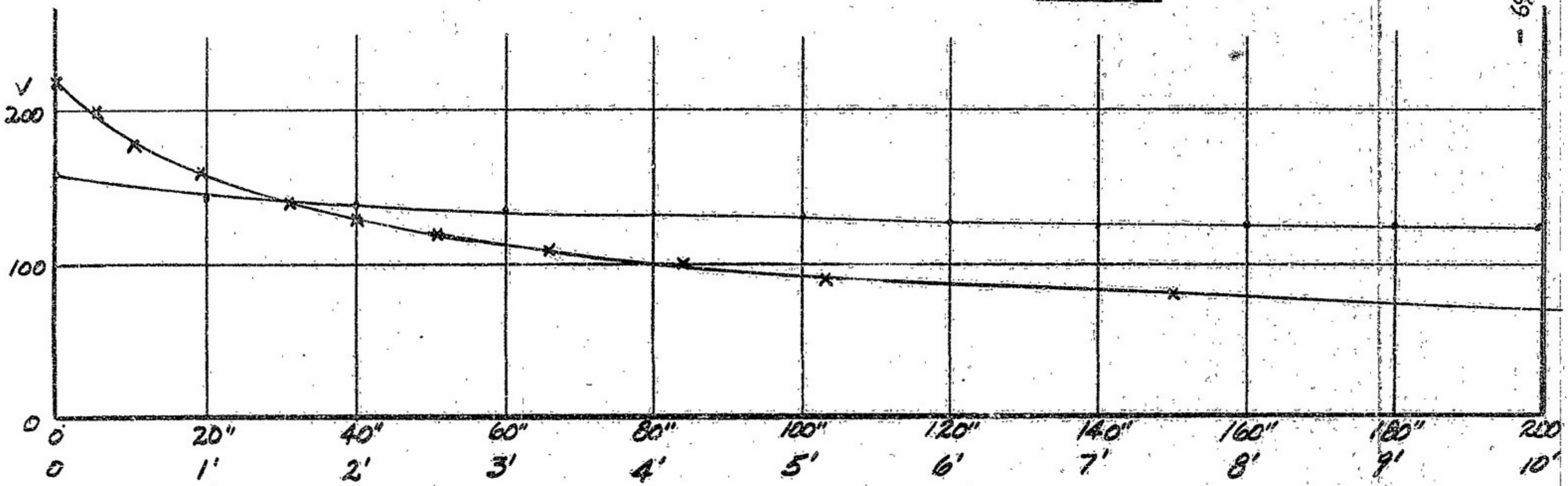

FIGURE NO. 13

1504 Plate 0.001" + 5000 V
+ 480 V

• Dark Decay, time in min.

X Light Decay, time in sec.

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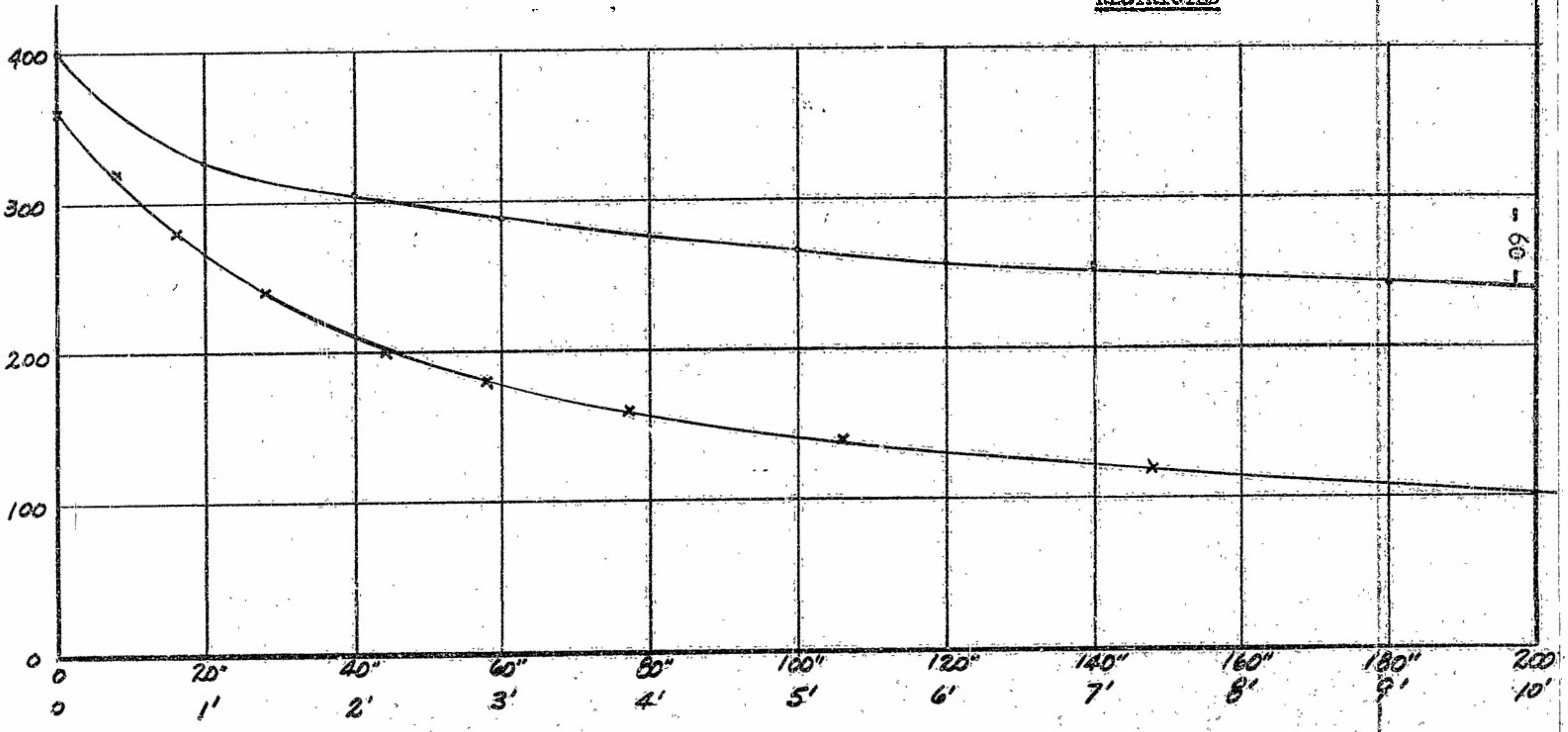

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FIGURE NO. 14

1504 plate 0.001"   + 5000 V
                              - 67.5 V

• Dark Decay, time in min.

✗ Light Decay, time in sec.

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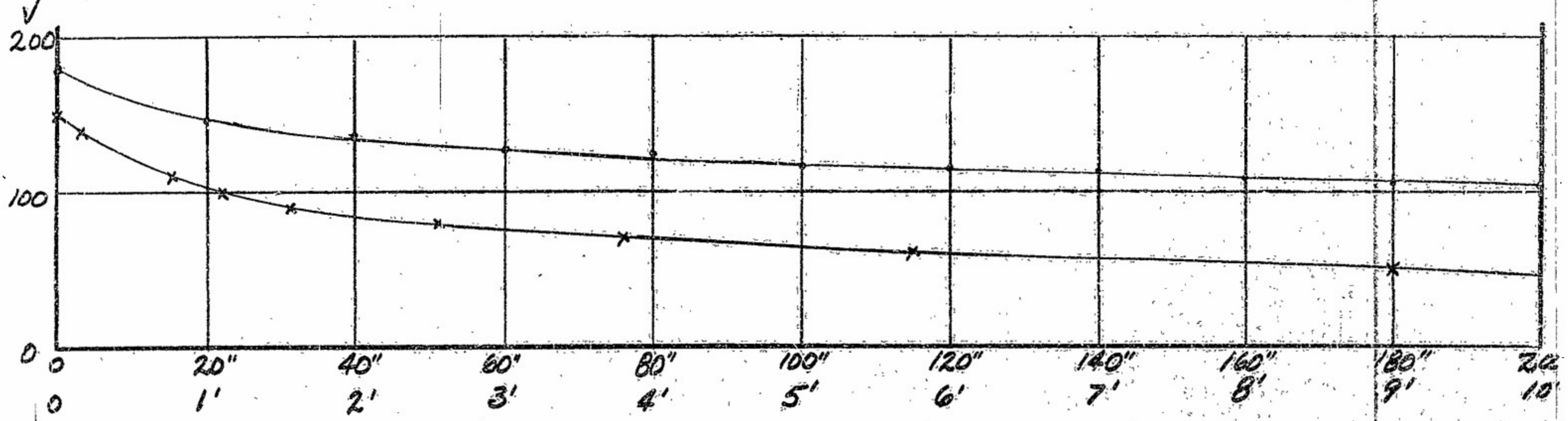

FIGURE NO. 15
Reverse Charging

+ 5000 V } with Light
− 480 V

− 5000 V
− 480 V

• Dark Decay, 1504 plate, 0.0025", time in min.
× Light Decay, 1504 plate, 0.0025", time in sec.

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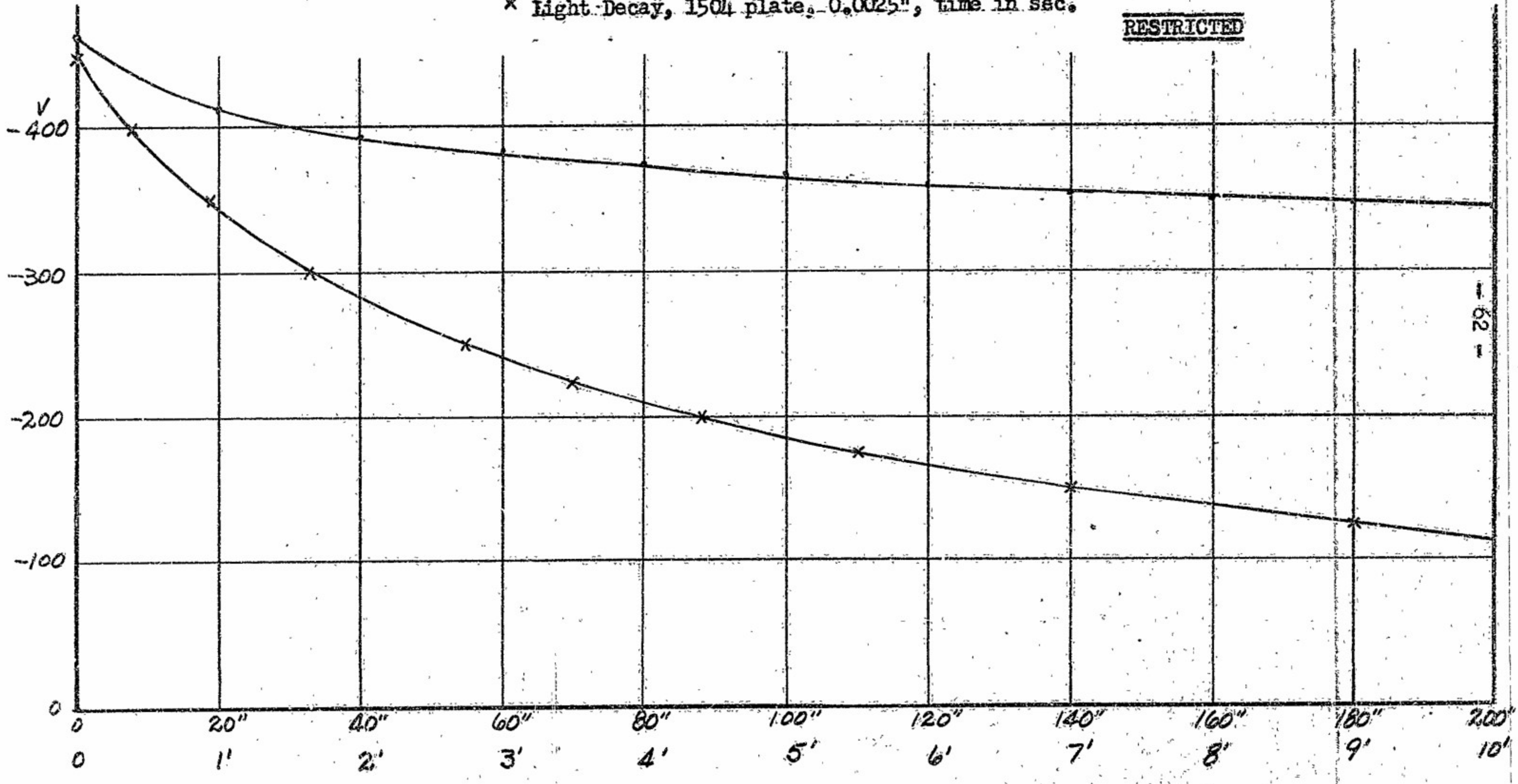

FIGURE NO. 16

Reverse Charging

+ 5000 V } with light
+ 480 V

- 5000 V
- 480 V

• Dark Decay, 1504 plate, 0.001", time in min.

X Light Decay, 1504 plate, 0.001", time in sec.

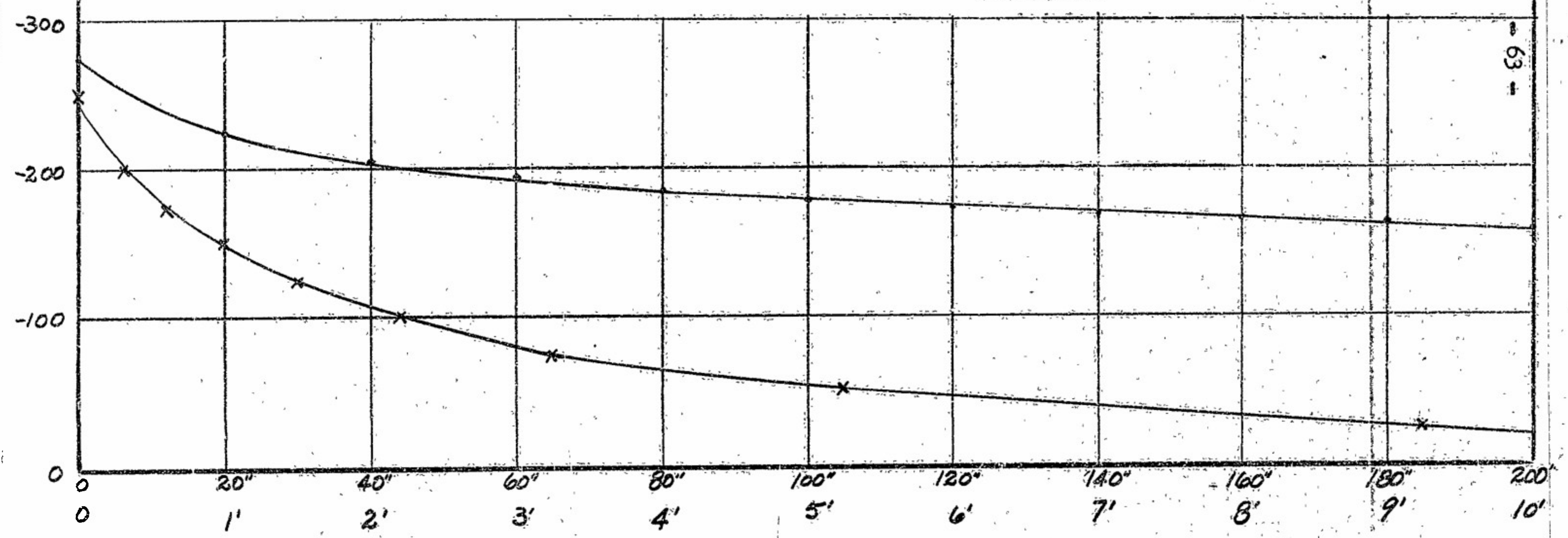

FIGURE NO. 17

No. 369 Slide: 0.1% CdS, 99.9% 2225, -5000 V
- 480 V

- • Dark Decay, time in min.
- x Light Decay, time in sec.
- ▣ Dark Decay, reverse charging, time in min.
- ⊙ Light Decay, reverse charging, time in sec.

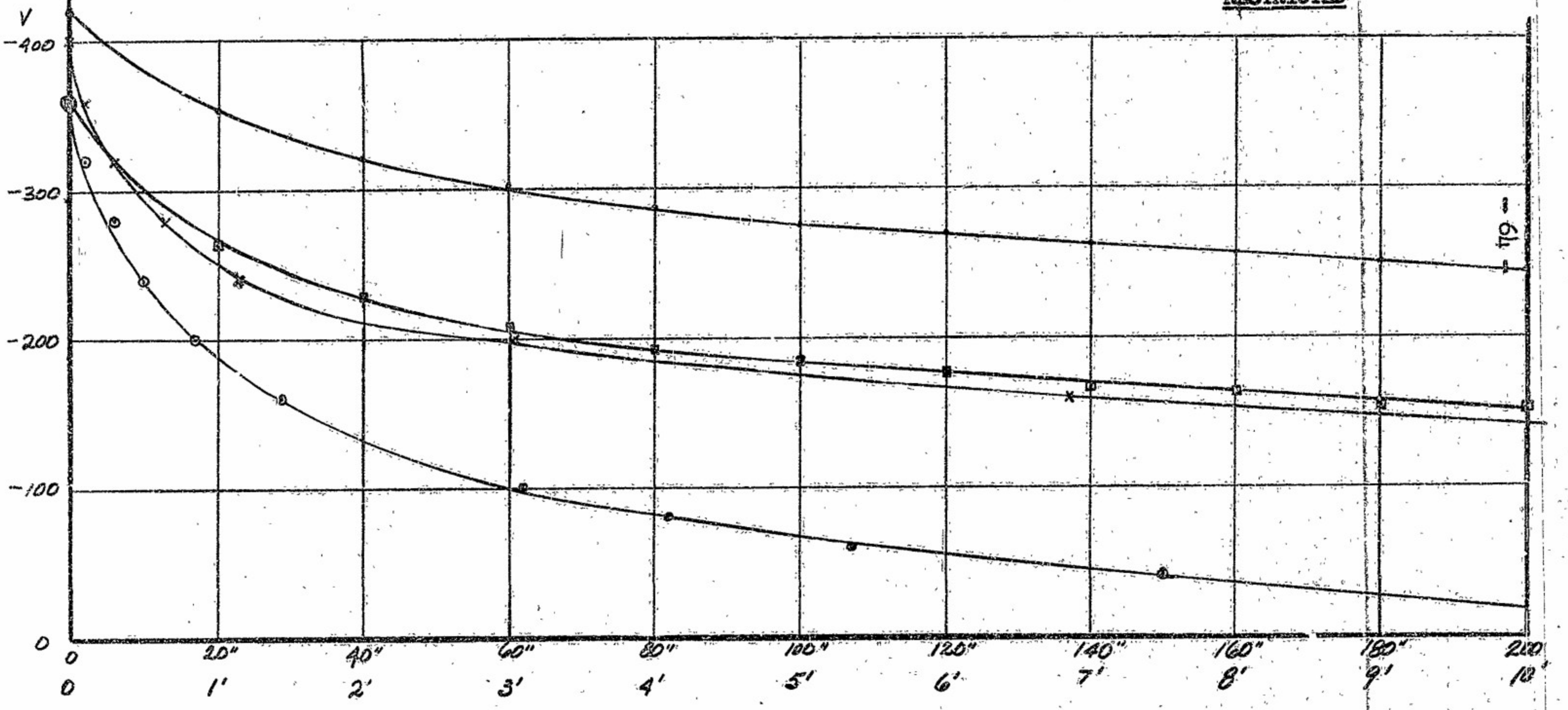

FIGURE NO. 18

No. 368 Slide: 0.2% CdS, 99.8% 2225, - 5000 V
- 480 V

- • Dark Decay, time in min.
- × Light Decay, time in sec.
- ▣ Dark Decay, reverse charging, time in min.
- ⊙ Light Decay, reverse charging, time in sec.

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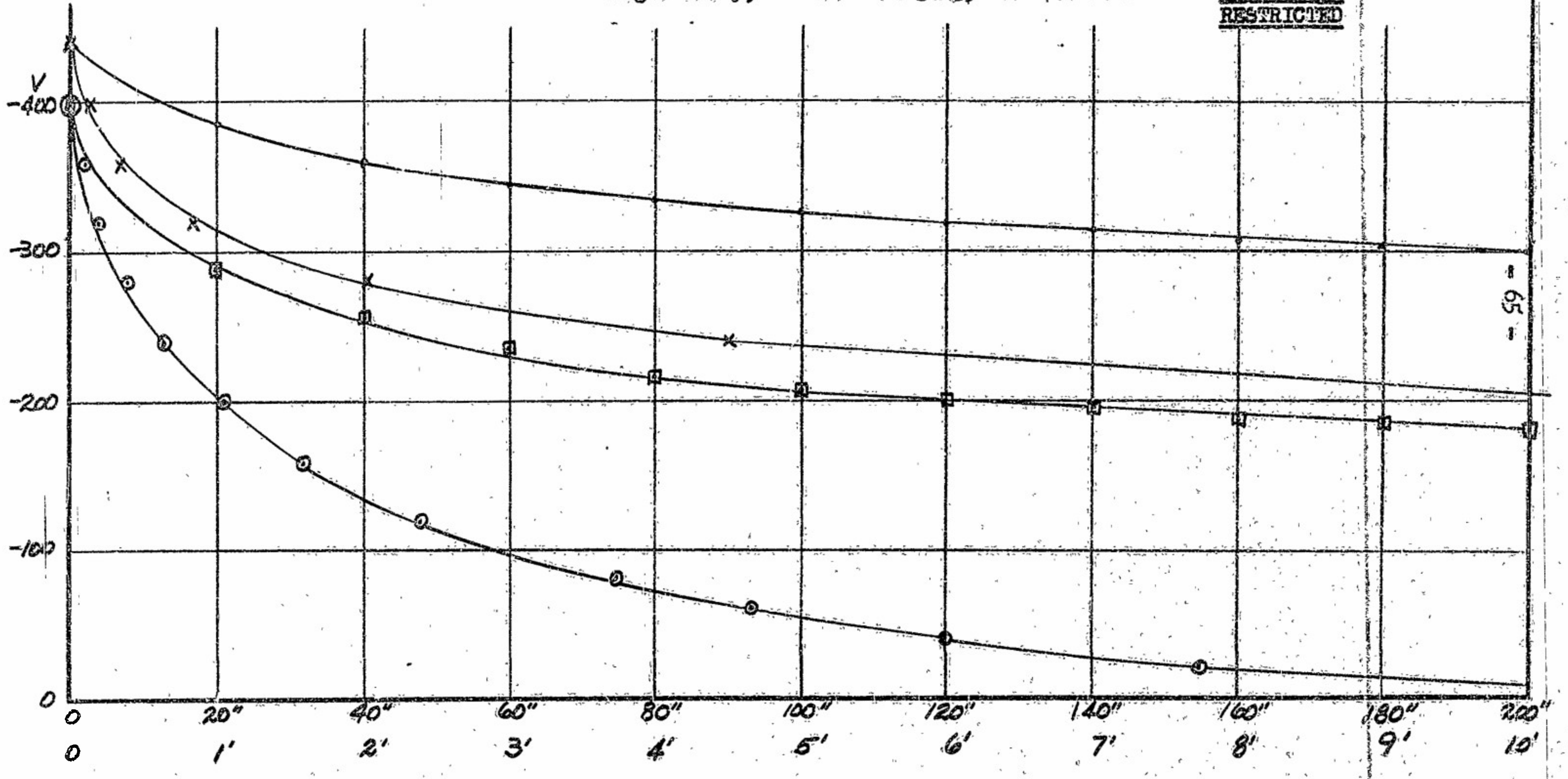

FIGURE NO. 19

No. 367 Slide: 5% CdS, 95% 2225, -5000 V
- 480 V

- · Dark Decay, time in min.
- × Light Decay, time in sec.
- ⊡ Dark Decay, reverse charging, time in min.
- ⊙ Light Decay, reverse charging, time in sec.

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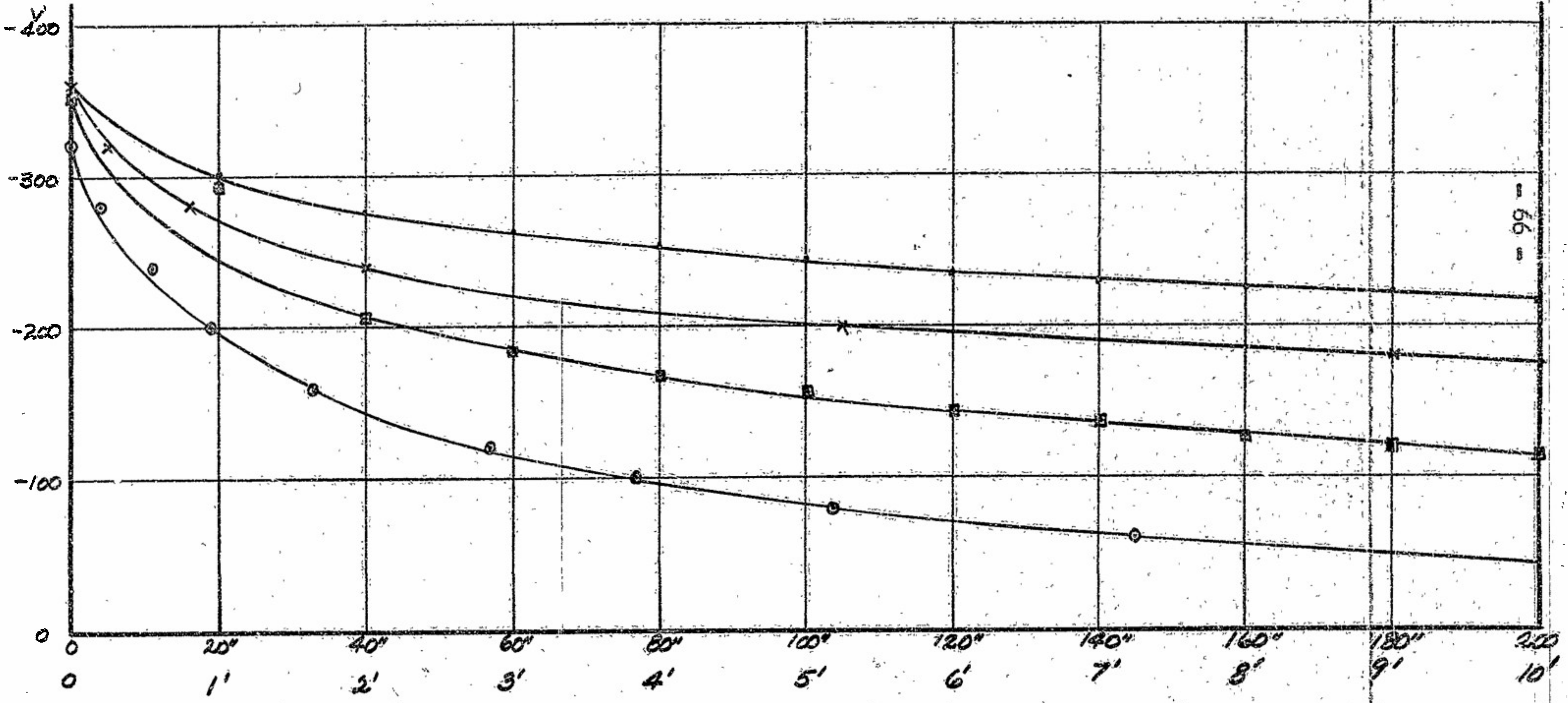

FIGURE NO. 20

No. 366 Slide: 9% CdS, 91% 2225, -5000 V
- 480 V

- · Dark Decay, time in min.
- × Light Decay, time in sec.
- ⊡ Dark Decay, reverse charging, time in min.
- ⊙ Light Decay, reverse charging, time in sec.

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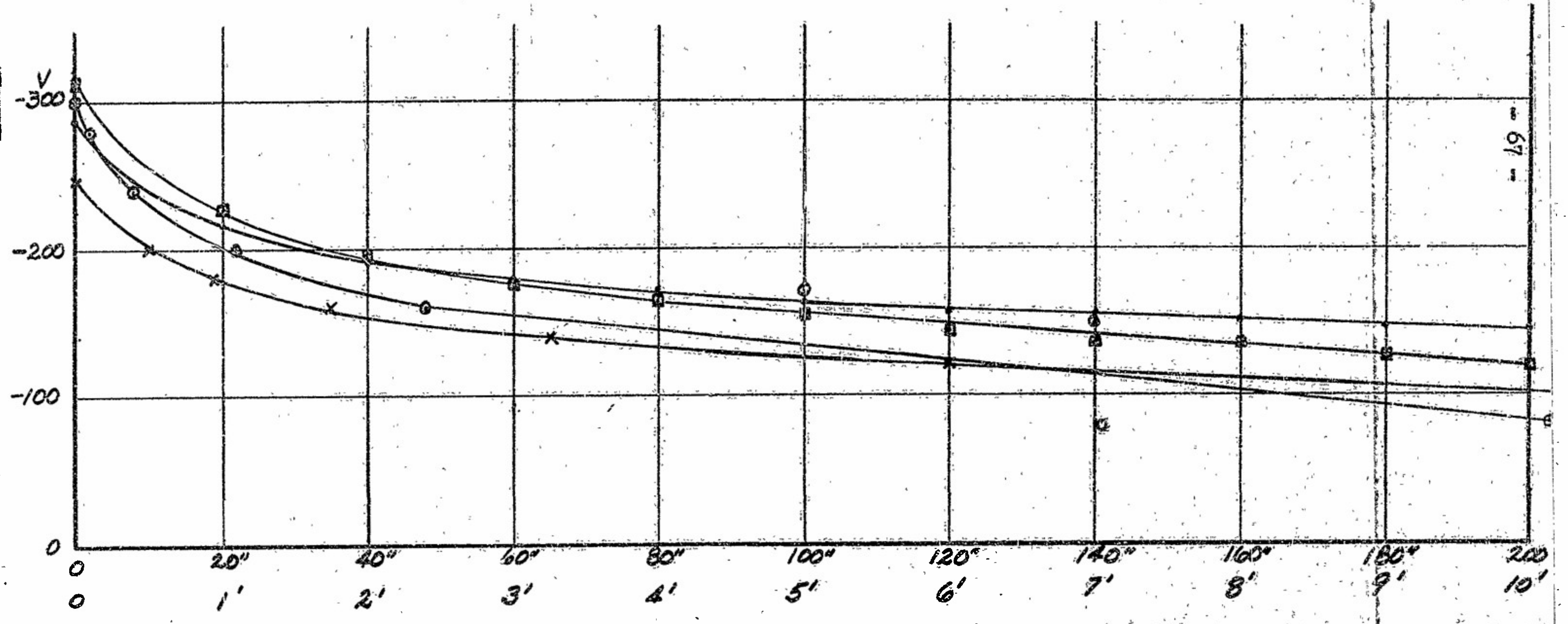

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FIGURE NO. 21

No. 362 Slide: 15% CdS, 85% 2225, -5000Ƒ
- 480V

• Dark Decay time in min.

× Light Decay time in sec.

⊡ Dark Decay reverse charging, time in min.

⊙ Light Decay reverse charging, time in sec.

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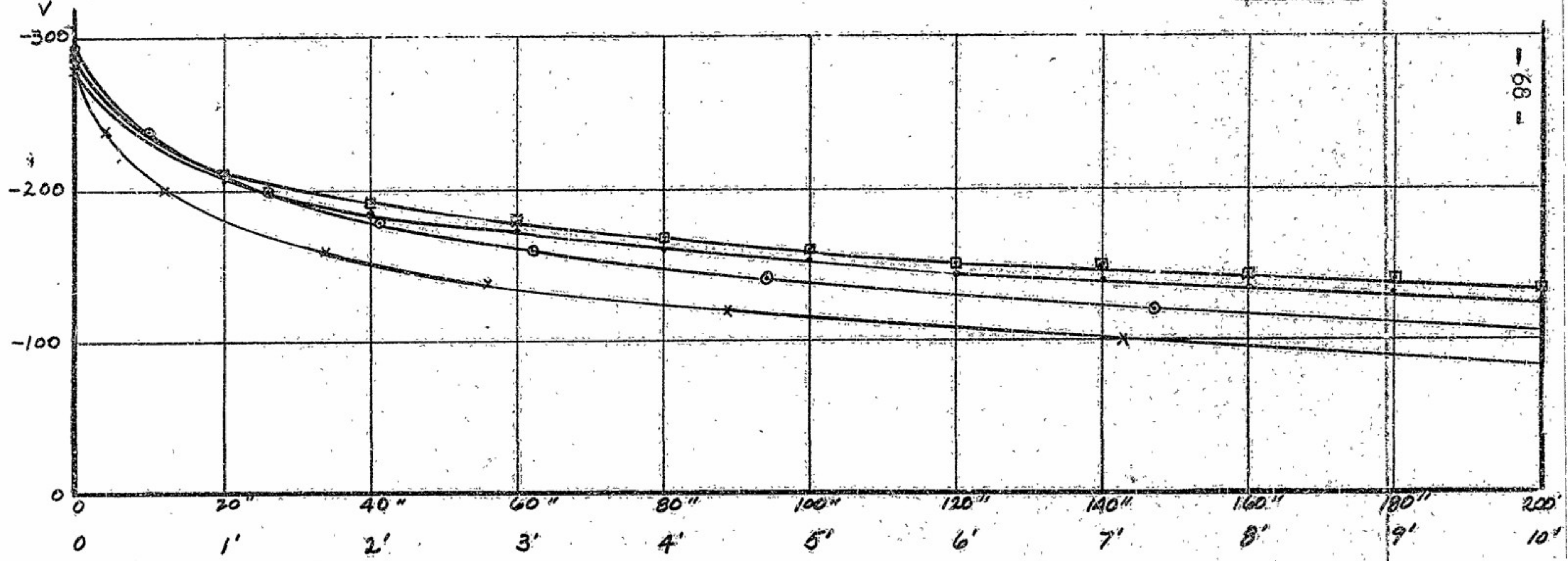
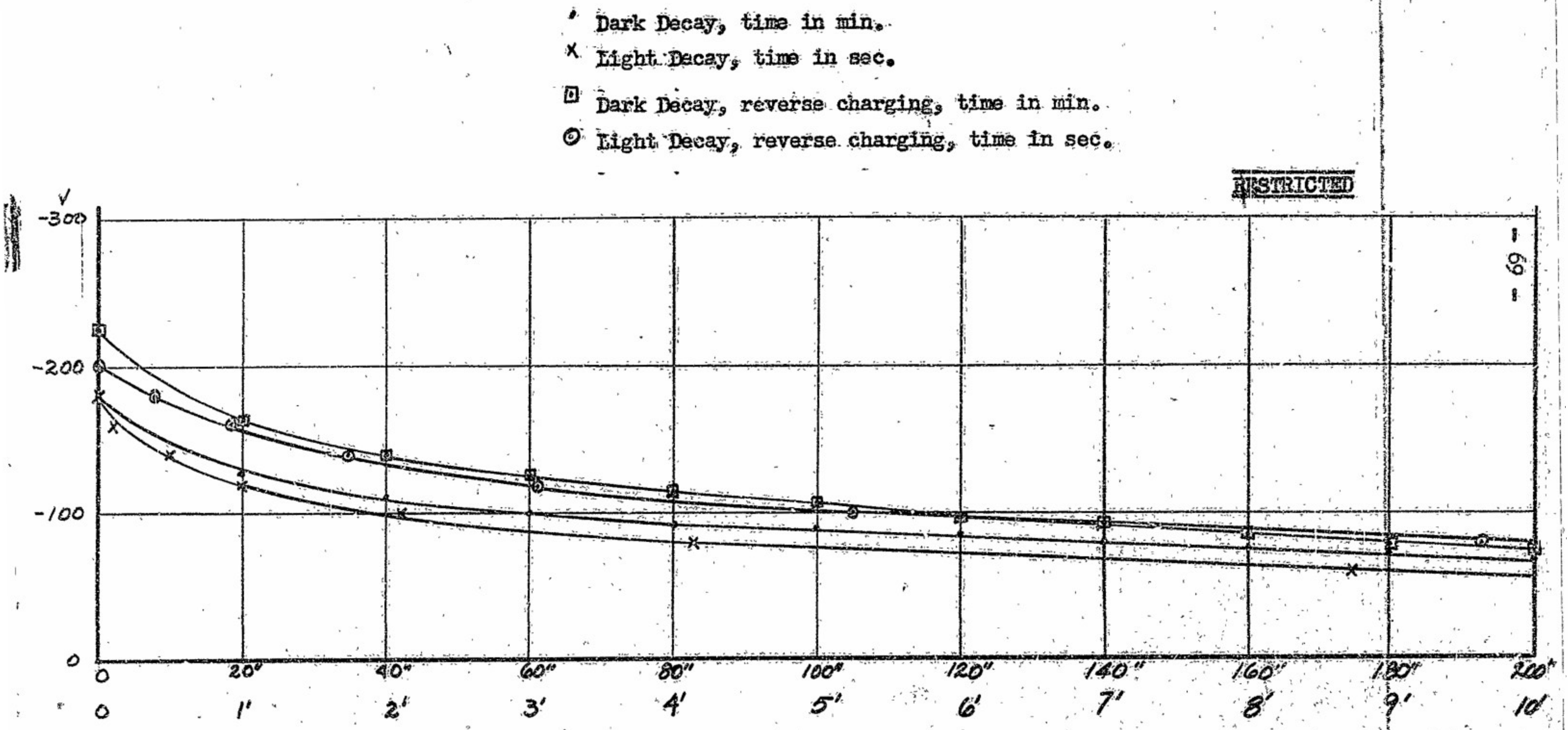


HORIZONS INCORPORATED

FIGURE NO. 22

No. 359 Slides: 20% CdS, 80% 2225, -5000 V
- 480 V



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TENTATIVE EVALUATION OF THE FACTORS AFFECTING THE ELECTROGRAPHIC PROCESS

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PREFACE

A tentative evaluation of the factors affecting the electrographic process is visualized as composed of three major steps. The first step may be a phenomenological model of the process, based merely on models using the results of experimental measruements, and attempting to correlate them with the electrographic process. The second step could be an attempt to look into the process from a microscopic viewpoint, this would form the basis of a solid state model.

The third step would then consist of an attempt to predict, on the basis of the solid state theory, the materials and processes to be experimented with. The following notes are a first attempt to lay down the foundations for the first two steps, primarily in connection with the exposure process. They are divided into:

- I. Phenomenological models
  - A. Introduction
  - B. Simplified equivalent circuit
  - C. Rise and decay of equivalent conductivity and dielectric constant of phosphors.
- II. Solid state models

I. Phenomenological Models

A. Introduction

Among the three major steps of an electrographic process, "preparation", "exposure," and "development," the second, exposure, appears to be the most significant, and will be the first to be considered. However, the development will be now briefly analyzed in connection with exposure.

An exposed plate carries on its surface a certain distribution of charges and potentials with respect to its back electrode. It will be the aim of the study of exposure to determine the nature of the distribution of charges. The question now is what determines the efficiency of development. Consider the plate under development (Fig. 1.) The phosphor is still undergoing a decay process so that its resistivity ρ_1 and dielectric constant ϵ_1, will not be the same as their initial values, ρ_0 and ϵ_0 before exposure.

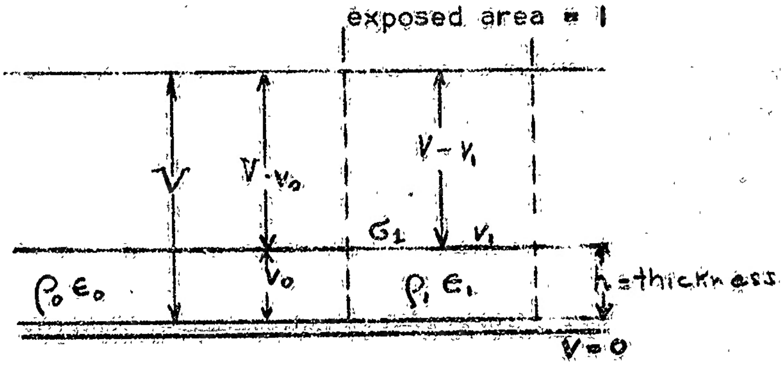

FIG: 1

The resistivities ρ_0 and ρ_1 are very high, so that they may be considered as infinite during the time of development. For the standard development process, one may now ask whether the voltage V_1 or the charge density σ_1 or what else is the determining factor for image resolution. The potential V_1 and the density σ_1 are <u>not</u>, in the general case, proportional to each other, since:

$$\sigma_1 = v_1 \epsilon_1 / t_2$$

EQUATION (1)

The simplest way out would be to reason that the charged particles will continue to deposit on the surface until all the surface charges are neutralized, so that the determining factor should be the charge density σ_1. However, there is reason to believe that the resolving power is determined by the different rates of powder deposition on the differently exposed regions on the surface of the phosphors, so that the resolution between two differently exposed points increases, during development, until the rates of powder fall become equal.

This criterion seems more satisfactory at the present time, but a complete analysis of the development will be attempted only when more insight will have been gained into the exposure process. At present it appears that the rate of powder deposition is a function of both voltage V_1 and charge density σ_1. The rate is probably mainly determined, at all times during development, by the field between plates, and hence mainly by $(V-v_1.)$ However, as time goes on and the deposited powder neutralizes the surface charges, both v_1 and σ_1, will decay, and the change of v_1 is directly affected by the decay of σ_1.

A tentative conclusion is, therefore, that both σ_1 and v_1 together with ϵ_1 have to do with the development.

The exposure process will now be considered from the viewpoint of determining σ_1 and v_1.

A phenomenological description of the exposure process may be based on two starting points. The first is based on an equivalent circuit, the second on a solid state model.

B. Simplified Equivalent Circuit Model

The exposed unit area of phosphorus may be considered equivalent to a resistance in parallel with a capacitance (Fig. 2.)

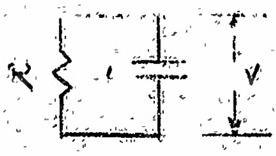

FIG. 2

If we knew independently how the resistance and the capacitance change during exposure, we could set up an equation for the voltage and the charge appearing on the surface. This is the well known equation for a condenser discharge:

$$\frac{q}{C} + R\dot{q} = 0$$

EQUATION (2)

where, in the present case, R and C are given functions of time. Of course one would have to be careful about the evaluation of R and C functions from the experimental results, in the sense that one should make sure that generalized Ohm's law applies to the quantities considered. This analysis should be the result of solid state theory applied to the phosphorus.

It is interesting, however, to develop an example of this procedure. Suppose we could approximate, for a given phosphor, the resistance and capacitance variations by means of linear diagrams (Fig. 3.)

$$R = R_o - \frac{\Delta R_o}{\Delta t_o} \qquad C = C_o + \frac{\Delta C_o}{\Delta t_o}$$ from t=o to t = t_m

$$R = Rm + \frac{\Delta R_{II}}{\Delta t_{I}} \qquad C = Cm - \frac{\Delta C_{II}}{\Delta t_{II}}$$ from t = tm to t = t_{II}

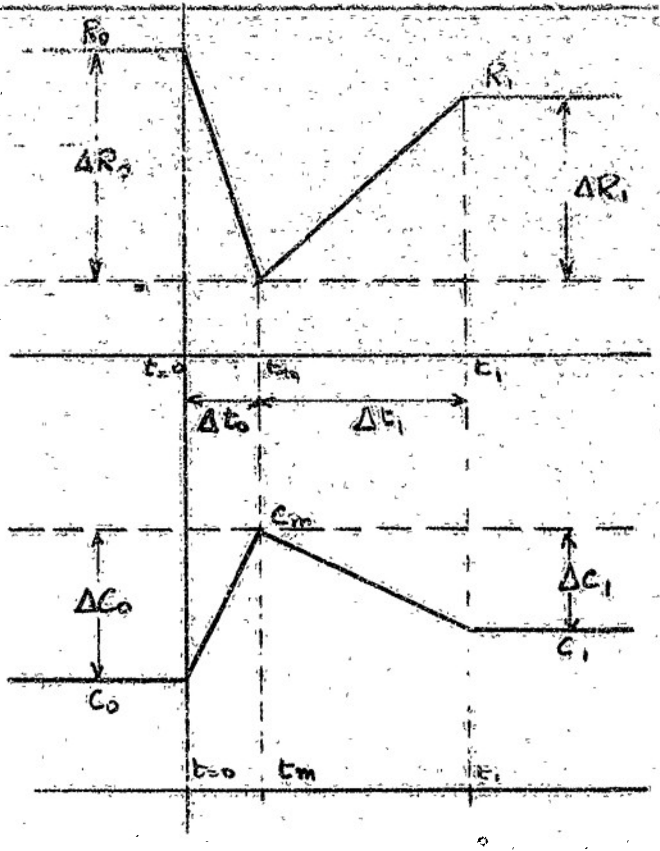

FIG. 3

Let us consider the simple case in which both resistance and capacitance are excited in the same time and decay in the same time. The laws of variation of R and C are then given together with Fig. 3. Then equation (2) yields:

$$\frac{q}{Co + \frac{\Delta Co}{\Delta t_o}} + \left(Ro - \frac{\Delta Ro}{\Delta t_o} t\right) \ddot{q} = o \qquad \text{between } t_o \text{ and } t_m$$

EQUATION 3a

$$\frac{q}{C_m - \frac{\Delta C_I}{\Delta t_I}} + \left(Rm + \frac{\Delta R_I}{\Delta t_{II}} t\right) \dot{q} = o \qquad \text{between } t_m \text{ and } t_{II}$$

EQUATION 3b

Let us solve (3a):

$$\frac{dq}{q} = -\frac{dt}{R_o\left[1-(r_o/\tau_o)t\right]\;C_o\left[1+(c_o/\tau_o)t\right]}$$

EQUATION (4)

where ($r_o = \frac{\Delta R_o}{R_o}$ = resistance variation in time τ_o

$c_o = \frac{\Delta C_o}{C_o}$ = capacitance variation in time τ_o

with the initial condition: $q = q_o$ at $t = o$

Now:

$$\frac{1}{\left(1-\frac{r_o}{\tau_o}t\right)\left(1+\frac{c_o}{\tau_o}t\right)} = \frac{A}{1-\frac{r_o}{\tau_o}t} + \frac{B}{1+\frac{c_o}{\tau_o}t}$$

where:

$$A = \frac{r_o}{c_o+r_o} \qquad B = \frac{c_o}{c_o+r_o}$$

Integrating (4):

$$\ln\frac{q}{q_o} = -\frac{\tau_o}{R_oC_o\,(c_o+r_o)}\,\ln\frac{1+\frac{c_o}{\tau_o}t}{1-\frac{r_o}{\tau_o}t}$$

$$\frac{q}{q_o} = \left(\frac{1+\frac{c_o}{\tau_o}t}{1-\frac{r_o}{\tau_o}t}\right)^{-\frac{\tau_o}{R_oC_o(c_o+r_o)}}$$

At $t = t_m = \Delta t_0 = \tau_0$

$$\frac{q_m}{q_o} = \left(\frac{1 + C_o}{1 - r_o}\right)^{-\frac{\tau_o}{R_o C_o (C_o + r_o)}}$$

EQUATION (5)

The corresponding voltage v_m will be:

$$v_m = \frac{q_m}{C_m} = \frac{q_o}{C_o (1 + c_o)} \left(\frac{1 + c_o}{1 - r_o}\right)^{-\frac{\tau_o}{R_o C_o (C_o + r_o)}}$$

EQUATION (6)

and since $V_o = \frac{q_o}{c_o}$

$$\frac{V_m}{V_o} = \frac{1}{1 + c_o} \left(\frac{1 + c_o}{1 - r_o}\right)^{-\frac{\tau_o}{R_o C_o (c_o + r_o)}}$$

EQUATION (7)

or:

$$\log \frac{V_m}{V_o} = \log \frac{q_m}{q_o} = \log (1 + c_o)$$

EQUATION (8)

Both charge and voltage decay, since all the right hand terms are negative.

$\tau_R = R_o C_o$, the time constant of the phosphor in the dark, must be as long as possible so that the phosphor charge will not decay substantially in the time interval between polarization and exposure. In any case τ_R is much greater than τ_o, and $(c_o + r_o)$ is a number greater than 1. It is therefore interesting to note that the voltage variation during the first time interval τ_o is greater than the charge variation, and that the variation in the voltage is almost exclusively due to the build up of dielectric constant (or capacitance) - From $(t = t_m)$ to $(t = t_1)$ the solution may be obtained by substitution of the symbols for R and C, since the equation is the same. The result is:

$$\frac{q}{q_m} = \left(\frac{1 - \frac{c_1}{\tau_1} t^*}{1 + \frac{r_1}{\tau_1} t^*} \right)^{-\frac{\tau_1}{R_1 C_1 \left(c^* + r_1^* \right)}}$$ between tm and t_1

where: $r_1^* = \frac{\Delta R_1}{Rm}$; $c_1^* = \frac{\Delta c_1}{Cm}$; $\tau_1 = \Delta t_{11}$ = decay time, and

$t^* = (t - tm)$ is the time being counted from tm, since q must be equal to q_m at $t = tm$ ($t^* = 0$.) It is now more convenient to use the fractions:

$r_1^* = \frac{\Delta R_1}{R_1}$; $c^* = \frac{\Delta c_1}{c_1}$, since then $r_1 = ro$ and $c_1 = co$ in the case of phosphors returning completely to their original conditions ($R_1 = Ro$; $C_1 = Co$.) We have:

$$r_1^* = \frac{\Delta R_1}{R_1} \frac{R_1}{R_m} = r_1 \frac{R_1}{R_1 - \Delta R_1} = \frac{r_1}{1 - r_1}$$

$$c_1^* = \frac{\Delta C_1}{C_1} \frac{C_1}{C_m} = \frac{c_1}{1 + c_1}$$

Hence:

$$\frac{q}{q_m} = \left(\frac{1 - \frac{c_1}{1+c_1} \frac{t^*}{\tau_1}}{1 + \frac{r_1}{1-r_1} \frac{t^*}{\tau_1}} \right)^{-\frac{\tau_1}{R_1 C_1 \left(\frac{r_1}{1-r_1} + \frac{c_1}{1+c_1} \right)}}$$

EQUATION (9)

$$v_1 = \frac{q_m}{c_m \left(1 - \frac{c_1}{1+c_1} \right)} \left(\frac{1 - \frac{c_1}{1+c_1}}{1 + \frac{r_1}{1-r_1}} \right)^{-\frac{\tau_1}{R_1 C_1 \left(\frac{r_1}{1-r_1} + \frac{c_1}{1+c_1} \right)}}$$

EQUATION (10)

and on log scale, at $t = t_1$:

$$\ln \frac{q_1}{q_m} = \frac{-\tau_1}{R_1 C_1 \left(\frac{r_1}{1-r_1} + \frac{c_1}{1+c_1} \right)} \ln \frac{1 + \frac{r_1}{1-r_1}}{1 - \frac{c_1}{1+c_1}}$$

EQUATION (11)

$$\ln \frac{v_1}{v_m} = \ln \frac{q_1}{q_m} + \ln \frac{1}{1 - \frac{c_1}{1+c_1}}$$

EQUATION (12)

Therefore, both charge and voltage increase again, the latter more than the former. Here again τ_1 is the decay time of the phosphor in this idealized case, and $R_1C_1 = \tau_R$ is the time constant in the dark after exposure.

Let us consider finally the overall charge and voltage variation:

$$\ln \frac{q_1}{q_0} = \ln \frac{q_m}{q_0} + \ln \frac{q_1}{q_m} = -\left[\frac{\tau_0}{\tau_R (r_0 + c_0)} \ln \frac{1+c_0}{1-r_0} - \frac{\tau_1}{\tau_R \left(\frac{r_1}{1-r_1} + \frac{c_1}{1+c_1} \right)} \ln \frac{1 + \frac{r_1}{1-r_1}}{1 - \frac{c_1}{1+c_1}} \right]$$

EQUATION (13)

$$\ln \frac{V_1}{V_0} = \ln \frac{q_1}{q_0} + \ln \frac{1}{\left(1 - \frac{c_1}{1+c_1}\right)(1+c_0)}$$

EQUATION (14)

These formulae indicate that the charge and voltage decay during the first period τ_0 is followed by a charge (voltage) rise during the second period τ_1. The relative importance of the capacitance versus resistance variation may be best evaluated in specific cases.

It may be noticed that the relative magnitudes of the decay time τ_0 and τ_1 bear a direct effect on the overall decay and that a small relative value of τ_1 is desirable, if the first term (decay) is to be greater than the second (rise.)

However, it should be kept in mind that this is only a hypothetical model; it may be more useful then at this point to examine the possible actual decay curves for R and C.

C. Rise and Decay of Equivalent Conductivity and Dielectric Constant of Phosphors

Some of the conclusions and hypothesis on conductivity and dielectric constant of phosphors may be summarized as presented mainly by Garlick (Luminescent Materials,) Garlick and Gibson (Proc. Roy. Soc. 1947, A 188, 485.)

In the band picture of phosphors, "impurity centres," impurity atoms or ions are dispersed in the lattice, and "electron traps" are potential defects in the periodic field of the lattice. The exact nature of the traps is not known, but there is some evidence that they are associated with the neighborhood of impurity centers. The heat treatment during preparation affects the dispersal of impurity centers and also gives rise to traps. The number of effective traps is about the same as the number of luminescence centers.

The cycle of excitation is briefly as follows: electrons are excited from the uppermost filled band of the lattice into the conduction band and from this they decay either into traps with no radiative emission or back into luminescence centers with radiative emission. The trapped electrons will then be thermally excited into the conduction band again and will decay with radiative emission into the luminescence centers. These had been previously emptied since their electrons had fallen into the holes left by the excited electrons of the filled band.

However, it should be kept in mind that this is only a hypothetical model. It may be more useful then at this point to examine the possible actual decay curves for R and C.

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During this process, together with emission of radiation, the conductivity and dielectric constant of the phosphor undergo a rise and decay process, generally ending with values other than their original ones. It is important that the variations in conductivity and dielectric constant be defined strictly in connection with the method by which they have been measured. The experimental setup of Garlick and Gibson consisted of an R.F. oscillator in which the phosphor was the reasonating R, C element. The phosphor was considered as equivalent to a capacity C in parallel with a resistance R; the C variation was measured as a change in resonant frequency, and the R as the Q of the phosphor condenser. Thus the R represented the equivalent resistance and included all the losses.

Since this RC model has proved to be convenient for a quantitative treatment of the exposure process, this operative definition for R and C will be maintained in the development of a phenomenological model for exposure.

As a consequence, it may be necessary to repeat Garlick's measurements, with the polarized phosphor, as prepared for electrography. This point will be referred to later.

The dielectric changes may be due to electrons in two different conditions:

a) Conduction electrons, if they are subject to suitable constraining forces do not move in phase with the field.

b) Trapped electrons (binding energy 0.1 to 0.8 ev.) whose displacement is not in phase with the field; this phase difference would be a maximum at a frequency close to the natural vibration of the filled trap.

Garlick showed that the second contribution is the most important, the best experimental proof of it being that the decay curve of the dielectric constant is parallel to the decay curve of trapped electrons. From these assumptions it follows that the dielectric changes are expected to be affected by the following factors:

a) Number of trapped electrons (not $\geq 10^{18}$ / cm^3)

b) Trap-depth distribution

c) Relaxation time of filled traps

d) Applied field frequency

e) Temperature and treatment

Both dielectric changes and losses have been measured and the experimental results are in agreement with a theoretical model developed by Murphy and Morgan.

The variations in the equivalent conductivity may be due also to electrons in two different states, namely:

a) Electrons in the conduction band

b) Electrons in traps

The second cause of in-phase current is proposed by Garlick in order to explain the increase in loss with frequency of the applied field. The trapped electrons are capable of absorbing small quanta of energy from the field. This would in turn require a large number of closely spaced energy states for trapped electrons, and hence, a large trap diameter. Garlick states that the large increase in dielectric loss which occurs when electrons are trapped may account for the large initial currents measured in photoconductivity experiments. In this case it is not necessary to assume that the "primary" photocurrent is due to conduction electrons. Garlick's conclusion on this subject is that electrons in the conduction band of a phosphor do not make significant contribution to photoconductivity and to dielectric charges at ordinary temperatures. This statement seems to be in contradiction with the generally accepted opinion that the primary photocurrent is due to electrons moving in the conduction band. These two viewpoints may be reconciled by keeping in mind the operational definition of photocurrent in terms of relative conductivity change that Garlick probably had in mind.

In Garlick's experiments the photocurrent, or in-phase-current, is provided by the external oscillating source. In measuring photocurrent only a D.C. voltage is normally used, or the phosphor is prepolarized, as it is the case for electrography. In these last cases there is a rapid variation of the internal electric field only during the fast rise period; this variation is due in the first case to the internal impedance of the source, in the second case to the voltage decay in the phosphor itself.

Therefore, the equivalent conductance during the rise period would be roughly equal to that measured with an A.C. field whose frequency is such that its rising time is equal to the rising time of the photocurrent. The decay time is relatively large and the field may be considered as approximately constant.

As for the decay of the photocurrent, it may be associated with the escape of electrons from traps and their subsequent return to the unexcited state via the conduction band.

It is now profitable to examine the nature of the curves of rise and decay of equivalent conductivity and dielectric constant during exposure of the electrographic plate, on the basis of Garlick's results. From these, it is not possible to deduce the rise curves for conductivity and dielectric constant of the excited electrographic plate. However, the formulae given for $\Delta\gamma$, variation in dielectric loss ohm^{-1} (or conductance), and $\Delta\epsilon$, variation in dielectric constants show that they are intimately connected, $\Delta\gamma$ being a function of $\Delta\epsilon$ and frequency. It probably is not too far from being true to assume that $\Delta\gamma$ and $\Delta\epsilon$ rise together and in the same time. This point, however, would deserve experimental check since a difference in rise time may have a sensible effect on the overall charge decay.

As for the decays, these are given in Garlick (Fig. 76). These decays seem to be completed in the same time; the slope of the dielectric loss change on the log paper is smaller than the slope of loss change.

As a conclusion, the representation of ρ and ϵ by means of two straight lines as given in the previous section may not be too far from reality. Such a representation may be improved by assuming for the decay curves functions of the type:

$$\Delta\epsilon = k\,t^{m}$$

$$\Delta\gamma = k'\,t^{n}$$

where according to Garlick the difference in slopes should be $n-m=1$ (Garlick, page 136). The part of the previous treatment relative to the rise period would then still hold. For the decay period, let us then assume again that both resistance and capacity decay in the same time τ_1. Their expressions will then be in a more general case than that given above:

$$R = \frac{1}{\Gamma_m - \Delta\Gamma}$$

$$C = C_m - k_1 \Delta C = C_m - \Delta C_1 \left(\frac{t}{\tau_1}\right)^m$$

where Γ_m is the maximum conductance and $\Delta\Gamma$ is the conductance variation; hence:

$$\Gamma_m = \frac{1}{R_m}$$

$$R_1 = \frac{1}{\Gamma_m - \Delta\Gamma_1} =$$

$$= \frac{1}{(1/R_m) - \Delta\Gamma_1}$$

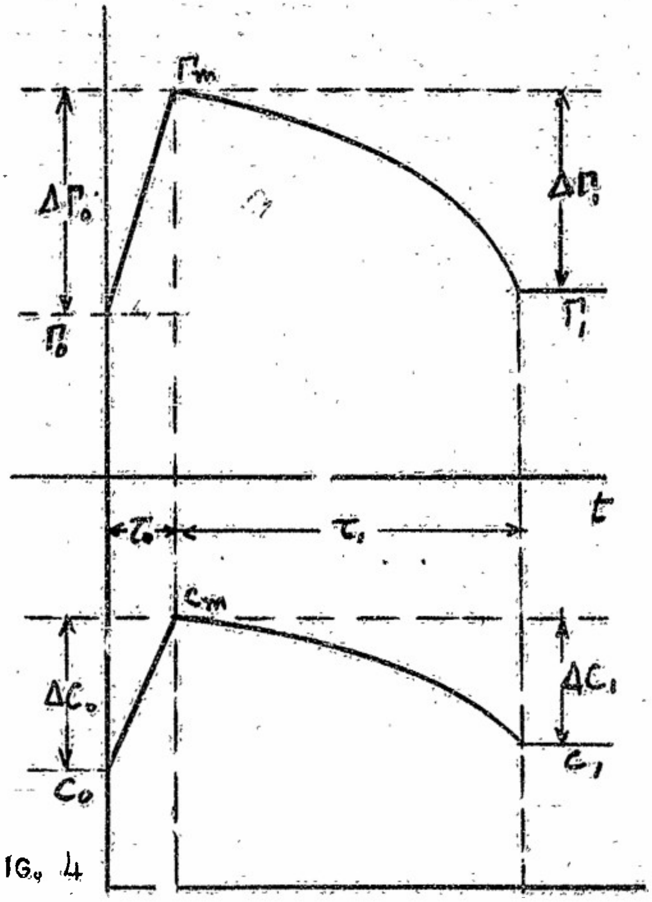

FIG. 4

Hence: $\Delta\Gamma_1 = \frac{1}{R_m} - \frac{1}{R_1}$

and: $\Gamma = \Gamma_m - \Delta\Gamma_1 \left(t/\tau_1\right)^n$ between t_m and t_1 where n is also a number ≥ 1 and such that $m<n$. The charge equation is then:

$$\frac{dq}{q} = -\frac{\Gamma_m - \Delta\Gamma_1 (t/\tau_1)^n \, dt}{C_m - \Delta C_1 (t/\tau_1)^m}$$

This integration may be rather laborious in the general case of m and n not integers. Let us try with $m = z$ and $n = m+1 = 3$. The result is:

$$\ln\frac{q}{q_m} = -\tau_1\frac{\Delta\Gamma}{\Delta C_1}\frac{\tau^2}{2} + \frac{\tau_1 C_m\Delta\Gamma_1}{2(\Delta C_1)^2}\ln\frac{1}{1-\frac{\Delta C_1}{C_m}\tau^2} + \frac{\tau_1\sqrt{\Gamma_m}}{2\sqrt{C_m\Delta C_1}}\ln\frac{\tau+\sqrt{\frac{C_m}{\Delta C_1}}}{\tau-\sqrt{\frac{C_m}{\Delta C_1}}}$$

Where: $\tau = t/\tau_1$

the overall charge decay may be obtained by putting $t = 1$.

If this calculation is correct, it seems off hand that we can neglect the ln terms with respect to the first term, so that:

$$\ln\frac{q_1}{q_m} \approx -\tau_1\frac{\Delta\Gamma}{2\Delta C_1} = -\tau_1\frac{\Delta\sigma_1}{\Delta\epsilon_1}$$

This result would show that the charge decay during the decay time is the most effective, the greater the decay time and the conductivity change, and the smaller the dielectric constant change. Of course this treatment would not hold for zero dielectric change.

If then we put together the results obtained in the previous paragraph for the rise time and the present result, we would come to the tentative conclusion that the dielectric change is beneficial to decay during rise time and non-beneficial during decay time. Of course more detailed evaluations could be attempted for specific cases.

In any case, before trying to evaluate for a specific case, the mutual effects of dielectric constant change and conductivity change, one should first find experimentally the variation of dielectric constant charge with light intensity, or exposure. In the case of a ZnS-A phosphor, Garlick (page 132, Fig. 73) reports that the dielectric constant is, on the other hand, proportional to the intensity of excitation provided that this is sufficiently small (Garlick 123). Therefore, in the case where the dielectric constant charges were saturated well before the conductivity change within the exposure range to be used in electrography, it is possible that the dielectric change would have a different importance at low or at high exposed sites on the plates.

II. Solid State Models

The previous models were based on the consideration of the phosphor as a whole, and disregarded what actually happened inside the phosphor. They were legitimate only insofar as logical deductions from the experimental results were made. A more ambitious plan would be to consider the internal processes in the phosphor during exposure. This might be attempted in accordance with the following. For a given intensity, during the time of exposure, radiation penetrated inside the phosphor only to a small depth, of the order of the inverse of the absorption coefficient. So one could write for the light intensity and depth x : $I = I_0 e^{-\mu x}$. (μ=absorption coefficient). The problem could be treated in one dimension. The next stop would be to establish a relation between conductivity, dielectric constant and light intensity during rise time as a function of depth. The same should be attempted for the decay period. Once the functions $e(x, t)$ and $\epsilon(x,t)$ are evaluated, one could write the field equations:

$$\operatorname{div}(\epsilon \vec{E}) = q_v$$

Where E is the electric field, q_v is the amount of charge freed per unit volume at a depth at time t. Furthermore

$$\frac{d}{dt} q_v = \vec{E} \gamma$$

(1) and (2) are a system of partial different equations involving the

coordinates x and t. If soluble, they would yield E (x,t) and hence $v_i(x,t)$, the voltage at the surface.

However, before pursuing this method, it may be better to have more definite data from the previous method.

APPENDIX II

NOTES ON A MACROSCOPIC THEORY OF ELECTROPHOTOGRAPHIC SPEED

A. The Quantum Yield

In Appendix I the possible aims of a theory of electrography were defined and the methods of attack divded into two major classes, one being the macroscopic, or phenomenological theory, based on experimental evidences and the second being the atomic or solid state theory.

The following notes will be mainly concerned with the correlation of experiments and the problem of electrographic speed. It has been reported elsewhere (Battelle Reports on "Continuous Tone Electrostatic Electrography"), that the speed depends primarily on the quantum yield, i.e., on the number of electrons freed per each quantum of radiant energy. It has also been hinted that a yield much greater than one is necessary to obtain high speed electrophotography. These conclusions were based on estimates on the number of quanta falling on the unit area of the plate, on the plate capacity and on the desired decay. Clearly, if the increase in photographic speed did depend only on an increase in quantum yield, only the collection of information on an "atomic" theory could be useful in giving hints as to the search for high speed materials. In such a case, a "macroscopic" theory could only determine the best operating conditions for a given phosphor. However, the hope of increasing the speed by development of new techniques is still worthy of exploration so as to obtain an increase in speed from materials having the same quantum yield. It has been reported (Battelle IX) that the reciprocity law is roughly observed, but not completely, since the product intensity $\times(\text{time})^n$ is constant ($n=1.2$ to 1.4) for equally satisfactory plates, in the range between 1/25 to 100 seconds. This means that for small times of aperture, the intensity required is higher than that corresponding to the reciprocity law. It is possible that at times smaller than 1/25 this law is even less observed.

In connection with this fact one may argue that the quantum yield is not the only factor affecting speed, (in conditions of optimum preparation and development of the plates), but there is some other factor involved, such as the lifetime of electrons (or holes.) For example, it may happen that surface electrons, excited by the light quanta, be retrapped in the body of the phosphor before reaching the back plate and having their charge compensated by a positive charge. The degree of retrapping might depend on the number of freed electrons, so that at higher intensities, the cloud of retrapped electrons would be responsible for higher residual voltages (less effective decay), than at low intensities. This model (and others could be imagined) shows that possibly a better use of the electrons freed by light may be made by means of improved techniques.

B. The Charge Decay During Exposure

The current diagrams described in Report No. 8 were obtained under substantially different conditions than those present during exposure of the photographic plate. An evaluation of these diagrams is now under way. At present, for the purpose of evaluating the parameters of charge decay to a first approximation, it will be assumed that the current diagram during photographic exposure has a shape similar to that of the experimental photocurrent diagrams. Furthermore, it is assumed that the shutter aperture time in the electrophotographic process to be considered here, is of the order of magnitude or less than the rise time of the current, so that the current diagram will substantially consist of a steep rise to a peak value followed by a slower decay.

The phosphor will be considered equivalent to a resistance in parallel with a capacitance initially charged and the current variation during exposure will be ascribed to a change in both resistance and capacitance.* The current diagram would be similar to the conductance diagram if there was no change in capacitance. For this approximation, it will be assumed that both conductance and capacity diagrams are approximated by two straight lines, and that the rise and decay times are respectively equal (as justified in Appendix I).

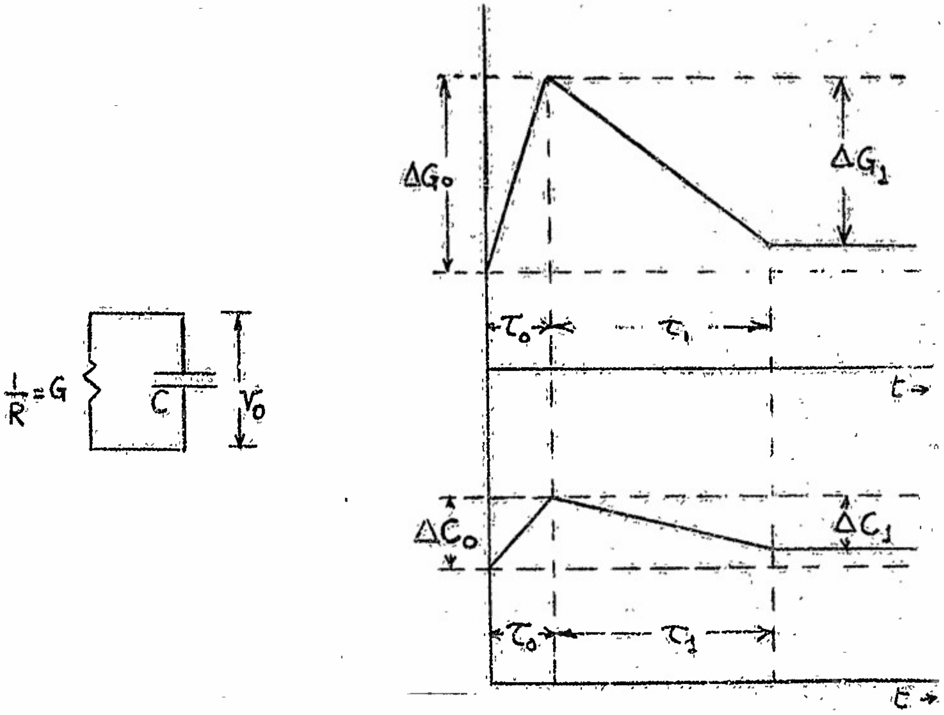

Fig. 1

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* This problem had been treated in Appendix I. The present treatment differs from the previous one in what conductivity rather than resistance changes are considered, and the effects of both changes are separated and compared.

It is now convenient to treat separately the following cases of charge decay: 1) G variation - 2) C variation - 3) G variation and C variation.

Let us then represent the conductance and capacitance variations as follows:

$$G = G_0 + \Delta G_0 \frac{t}{\tau_0} = G_0 \left(1 + g_0 \frac{t}{\tau_0}\right) \qquad \text{rise}$$

$$G = G_0 + \Delta G_0 - \Delta G_1 \frac{t}{\tau_1} = G_0 \left(1 + g_0 - g_1 \frac{t}{\tau_1}\right) \qquad \text{decay}$$

where: $g_0 = \frac{\Delta G_0}{G_0}$; $g_1 = \frac{\Delta G_1}{G_0}$

and analogously for the capacitance:

$$C = C_0 \left(1 + c_0 \ t/\tau_0\right) \qquad \text{rise}$$

$$C = C_0 \left(1 + c_0 - c_1 \ t/\tau_1\right) \qquad \text{decay}$$

where: $c_0 = \frac{C_0}{C_0}$; $c_1 = \frac{C_1}{C_0}$

The equation to be applied in any case is:

$$\frac{q}{C} + \frac{\dot{q}}{G} = 0$$

with the initial condition $q = q_0$.

<u>1) G varies ; C = C₀ = const.</u>

The q equation is integrated separately for rise and decay, and yields:

$$\ln \frac{q_m}{q_d} = - \frac{\tau_0}{\tau_D} \left(1 + \frac{g_0}{2}\right) \qquad \text{: during conductivity rise}$$

$$\ln \frac{q_1}{q_m} = - \frac{\tau_1}{\tau_D} \left(1 + g_0 - \frac{g_1}{2}\right) \qquad \text{: during conductivity decay.}$$

where $\tau_D = \frac{C_0}{G_0}$ = dark decay constant

In the case when the phosphor comes back to its original conductivity ; $g_0 = g_1 = g$, and the overall charge decay is:

$$\ln \frac{q_1}{q_0} = - \frac{T_0 + \tau_1}{\tau_D} \left(1 + \frac{g}{2}\right)$$

2) C varies: $G = G_0$ = const. This of course is a purely

hypothetical case but its treatment will be useful for comparison purposes.

In this case:

$$\ln \frac{q_m}{q_0} = -\frac{\tau_0}{\tau_D c_0} \ln (1 + c_0) \quad : \text{ during capacitance rise}$$

$$\ln \frac{q_{II}}{q_0} = -\frac{\tau_1}{\tau_D c_1} \ln \frac{1 + c_0}{1 + c_0 - c_{II}} \quad : \text{ during capacitance decay}$$

and in the case $c_0 = c_{II} = c$, the overall charge decay is:

$$\ln \frac{q_{II}}{q_0} = -\frac{\tau_0 + \tau_1}{\tau_D} \frac{\ln (1 + c)}{c}$$

This decay would be much smaller than the previous one

3) Both G and C vary: In this case one obtains

$$\ln \frac{q_m}{q_0} = -\frac{\tau_0}{\tau_D} \left[g_0 c_0 - \frac{g_0 - 1}{c_0} \ln (1 + c_0) \right] \quad \text{during G and C rise}$$

$$\ln \frac{q_{II}}{q_m} = -\frac{\tau_1}{\tau_D} \left[g_1 c_1 + \left(\frac{1 + g_0}{c_{II}} - g_1 (1 + c_0) \right) \ln \left(\frac{1 + c_0}{1 + c_0 - c_1} \right) \right]$$

during G and C Decay

In the case $g_0 = g_{II} = g$: $c_0 = c_{II} = c$; the overall decay is:

$$\ln \frac{q_{II}}{q_0} = -\frac{\tau_0 + \tau_1}{\tau_D} gc + \left[\frac{\tau_0}{\tau_D} \frac{g-1}{c} + \frac{\tau_1}{\tau_D} \left[g(1+c) - \frac{1+g}{c} \right] \ln (1+c) \right]$$

This expression can be simplified further if one uses it for practical values of $g \gg 1$, and $\tau_1 \gg \tau_0$, and $c \approx 1$, obtaining:

$$\ln \frac{q_{II}}{q_0} \cong -\frac{\tau_0 + \tau_1}{\tau_D} g \left[c - \left(1 + c - \frac{1}{c} \right) \ln (1 + c) \right]$$

where it will be noticed that the effect of the capacity change is now separated from that of the conductivity, and that the former is composed of two terms of opposite signs. To evaluate the previous expressions let us consider the following example, which represents average values:

$$\frac{\Delta G}{G} = g = 100 \; ; \quad \frac{\Delta C}{C} = c = 1$$

A pure G change would yield: $\ln \frac{q_{II}}{q_0} \cong -50 \frac{\tau_0 + \tau_1}{\tau_D}$

A pure C change would yield: $\ln \frac{q_{II}}{q_0} \cong 0.7 \frac{\tau_0 + \tau_1}{\tau_D}$

A G and C change would yield: $\ln\frac{q_t}{q_0} = -30\,\frac{\tau_0+\tau_1}{\tau_D}$

The dark decay is $\ln\frac{q_t}{q_0} = -\frac{\tau_0+\tau_1}{\tau_D}$

These results show that within the range of values of conductivity and capacity changes given above, and within the limitations of the present assumptions, the capacity change is to be considered as a disadvantage with respect to the overall charge decay. This conclusion is intuitively justified by the fact that an increase in capacitance tends to keep charges from flowing out of the condenser plates, as it is also shown by the decay in the case of a change in C only, which is slower than the dark decay in the same time $(\tau_0 + \tau_1)$. Actually, the above decay formula shows that the C variation may compensate for the G variation. This would happen for a value of c around 1.3, for which the c dependent term in the decay vanishes. For values of c> 1.3 there would result a build up of charges rather than a decay, regardless of how big g may be. On the other hand, a capacity decrease, rather than increase, would probably enhance the decay.

The reason why plates showing a relatively high change of capacity (in bridge measurements from dark to light,) had relatively good photographic speed, may perhaps be ascribed to the fact that a high capacity change is normally accompanied by a high conductivity change. This fact is recognized also by the macroscopic theory of dielectrics, which proves that both real and imaginary component of dielectric constant are intimately connected and derivable the one from the other by means of a common decay function (Frohlich - "Theory of Dielectrics" - Oxford 1949, Ch. 1.)

C. The dark Time Constant

The previous decay formulae show that, every other parameter being the same, the charge decay is inversely proportional to the dark time constant. It would, however, be misleading to conclude that if one could obtain, by proper treatment of the phosphor, a decrease in the dark time constant compatible with other requirements, then the speed would be increased. A decrease in time constant would probably be accompanied by a decrease in the conductivity change g, and it is obviously difficult to say whether the overall charge decay will be increased or not. Here again, if the reciprocity law for exposure was exactly obeyed in a broad range of dark time constants, the answer to such a question would be clearly that no change in overall decay should be observed. However, it still is tempting to investigate further this possibility. For example, the reversal technique described in Report No. 8 may be classified as a means of reducing the dark time constant. In fact, voltage decay curves given in this report prove that the effect of reversal is not only to increase the light current in C.R.O. measurements, but also to decrease the dark time constant, so that the former effect may be, at least partly, ascribed to the latter.

To decide whether the reversal technique is a real advantage one should compare the charge decays obtained with: a) a plate subjected to reversal, b) a plate of the same type of phosphor previously doped in such a way as to obtain the same dark time constant as the previous plate after reversal. From this viewpoint, it appears that the only conclusive test (besides actual photography of course) is the measurement of voltage decay.

The previous considerations lead to the tentative conclusion that techniques, such as reversal, tending to decrease the dark time constant may have practical application only if they could be used in the camera itself, shortly before exposure. If it was possible to apply a potential during exposure, some interesting possibilities could be investigated, such as reversal, the application of high voltage pulses, or A.C. pulses. The following arrangement is suggested for this purpose:

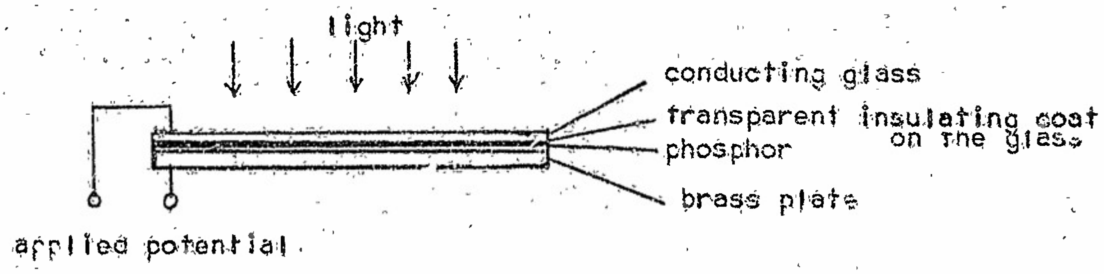

Fig. 2

A thin slab of conducting glass coated with a transparent insulating coat could be layed against the phosphor plate, and potential applied during exposure between the glass and the plate.