UNCLASSIFIED

| AD NUMBER |
|---|
| ADA800084 |
| CLASSIFICATION CHANGES |

| TO: | unclassified |
|---|---|
| FROM: | restricted |

| LIMITATION CHANGES |
|---|

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to DoD only; Administrative/Operational Use; 15 DEC 1949. Other requests shall be referred to Signal Corps Engineering Laboratories, Fort Monmouth, NJ. Pre-dates formal DoD distribution statements. Treat as DoD only.

| AUTHORITY |
|---|

E.O. 10501 dtd 5 Nov 1953; USAEC ltr dtd 29 Jun 1965

THIS PAGE IS UNCLASSIFIED

# UNCLASSIFIED

# ATI 178 566

## DEFENSE DOCUMENTATION CENTER

FOR

### SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

# UNCLASSIFIED

# REPORT

## TO

## THE HALOID COMPANY

### (UNDER PRIME CONTRACT NO. W-36-039

### sc-38551 WITH THE U. S. ARMY

### SIGNAL CORPS ENGINEERING

### LABORATORIES, BRADLEY BEACH, N. J.)

# CONTINUOUS-TONE ELECTROSTATIC

# ELECTROGRAPHY

## BATTELLE MEMORIAL INSTITUTE

# BATTELLE MEMORIAL INSTITUTE
## INDUSTRIAL AND SCIENTIFIC RESEARCH
### COLUMBUS 1, OHIO

January 9, 1950          <u>RESTRICTED</u>

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

Dear Dr. Dessauer:

We are enclosing 56 copies of Quarterly Progress Report No. 6 on Continuous-Tone Electrophotography. This report covers work for the three-month period from September 15, 1949, to December 15, 1949.

A marked improvement in the quality of continuous-tone pictures, produced by powder-cloud techniques, has been achieved. This improvement is due principally to the use of plates with thicker selenium coatings combined with particular care to prevent overcharging.

A spray-development technique has been devised which produces the best pictures produced to date by electrophotography.

The work for the next quarter will be concentrated on getting specific engineering data to enable the camera design to be completed in detail.

Very truly yours,

*Lewis E. Walkup*

Lewis E. Walkup
Assistant Supervisor
Graphic Arts Research Division

LEW:swr
Enc.

<u>RESTRICTED</u>

QUARTERLY PROGRESS REPORT NO. 6
(September 15, 1949, to December 15, 1949)


on


CONTINUOUS-TONE ELECTROSTATIC ELECTROGRAPHY


to


THE HALOID COMPANY

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

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

(Signal Corps Project: 195 B)


by


R. M. Schaffert, D. T. Williams, and L. E. Walkup


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


BATTELLE MEMORIAL INSTITUTE

December 15, 1949

## TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

QUARTERLY PROGRESS REPORT NO. 6
(September 15, 1949, to December 15, 1949)

on

CONTINUOUS-TONE ELECTROSTATIC ELECTROGRAPHY

to

THE HALOID COMPANY

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

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

(Signal Corps Project: 195 B)

from

BATTELLE MEMORIAL INSTITUTE

by

R. M. Schaffert, D. T. Williams, and L. E. Walkup

December 15, 1949

## SUMMARY

This report covers experimental work on continuous-tone electro-photography from September 15, 1949, to December 15, 1949.

A decided improvement in the quality of continuous-tone images developed by the powder-cloud technique has been achieved. It consists primarily in a great reduction in the graininess of the powder deposit and an almost complete elimination of powder-deficient spots in the prints. This improvement in both grain and powder-free areas is attributable to three factors: (1) a control of potential during sensitizing the plates

so as not to overcharge them, (2) the use of plates with thicker selenium coatings which can accept a greater charge without breakdown, and (3) a general improvement in powder-cloud developing techniques.

The study of particle-size distribution in powder-cloud development work has been continued. It shows that particle size in the deposited powder is dependent on the moisture content of the powder, excess moisture causing coarser grain or "treeing". It also shows that the average particle size in the deposit does not go below three microns even though the powder has originally been ground much finer.

Work on gray-scale exposures of selenium plates has yielded valuable information about the dependence of plate voltage on plate exposure. Using this information, a definite plan has been worked out for cycling the voltage on the development grid during powder-cloud development. This development-grid cycling should make possible a much more faithful tonal rendition than has been obtainable to date.

A spray-development technique has been developed which produces prints having the finest texture and best tonal gradations yet attained in the electrophotographic process.

A smoke cloud containing vaporized dye has been used to develop continuous-tone images. Though these prints are of very low contrast, the grain texture and resolution are very good.

Work was initiated on adhesive transfer and fixing of electrophotographic prints. The best results were obtained using gelatin-coated photographic paper.

It was found that brass is much superior to 2SH 14 aluminum as a backing-plate material. It gives rise to slower dark-decay rates and greatly decreases the tendency of plates to form powder-deficient areas.

Plates using phosphors as the photosensitive element have been prepared and tested. Though prints made with these plates do not have the fine grain quality now obtainable with selenium-coated plates, the plates do have fair speed and give reasonable image quality. They also offer potentialities for providing a greater variety of spectral sensitivities than selenium plates. Pictures of comparable speed and quality have been produced both by the Carlson (charge before exposing) and the Kallman (expose before charging) methods.

The emphasis of work on this project has been changed from general development work to obtaining more specific information on the processes as they now stand. This should provide the data needed by the camera-design engineers to prepare drawings for a practical electrophotographic camera.

## FUTURE WORK

All work for the next quarter will be directed, in so far as is practicable, toward obtaining the specific information still required by the camera designers. This consists, with regard to plates themselves, in determining the optimum thickness of selenium to be used, and in determining the decay and fatigue characteristics of these plates. Work will also be done to find the optimum plate-preparation temperature.

With regard to plate sensitization, future work will consist in determining the best plate potential and the corona and potential-control-grid voltages to use.

Limits of exposure will be set up for several exposure conditions. The final design of a powder-cloud box will be fixed and its most effective geometry determined. This includes development-grid-wire diameter and spacing, and the spacing between the grid and the plate. Recommendations will be made with regard to voltage cycling on the grid, as well.

The study of adhesive transfer and fixing will continue as outlined in this report.

Some further work will also be done with spray development along the lines of more faithful tonal rendition and a simpler transfer operation.

More phosphor plates will be made for the purpose of getting engineering-type information on best methods, best thickness, best phosphor-to-binder ratio, etc. Only those phosphors which have been used to date will be studied.

## PUBLICATIONS AND REPORTS

(None)

-478-

EXPERIMENTS ON CONTINUOUS-TONE DEVELOPMENT

(P. G. Andrus, S. J. Czyzak, D. L. Fauser, R. B. Landrigan,
D. Reynolds, E. Ricker, and R. Tom)

Production of Gray Scales with the Powder Cloud

The electrophotographic process is capable of producing continuous-
tone reproductions with high contrast. The tonal rendition is non-linear,
however, the middle and lighter tones being developed to a higher
contrast than the darker tones. The reason for this was found to be that,
while density of powder deposited is substantially proportional to plate
potential, the potential decay of an exposed plate is not proportional
to subject density. The decay is more nearly a linear function of
exposure, over a wide range.

A correction for this lack of contrast in the higher density area
can be effected by means of the development-control grid. The use of
this grid has been described in Quarterly Progress Report No. 3, page
292. There it was stated that development of any particular plate area could
be stopped by applying to the grid a potential equal to or greater than
the potential which exists on the particular area. Actually, powder
deposition is not completely stopped by this potential, but nearly so.
The procedure for correcting the lack of contrast in high-density areas
is as follows: after sufficient contrast has developed in the middle-
and light-tone areas, the grid potential is increased to such a point as
to almost completely stop development of these middle- and light-tone
areas. The darker areas will then continue to be developed.

It was not possible to correct the non-linear contrast by simple trial and error methods. It was necessary to break the problem into two parts. These consisted of (1) determining the relation between subject density and potential on the exposed electrophotographic plate, and (2) determining the relation between potential on a surface and the amount of powder deposited on it.

In determining the relation between subject density and plate potential, the charged plate was first exposed in a camera to a gray scale. The densities on this gray scale ranged from zero to 1.7. The potentials on the exposed plate corresponding to the gray-scale steps were then measured on the point-probe electrometer (described on page 519 of this report). A plot of potential versus subject density is shown in Figure 140. Corresponding relative-intensity values are included along the abscissa. Kenny flash lamps were used and curves are drawn for three different stop openings of the lens. The curve for f-5.6 is drawn as gradually sloping to the origin, rather than intersecting the density axis at some value of density other than zero. Though the data do not distinctly indicate this choice as the proper one, knowledge that practically all plates have very slow light-decay characteristics near zero potential make it the most likely one.

The f-11 curve in Figure 140 gives an indication of the relative exposure for highlights and shadows. For the plate tested, the relative exposure is about 50 to 1. The curves for f-5.6 and f-32 show over exposure and under exposure.
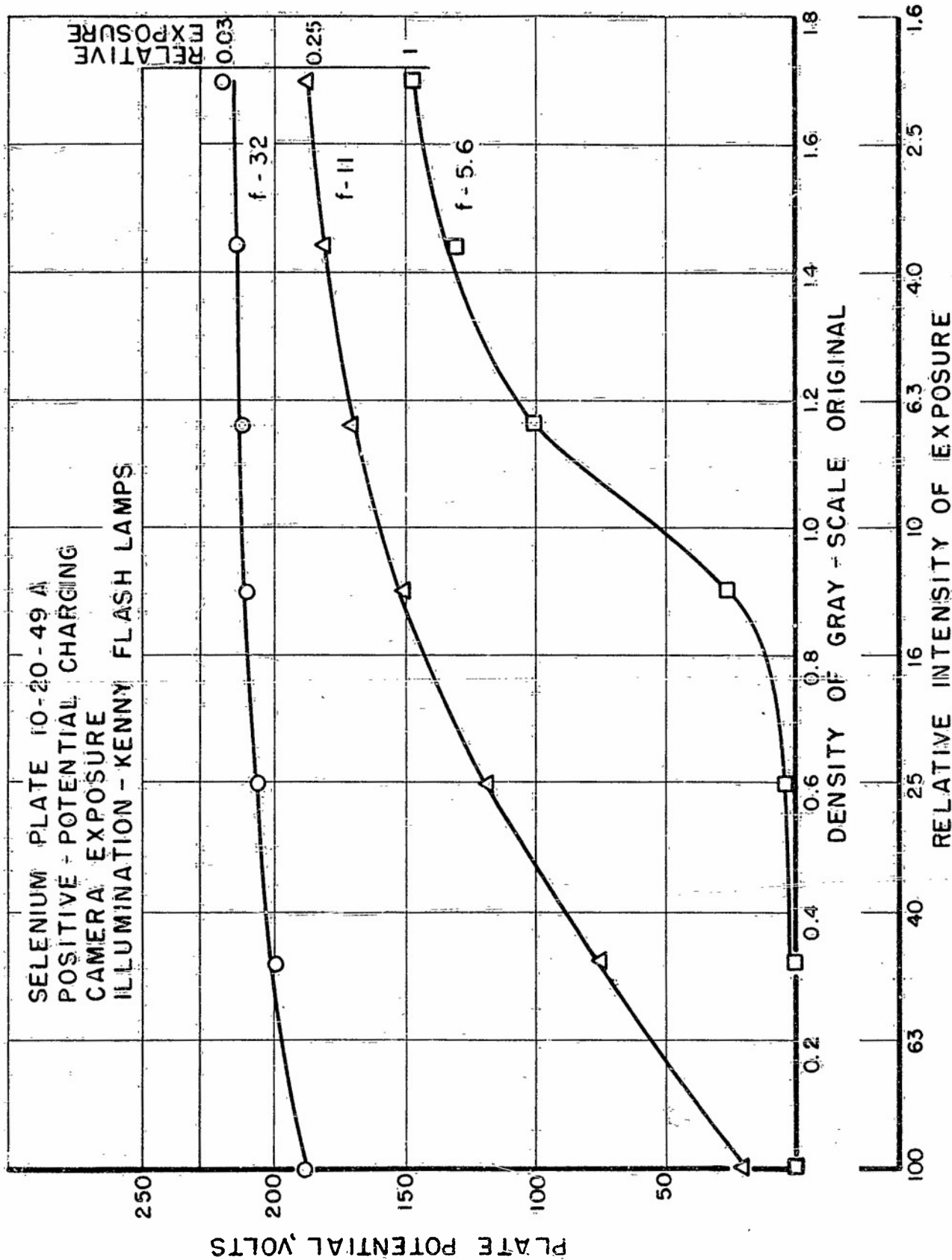
O-14176



FIGURE 140. PLATE POTENTIAL VERSUS GRAY-SCALE DENSITY.

-480-

The effect of different intensities is given in Figure 140, both by the intensity axis and by going from one curve to another. A comparison of voltage drops caused by a decreasing subject density with voltage drops caused by a change in stop opening (at constant subject density) gives an indication of the reliability of the data; though the curves checked in this way are not completely selfconsistent, they do give valuable information on latitude of exposure.

In determining the relation between potential on a surface and the amount of powder deposited on it, the development-test plate was used. The use of such a plate was described in Quarterly Progress Report No. 5, pages 401-406. A new development-test plate was made for the work reported here. This plate differed from the original only in the size and spacing of the different sections. Various voltages were applied to various areas on the plate during development. A transfer of the deposited powder to white paper was made and the densities of the different areas were measured on a reflection densitometer. The curves in Figures 141 and 142 show the relation between powder deposited (and transferred) to potential on the area. Reproductions of the powder deposit transferred from the test plate are also shown in Figures 141 and 142. Figure 141 covers a potential range from zero to 425 volts, with 25 volts on the development-control grid. Figure 142 covers a potential range up to 80 volts, with 51 volts on the grid. Note that the curve for the shorter potential range does not show zero density for a plate potential equal to the grid potential. This is due to the presence of uncharged and negatively charged particles in the space between the plate and the grid.

| 85 | 185 | 318 | 418 | VOLTAGE ON PLATE |



| 25 | 125 | 250 | 380 | VOLTAGE ON PLATE |



25 VOLTS ON GRID

DENSITY OF IMAGE (TRANSFERRED)

POTENTIAL ON PLATE, VOLTS
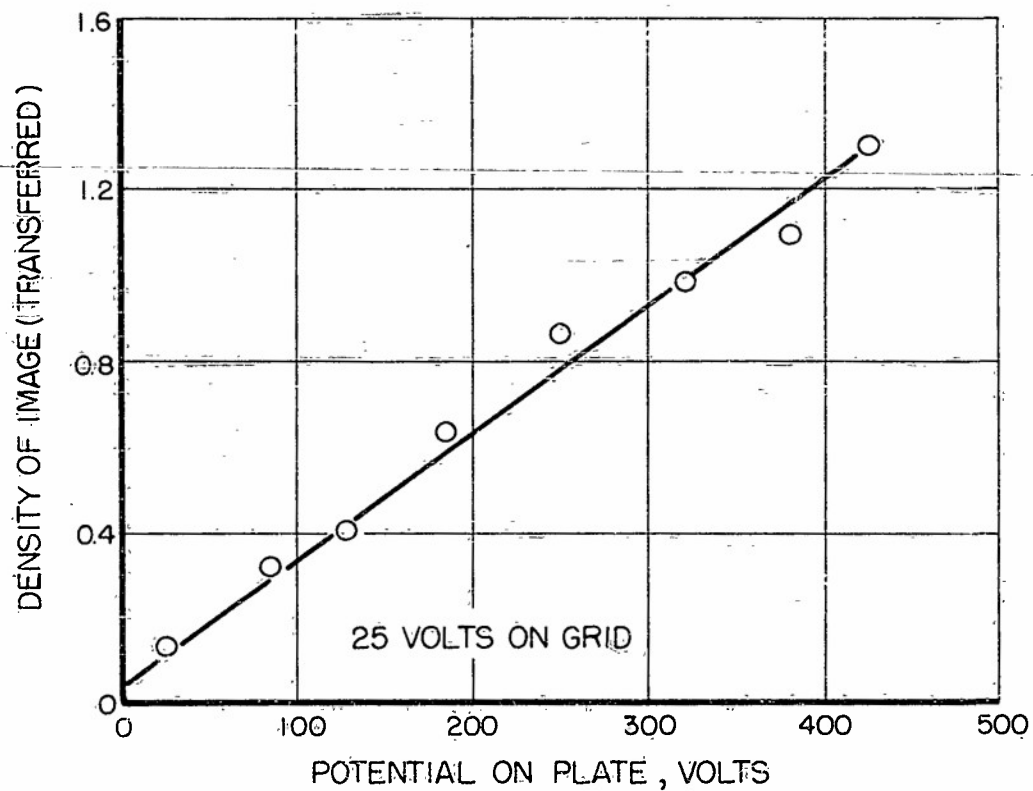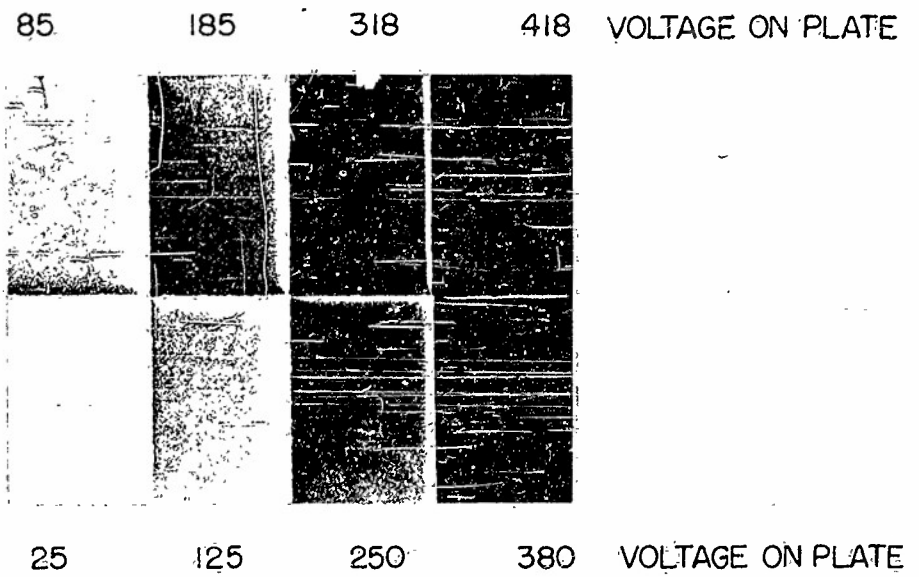
FIGURE 141. DENSITY OF IMAGE VERSUS DEVELOPMENT-TEST PLATE
POTENTIALS USING POWDER-CLOUD DEVELOPMENT

O-14232

| 55 | 63 | 70½ | 79½ | VOLTAGE ON PLATE |
|---|---|---|---|---|

| 51 | 59 | 66½ | 75 | VOLTAGE ON PLATE |
|---|---|---|---|---|



51 VOLTS ON GRID

POTENTIAL ON PLATE, VOLTS

FIGURE 142. DENSITY OF IMAGE VERSUS DEVELOPMENT-TEST PLATE
POTENTIALS USING POWDER-CLOUD DEVELOPMENT

0-14233

-481-

This effect is shown particularly well in Figure 143, in which a relatively high grid voltage was used. Here, a difference in concentration of positively and negatively charged powder particles is demonstrated by the difference in the slope of the two sections of the curve. The change in slope occurs approximately at the point where the grid potential equals the plate potential.

The following information results from a study of the curves in Figures 140, 141, 142, and 143.

1. The relation between subject density and plate potential after exposure is not linear over most of the density range. This means that, since the density of powder deposited (and transferred) is essentially proportioned to the plate potential, a true reproduction by powder-cloud development can be made only by correcting for this non-linearity in the development step. However, the curves are nearly linear over a short density range, from zero to 0.6. It has not yet been established what degree of non-linearity can be tolerated in producing a satisfactory print.

2. It should be possible to compensate for the potential-decay characteristics by varying the potential on the development-control grid. On the plate used for these tests, it appears that the maximum density range attainable is from zero to about 1.5, unless a development-grid potential cycle is used.

This work was carried out using glass bead-Alj developer (approximate ratio - 15 to 1) in the motor-driven, compartmented developing box. A potential-control grid was used for charging the plate in the

85      185      318      418      VOLTAGE ON PLATE

25      125      250      380      VOLTAGE ON PLATE

250 VOLTS ON GRID

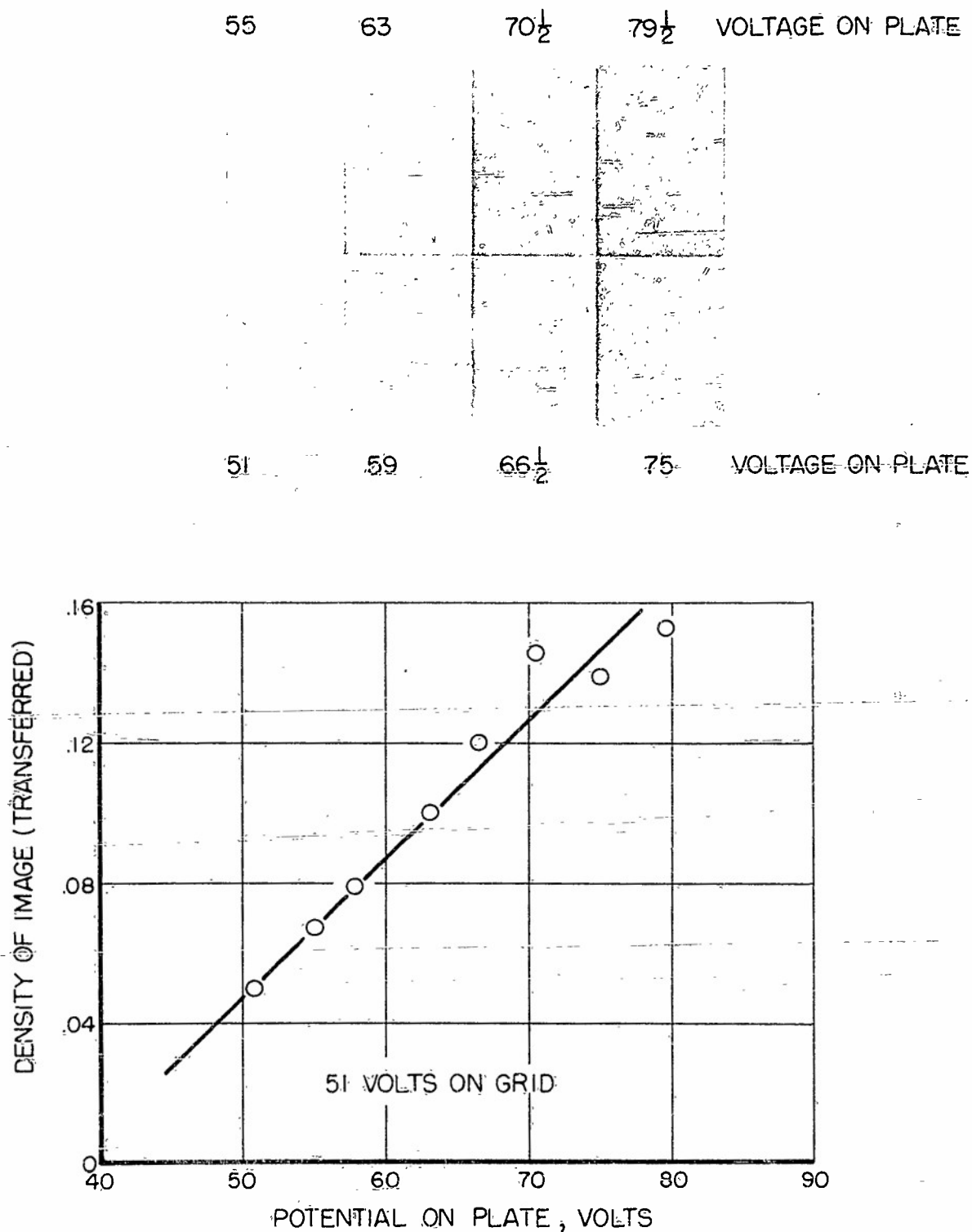DENSITY OF IMAGE (TRANSFERRED)

NEGATIVE POWDER
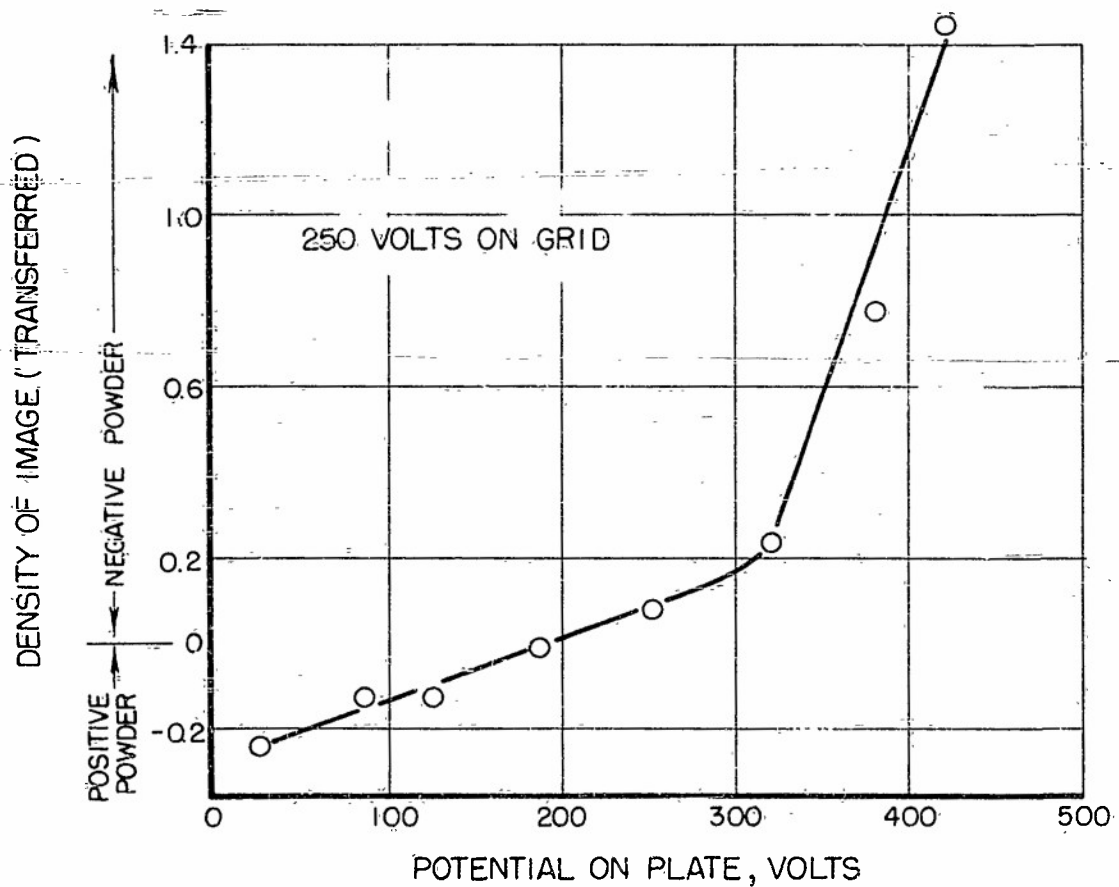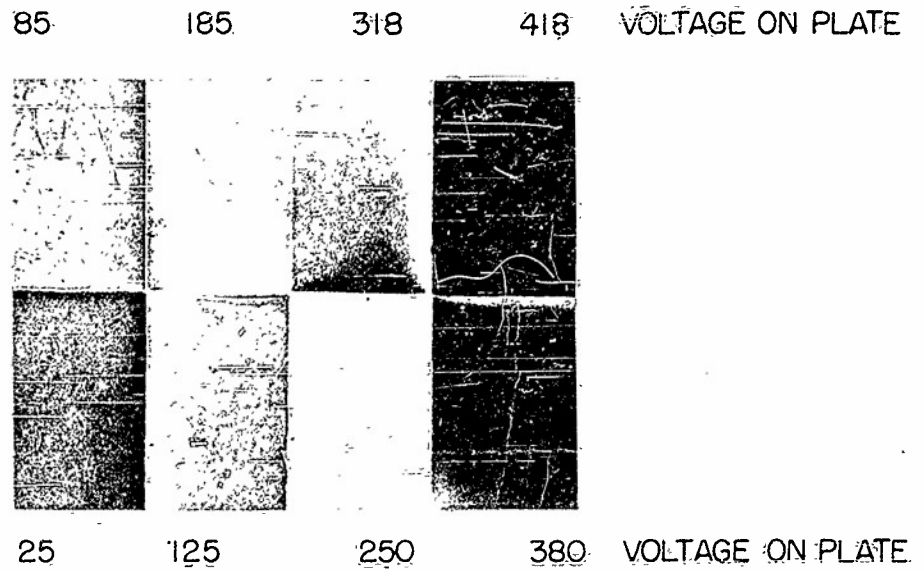
POSITIVE POWDER

POTENTIAL ON PLATE, VOLTS

FIGURE 143. DENSITY OF IMAGE VERSUS DEVELOPMENT-TEST PLATE
POTENTIALS USING POWDER-CLOUD DEVELOPMENT

0-14234

-482-

experiments showing the relation of plate potential to subject density. These data are the result of comparative tests on only one plate. They are to be taken only as representative of the type of results one can expect and should not be considered as quantitatively representative of most plates.

## Potential Cycling on Development Grid

It has been known for some time that electrophotography does not produce a true representation of an original gray scale in the final print when development is done with a single potential on the development grid throughout the development period. It has also been suspected that, if the potential on the development grid were cycled during development, it would be possible to produce a print having a density scale much closer to the density scale of the original subject. The following is a basic explanation of why this is true and of the method which would be used to arrive at the potential cycle to be used on the development grid.

For this analysis, it is assumed that the powder which deposits on a plate does not alter the potential on the plate, and that the density which deposits on a given area of the print (image) is proportional to the potential of that area.

The calculation is started with the data given in plots A and B of Figure 144. (All further references in this section will be made to the three plots in this Figure.) Plot A gives the potential of the electrophotographic plate as a function of the optical density of the original to which it was exposed. This plot is not a straight line,
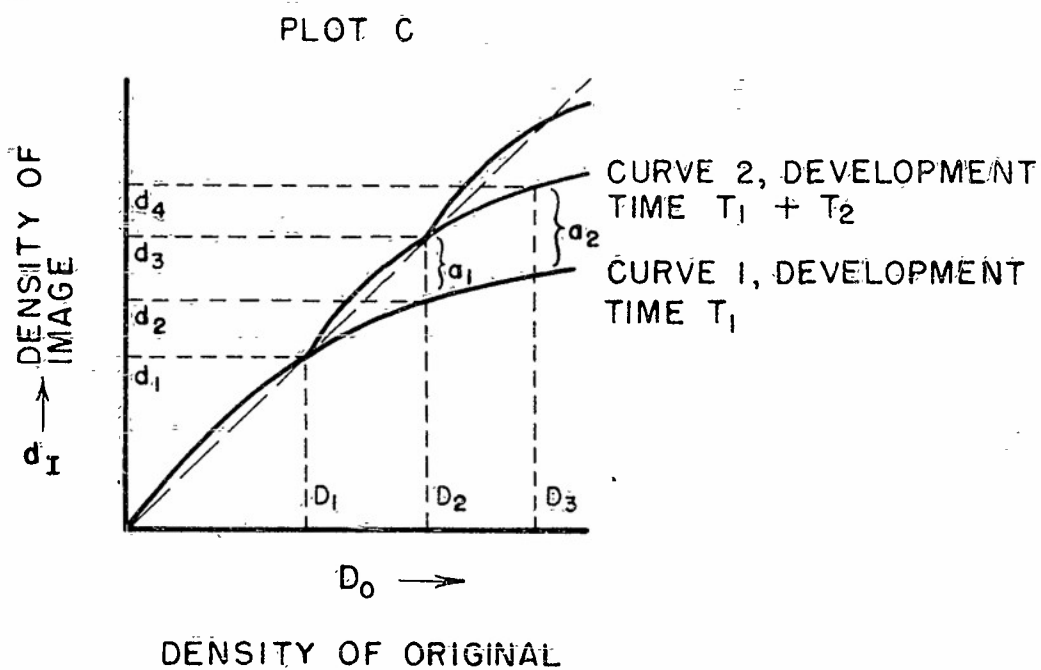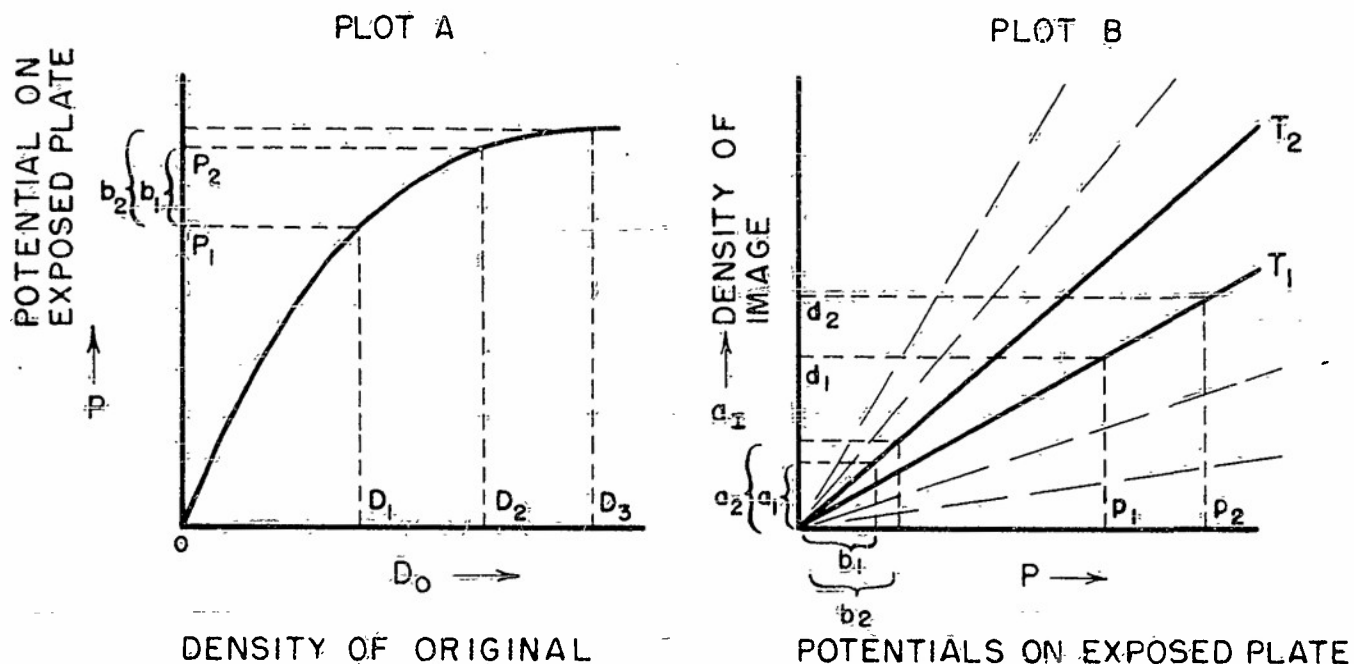
PLOT A

PLOT B



FIGURE 144. PLOTS USED TO DETERMINE DEVELOPMENT —
GRID POTENTIAL CYCLING TO IMPROVE
CONTRAST RENDITION.

since potential decay is nearly a straight-line function with exposure rather than optical density in the original. (Density varies inversely as the logarithm of the exposure.) Plot B shows the straight-line relationship between potential on the electrophotographic plate and the optical density of the final print for various times of development, $t_1$ to $t_6$. This relationship would have to be determined by experiments on actual plates. Enough is known about this relationship, however, to show that it agrees reasonably well with the curves given.

From the data described above, it is desired to specify a development cycle which will give a density scale in the final print as closely as possible equal to the density scale of the original. This derived function is to be produced in Plot C as the calculation progresses.

As the first step in the calculation, it is seen that the curve in Plot A can be reasonably well represented by a straight line up to a point corresponding to a density $D_1$, and a potential $P_1$. Density $D_1$ is then marked off on the abscissa of Plot C. If the final print is to be a true representation of the original, then this point should correspond to a density of $D_1$ on the final print and it can be so marked on Plot C. Furthermore, the dashed line on Plot C is the line which we would like to follow for the whole relationship of density of original to density of the finished print.

Next, the value of potential $P_1$ and the value of $D_1$ (same as $d_1$) is marked on the appropriate axes of Plot B. These two values determine

-484-

a point on this plot and this point determines the proper development time, $T_1$, required to achieve this relationship of density and potential.

At the same time this one point is being developed, the other density areas of the plate are also being developed. These areas will generally have optical densities from zero up to some value between one and two, on the conventional scale. To find the densities resulting from developing for a time $T_1$, it will be necessary to take other values on the scale of densities of the original and repeat the calculation outlined above to get additional points on the curve. In calculating these additional points on curve 1, it will be necessary, of course, to use the same development time, $T_1$, as was arrived at in the original calculation.

At the end of this first development period, the density of the image on the plate will be represented by Curve 1 on Plot C. For the second period of the development cycle, it will be necessary to raise the potential on the development grid to the value $P_1$. When this is done, it is assumed that there will be no further development in any areas on the plate which have potentials lower than $P_1$. These areas are now completely developed.

For the second period of the development cycle, the value $D_2$ is selected so that the curve in Plot A and Curve 1 in Plot C are both reasonably well represented by straight lines between the values $D_1$ and $D_2$. Now, to bring the density of the print up to the desired straight line in Plot C for density $D_2$, it will be necessary to add to the image an increment of density equal to $a_1$. When the development grid is raised to the potential $P_1$, then the area corresponding to $D_2$ will have an

-485-

effective potential of $b_1$. These two values can be marked off on Plot B and the necessary development time $T_2$ determined for the second period of the development cycle. When this second development period is completed, the final density of the print corresponding to the original density of $D_2$ will fall on the desired straight line. The rest of Curve 2 on Plot C can be drawn by chosing other values of original density and carrying them through the calculation involving Plots A and B. In each case, the value of $T_2$ is used on Plot B.

An extension of the process outlined above can make better and better approximations to the straight line desired between original and final density. However, it is believed that from three to five values of development-grid potential should be sufficient for practical purposes.

The above exposition of the method of arriving at the proper development cycle can be modified in actual practice, depending on the nature of the functions finally determined in Plots A and B. It may even be possible to write out differential equations and solve them for the ideal development cycle. On the other hand, it may be more practical to determine the development cycle from purely empirical tests on the process.

In any case, the development cycle will be determined only once for a particular combination of plate, total exposure, and development operation. It will not be necessary to repeat the process for each picture made.

Actual application of the method outlined above indicates that practical values of development time result.

-486-

## Control of Graininess in Prints Made by Powder-Cloud Development

One of the outstanding defects of continuous-tone electrophotography has been the graininess of the prints. This defect can possibly be attributed to one or more of the following:

1. Nonuniform initial plate potential.

2. Different rates of light and dark decay on different small areas of the plate.

3. Uneven deposition of powder on the plate as a result of the development process itself (i.e., such as the treeing effect of the powder).

One test for the first point above, nonuniformity of potential on the plate, is to make the plate surface slightly dark conducting. This will tend to equalize local potential differences. Slightly conducting mixtures of Glo-Coat Wax Polish* plus Arquad**, Sunoco Auto Polish*** plus glycerine, and Sunoco Auto Polish plus Arquad or Glass Wax**** will accomplish this. These coatings apparently allow some surface conduction, thus producing a more uniform initial potential on the plate. They also may cause the plate to discharge more uniformly and allow surface conduction after exposure to give a more uniform image potential. In this way, it was possible to produce gray-scale areas equal in grain quality to the grays produced on the development-test plate. Images produced by this method lacked definition, however.

---

| * | S. C. Johnson and Son, Inc., Racine, Wisconsin. |
| ** | Armour and Company, Chicago, Illinois. |
| *** | Sunoco Oil Company, Philadelphia, Pennsylvania. |
| **** | Gold Seal Company, Bismarck, North Dakota. |

BATTELLE MEMORIAL INSTITUTE

-487-

Figure 145 shows two prints made using Plate Number 9-6-49-A. Both prints were prepared in the same manner, using positive sensitization and contact exposure. Print 145-A is representative of prints produced on the plate after it had been coated with Glo-Coat floor wax plus Arquad. Print 145-B is representative of prints produced before the plate was coated.

It was found that graininess of prints can also be reduced if the potential to which the plate is charged is held to some value well below the maximum which the plate can accept. This control of plate potential can be accomplished using a potential-control charging grid as described in Quarterly Progress Report No. 5, pages 414-417.

A plate which has never been subjected to breakdown voltages from an open-wire corona charging unit will show good grain quality through the use of the potential-control grid. However, a plate which has been subjected to breakdown potentials will not show so much improvement in grain quality when charged with the potential-control grid. An example of this is given in Figure 146. Figure 146-A is a gray scale made with the first charging to which the plate was ever subjected; Figure 146-B was made after the third charging; and Figure 146-C was made after the fourth charging. The potential-control grid was used on the first and fourth chargings (146-A and 146-C), and open corona wires were used for the second and third chargings (Figure 146-B). It is apparent that the open-wire charging has caused damage to the plate which the potential-control grid cannot correct. Further subjection to open-wire charging will damage the plate still more. The improvement in grain quality

67 II 18

(b) PRINT PRODUCED FROM THE
UNCOATED SELENIUM PLATE

(a) PRINT PRODUCED FROM SELENIUM
PLATE COATED WITH GLO-COAT
FLOOR WAX PLUS ARQUAD

FIGURE 145. SHOWING THE EFFECT OF A SLIGHTLY CONDUCTING SURFACE COATING ON
IMAGE QUALITY (PLATE 9-6-49A)
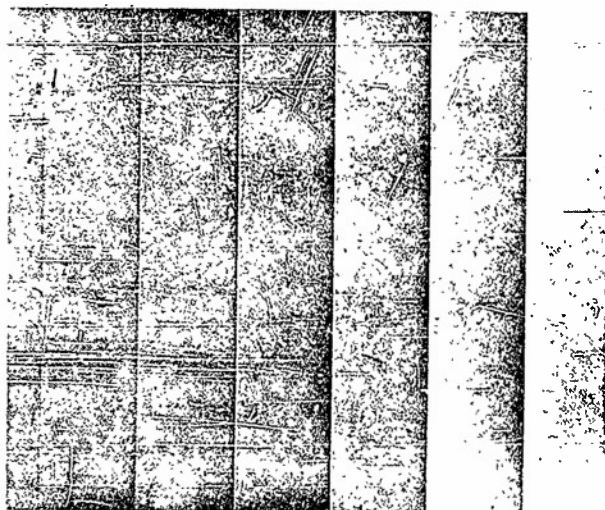
67117



a

FIRST CHARGING, POTENTIAL-
CONTROL GRID, 200 VOLTS
POSITIVE
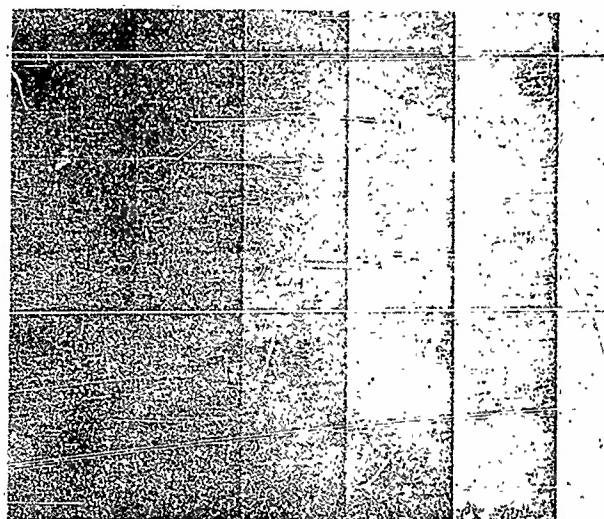
b

THIRD CHARGING,
OPEN-WIRE, 7000
VOLTS POSITIVE

c

FOURTH CHARGING, POTENTIAL-
CONTROL GRID, 200 VOLTS
POSITIVE

(CAMERA EXPOSURE -PLATE 10-28-49 (B))

FIGURE 146. COMPARISON OF POTENTIAL-CONTROL GRID CHARGING AND OPEN-WIRE
CORONA CHARGING

-488-

brought about by the potential-control grid is always much more pronounced in the denser areas of the prints.

The effect of the powder itself on grain texture is comparatively slight. This is discussed in the following section of this report.

## Particle-Size Distribution in Powder Clouds

### Summary of Results

In Quarterly Progress Report No. 5, page 412, it was recommended that the following factors be evaluated before any measurements could be made, to determine the effect of particle size on continuous-tone quality: (a) Effect of moisture on particle-size distribution; (b) type of cloud deposit produced by a powder whose composition consists mainly of one-micron particles; (c) type of cloud deposit produced by powder-carrier clouds; and (d), since clouds are known to possess negative, positive, and uncharged particles, the predominant polarity should be determined.

An investigation of the above-mentioned factors was made. It was observed that, of three powders examined [Alj (wet), Alj (dry), and Alj fines (dry)] using both the development-test plate and a selenium plate, the Alj fines (dry) gave the most uniform deposit and smoothest particle distribution (Figures 147-B and 148). This distribution differs considerably from that of the powder before being used to generate a cloud (Figure 147-A). From Figures 148, 149, and 150, it can be seen that the "treeing" effect is eliminated when dry powders are used.

BATTELLE MEMORIAL INSTITUTE
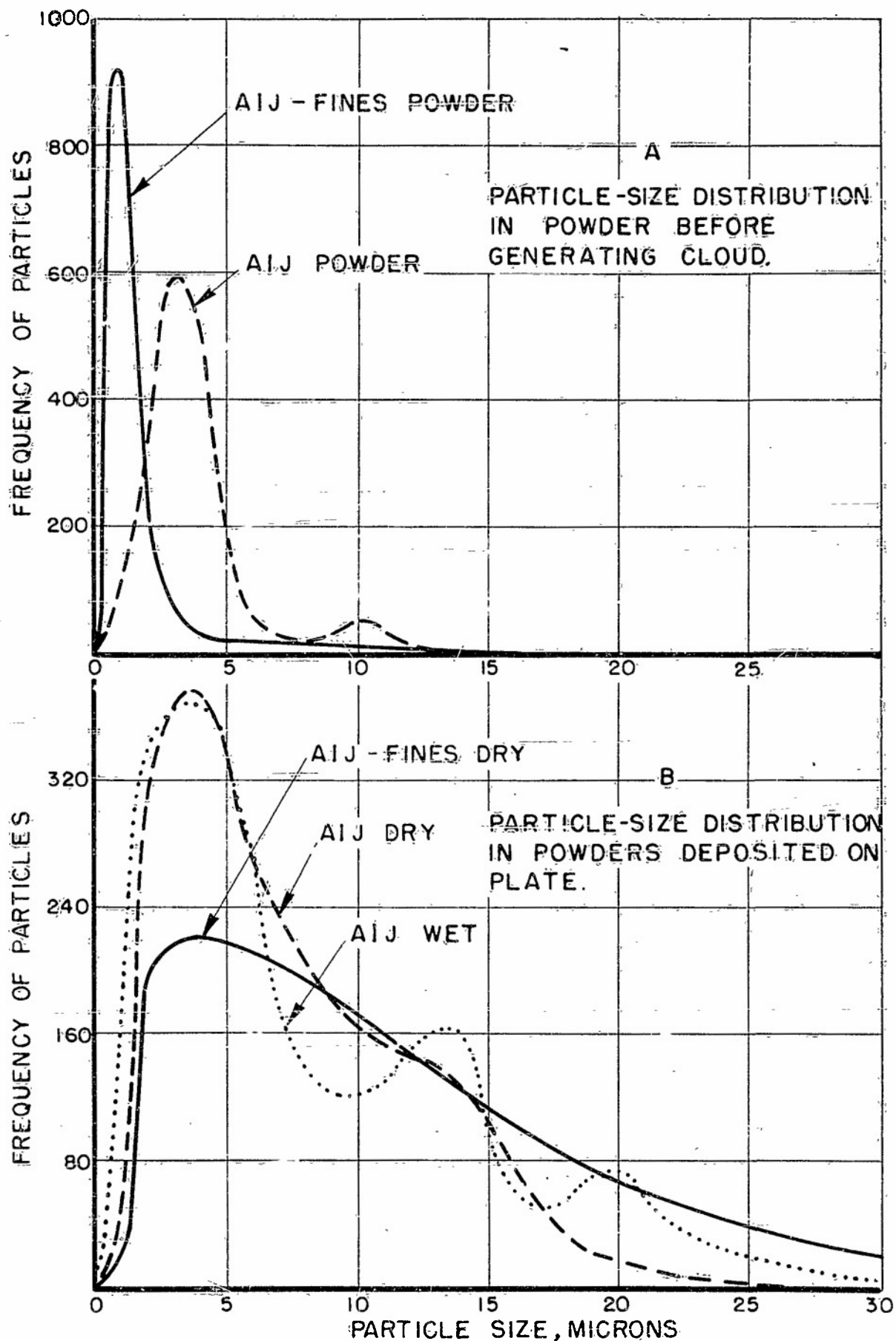
FIGURE 147, PARTICLE-SIZE DISTRIBUTIONS IN POWDER SAMPLES. A- BATCH B-DEPOSITED FROM CLOUD

DEVELOPMENT-TEST PLATE          SELENIUM PLATE
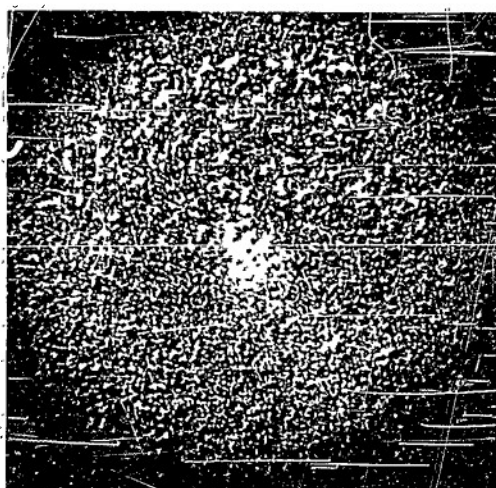


2.17 VOLTS          C                                    F

98 VOLTS          B                                    E

O VOLTS          A                          D                          67103

FIGURE 148. POWDER-CLOUD DEPOSITION OF Al j - FINES DRY POWDER
ON DEVELOPMENT-TEST PLATE AND SELENIUM PLATE

DEVELOPMENT-TEST PLATE                SELENIUM PLATE



215 VOLTS          C                              F
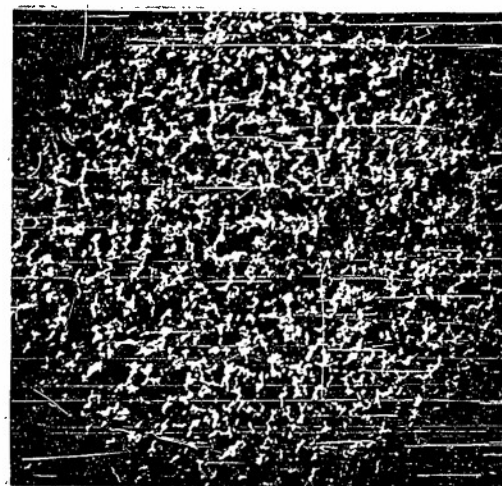
157 VOLTS          B                              E

98 VOLTS           A                              D                    67104

FIGURE 149.   POWDER-CLOUD DEPOSITION OF Alj-DRY POWDER
          ON DEVELOPMENT-TEST PLATE AND SELENIUM PLATE

DEVELOPMENT-TEST PLATE          SELENIUM PLATE
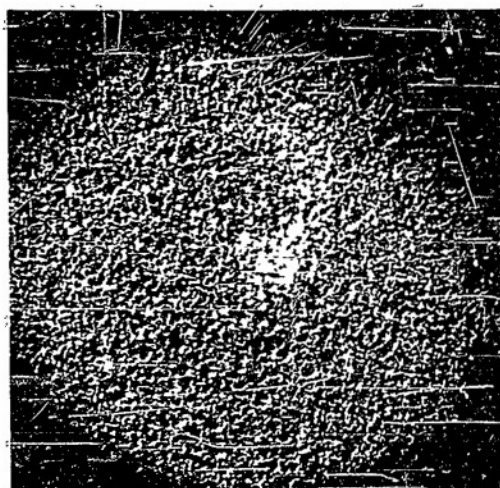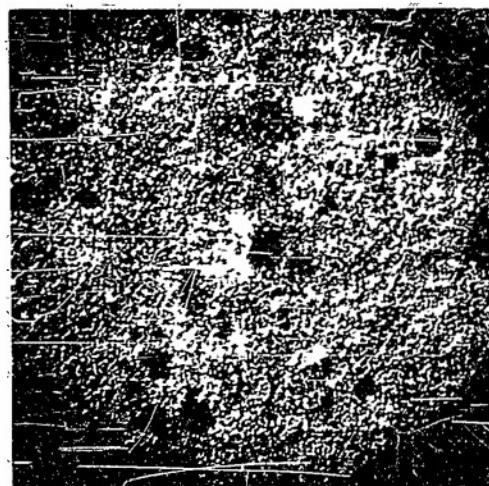


305 VOLTS          C                              F
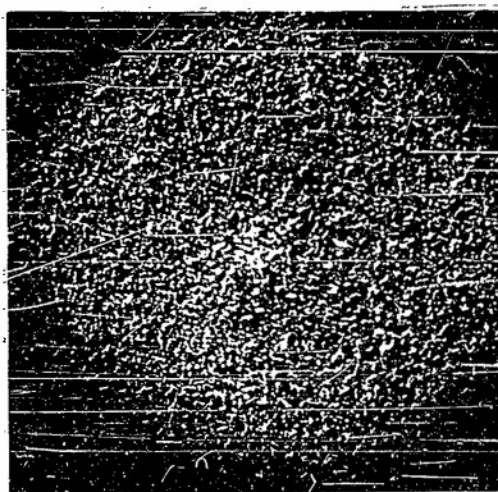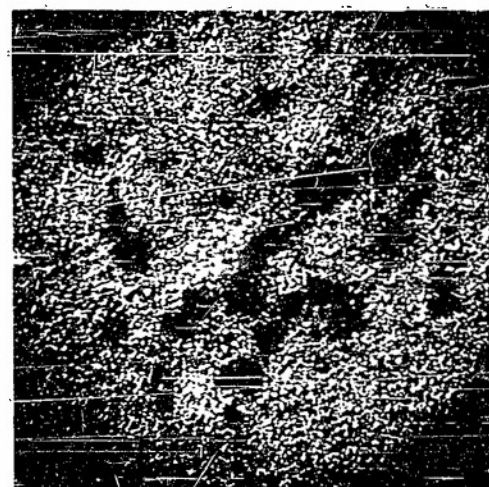
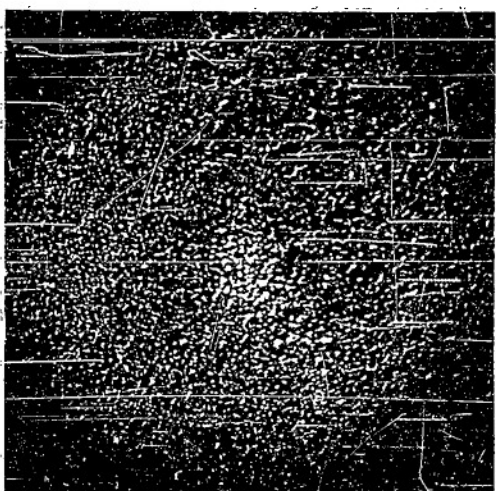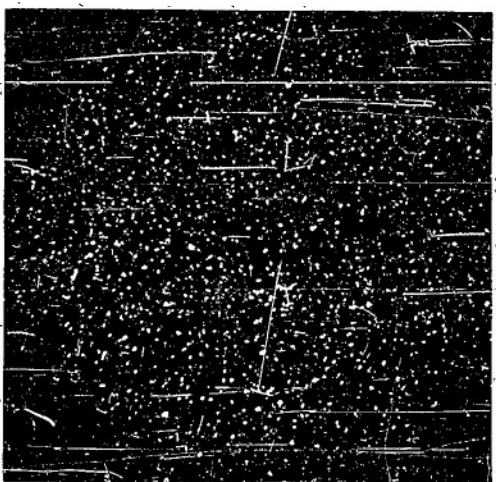151 VOLTS          B                              E
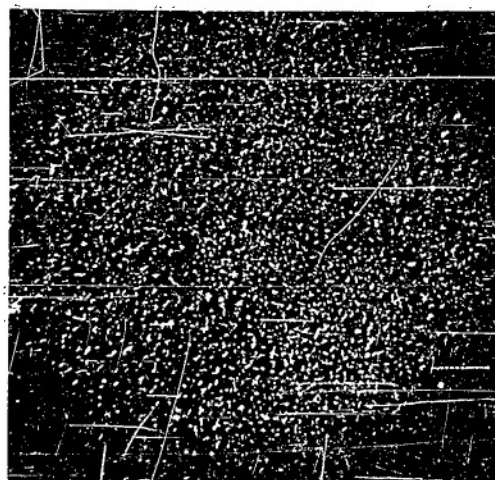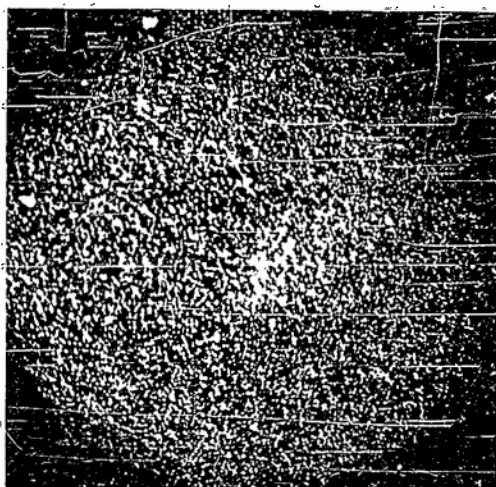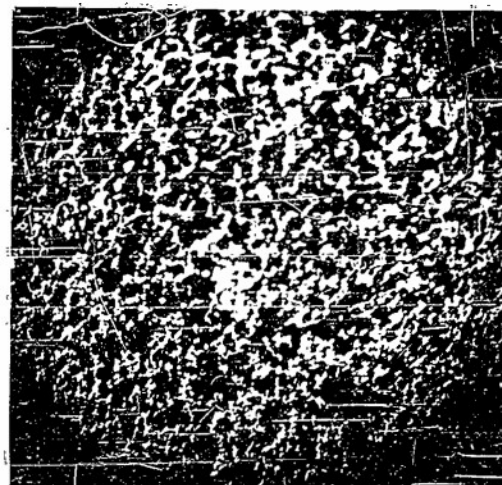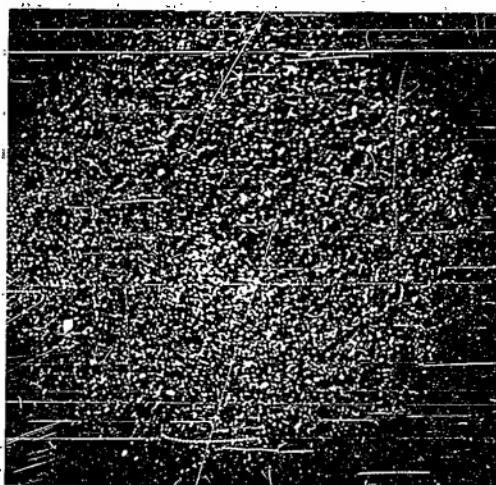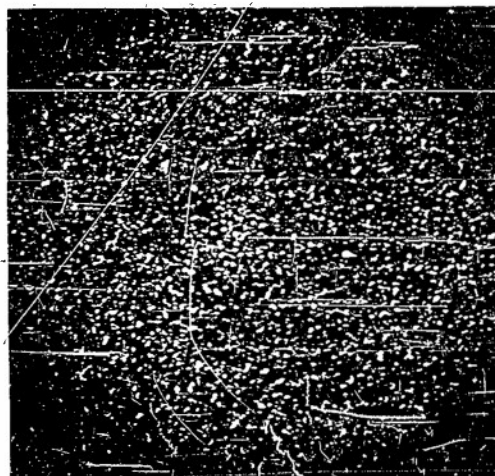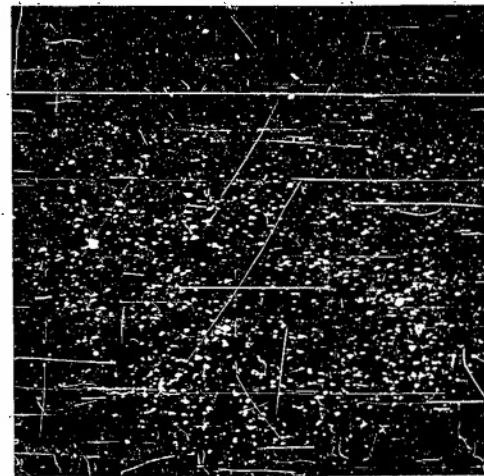
57 VOLTS          A                              D          67105

FIGURE 150.  POWDER-CLOUD DEPOSITION OF Aij-WET POWDER
              ON DEVELOPMENT-TEST PLATE AND SELENIUM PLATE

-489-

Tests on the polarity of cloud showed that polarity was dependent both upon the manner in which the cloud was produced and the moisture content of the powder. In these tests, the cloud was created using the motor-driven, compartmented, developing box. The polarity was mostly negative (3:1) for the Alj fines (dry) powder. The grid had no effect on the polarity of the cloud, and clouds deposited from wet powders were more negative than those of dry powders.

## Experimental Work on Cloud-Particle Studies

Samples were taken from Alj powders and Alj fines. The powders were prepared as described in Quarterly Progress Report No. 5, page 407 and the Appendix. The Alj fines and part of the Alj sample were dried in a vacuum oven at 60°C. for four days. They were then transferred to a vacuum desiccator until ready for use. The other part of the Alj sample was placed in a humidity chamber for four hours at 75 per cent relative humidity before using.

Powder clouds of the above samples were created by using the motor-driven, compartmented box (for details, see Quarterly Progress Report No. 5, page 401) and were deposited on selenium Plate 10-3-49A and the development-test plate. The plates for both the wet and dry powder-cloud tests were cleaned and vacuum dried in a vacuum oven at 60°C, and kept in a vacuum desiccator until ready for use. On the development-test plate, the cloud was deposited on the metal areas which were maintained at the following approximate potentials: 0, 60, 100, 160, 215, 275, 300, and 350 volts. The selenium plate (10-3-49A) was

-490-

exposed in a camera to a gray scale and then developed. After the development-test plate and the selenium plate had been developed, they were examined under a stereoscopic microscope at a magnification of 40X and a monocular microscope at a magnification of 50X and 150X. The particle size and distribution were determined from the microscopic examination. For each powder and plate, approximately 1000 particles were observed. From these counts, the data in Figure 147, parts A and B, were plotted. In addition, micro- and macrophotographs were taken, some of which are shown in Figures 148, 149, and 150. The cloud deposit from all plates was electrostatically transferred and fixed on paper which had been previously vacuum dried.

In the experiments on polarity of the various powder clouds, the following procedure for testing was employed. The apparatus is shown in Figure 151. A bell jar with a narrow opening at the top was used. Through this opening, two copper wires were inserted, on the ends of which were suspended two copper electrodes (2-1/2 x 1-1/2 x 1/64 inches). The other ends of the copper wires were connected to the battery to maintain the electrodes at a potential difference of 180 volts (+90 volts and -90 volts). The bell jar rested on a wooden frame to permit the opening (9-1/2 inches in diameter) at the bottom of the jar to be sufficiently high to allow the various cloud generators to be inserted. The electrodes were suspended one inch above the bottom opening of the jar. They were carefully cleaned, weighed, and dried before using. After each test, the electrodes were immediately weighed and the ratio of positive to negative determined. The data in Table 40 show the results under various conditions.

+ 90 V.    − 90 V.

COPPER ELECTRODES

CLOUD GENERATOR
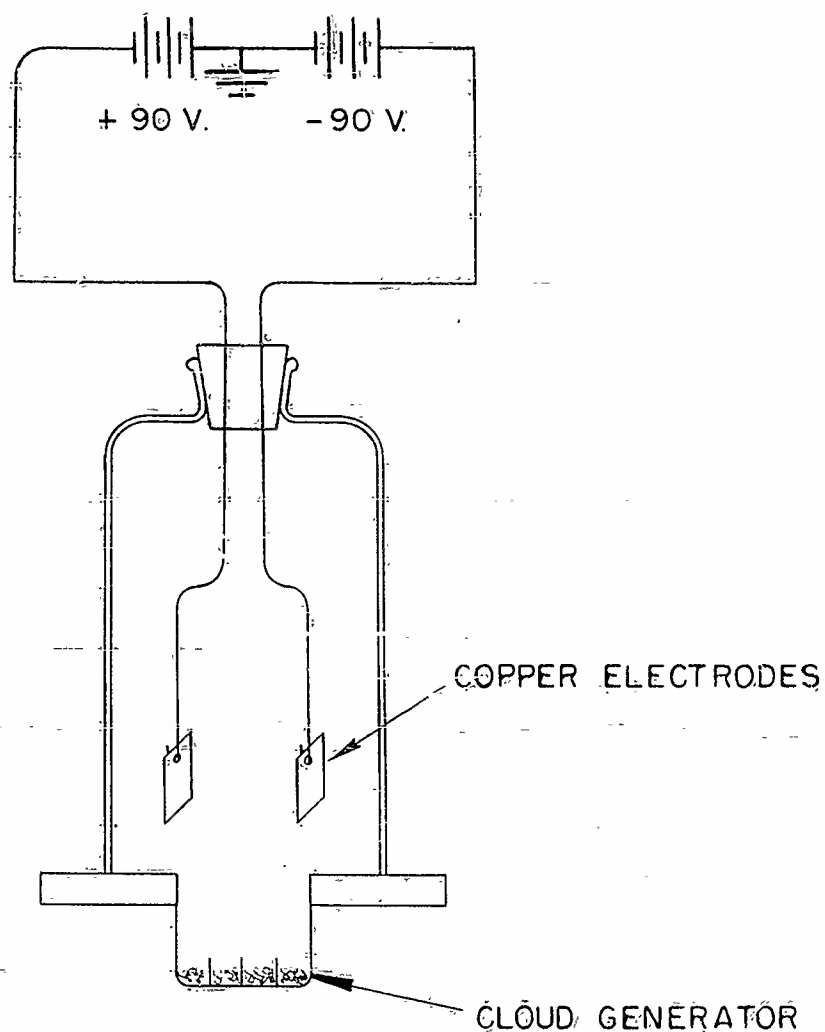
FIGURE 151. APPARATUS FOR DETERMINING THE RATIOS OF POSITIVELY AND NEGATIVELY CHARGED PARTICLES.

TABLE 40.   POLARITY OF POWDER-CLOUD DEPOSITS

| Method of Cloud Development | Powders | | | |
| --- | --- | --- | --- | --- |
| | Aly (wet) Negative:Positive | Aly (dry) Negative:Positive | Aly fines (dry) Negative:Positive | AG-1 (wet) Negative:Positive |
| 1. Air Blown | | | | |
| Grid | — | — | — | — |
| No grid | 1:2 | — | — | 1:1.6 |
| 2. Hand-operated, compartmented, development box | | | | |
| Grid | 22:1 | 11:1 | — | — |
| No grid | 22:1 | 11:1 | — | — |
| 3. Motor-driven, compartmented, development box | | | | |
| Grid | — | 1.7:1 | — | — |
| No Grid | 2.3:1 | 1.4:1 | 3.0:1 | — |

-492-

Discussion of Cloud-Particle Experiments

From the photographs in Figures 148, 149, and 150, it can be seen that the treeing effect is virtually eliminated when dry powders are used. The deposits from each of the three powder clouds on the development plate are uniform regardless of the powder used, i.e., wet or dry (see Figure 148, plates A, B, and C; Figure 149, plates A, B, and C; and Figure 150, plates A, B, and C). This, however, is not the case for the deposits on selenium plates, where a great number of powder-deficient areas are observed. The Alj fines (dry) deposit on the selenium plate, while not entirely devoid of powder-deficient areas, is definitely finer textured than deposits from the other powders. The powder-deficient areas for the "fines" are, on the average, at least an order of magnitude smaller. The distribution curves of the three types of deposited powder show a great predominance of particle sizes in the three-micron range, Figure 147, part B. The curves for the powders before deposition, Figure 147, part A, show maxima at 0.8 microns for the Alj fines and 3.0 microns for the Alj. The significant differences between the two sets of curves (Figure 147, parts A and B) are: (a) The maximum in the Alj fines powder has shifted from 0.8 microns to 3.0 microns, (b) in the case of the Alj powders, the maximum has not been altered, and (c) smaller maxima appear at the larger particle sizes for the wet Alj powder. These seem to be real rather than a peculiarity of the statistical method of counting or preparing the data. There is no good explanation for the appearance of these smaller maxima.

-493-

At the present time, no fundamental information is available to explain the fact that particle-size distributions are so nearly the same in the powder deposit when they are so different before the cloud is created. The two possibilities stated in the last Quarterly Report, i.e., aggregation and selection, still seem to offer the best explanations.

The aggregation hypothesis has a evidence in the literature[*] to support it. In creating the powder cloud, particles of both positive and negative charge are produced. Either through attraction of these oppositely charged particles, gravitational attraction, or through the normal agitation of the cloud, particles will collide. In such a collision, it is possible that local and temporary heating occurs at the contact surface. It can be sufficiently high to cause the particles to fuse the resin.

It is also possible that with the voltages, geometry, and method of cloud production used, there may be a strong selective attraction of particles in a given size range. Particles in the three-micron range may experience much stronger forces pulling them out of the cloud, perhaps by reason of a higher charge-to-mass ratio, than particles in other size ranges. This would mean that, though there were a great many more particles less than three microns in size in the case of the fines, the majority of particles deposited would still be taken from the three-micron range. This too could aid the agglomeration.

The experiments show that the Alj fines (dry) powder will produce the most uniform deposit and that particle size and distribution have a bearing on the type of deposit produced.

[*] J. Frenkel, Jour. Appl. Phys., 5, 25 (1941).

Another significant factor to be considered is the serious differ= ence between the deposits on the development-test plate and the selenium plate. Since the deposits on the development-test plate are uniform whether the powder is wet or dry and the deposits on the selenium plate are affected both by the wetness and particle-size distribution of particles, it would seem that the selenium plate possesses potential gradients which are responsible for the nonuniform deposit.

In so far as further work on the powder cloud is concerned, it is believed that the following should be considered:

(a) Alj fines (wet) powder-cloud deposits should be made on both the development-test plate and a selenium plate, since the Alj fines (dry), which is vacuum dried and maintained in that state, is not too practical for use in the field.

(b) Powders with still finer particle-size distributions should be made and tested.

(c) Tests with the hand-operated, compartmented box should be run for polarity, particle-size distribution, and wetness to determine the effect of a very predominant polarity (minus, see Table 40) on deposits.

(d) Other powders, such as AG-1 and AG-1 fines, should be tested to see if any correlation between compositions can be found.

(e) Investigate new carriers to determine their effect on polarity of the powders.

(f) Investigate the use of materials other than aluminum for use in the development box to determine the effect on the polarity and charge.

(g) Determine the magnitude of the charge on individual particles and the total charge that would occur in a powder cloud.

## Cascade Development

Previous experiments have indicated that the powder-carrier cascade method of developing electrophotographs has certain advantages over powder-cloud methods. The most important advantage is the simplicity of the method. The chief disadvantages are slower photographic speed and inferior definition in the final print. (See Quarterly Progress Report No. 5, pages 412-414.)

In the previously reported experiments, the cascade method was evaluated using positively charged plates and a powder-carrier combination formulated to develop positively charged images. In the work reported here, plates were charged negatively, and a negative powder-carrier combination was employed. Results indicate that the powder-carrier method has a slightly slower photographic speed than powder-cloud methods and the latitude of the method is somewhat limited, but that definition and picture quality of cascade-developed pictures are comparable to those of powder-cloud pictures.

The cascade method used was similar to the method described on page 413 of Quarterly Progress Report No. 5 except that negative charging and developers were used. The developers consisted of 5.6 per cent of

either G-1* or Magnetic** powder mixed with 94.4 per cent polystyrene*** carrier.

The subjects photographed included both outdoor scenes and gray scales. The curves in Figure 152 were plotted from reflection densitrometric measurements on the original gray scales and their reproductions. These curves indicate (1) a variation in black-area density from print to print [which has not been accounted for] and (2) a latitude of density range of about 0.6.

A study of the outdoor scene photographs showed that the photographic speed of the method was slower than that of powder-cloud development. This slower speed was apparently due to the fact that negative light decays for all selenium plates are slower than the positive light decays. Comparison between positive powder-carrier cascade development and positive powder-cloud development show that those two processes have roughly the same speed.

Figure 153 is an outdoor picture developed from a negatively charged plate by powder-carrier cascade. This picture shows the limited latitude of the cascade process. However, the picture also shows the fine definition and detail that can be obtained with the cascade method, and the intermediate grays that the method can produce.

---

\* See Quarterly Progress Report No. 5, page 471.

\*\* Magnetic Powder No. 10 as described in Progress Report No. 43 on Xerography to The Battelle Development Corporation, page 770; 60 per cent Manjak (Allied Asphalt and Mineral Corporation, New York, New York); 40 per cent Mapico Black (Binney and Smith Company, New York, New York) mixed on a rubber mill and micropulverized.

\*\*\* Polystyrene Beads, Type P-8 (The Koppers Company, Pittsburgh, Pennsylvania), screen cut above 35 mesh.

BATTELLE MEMORIAL INSTITUTE

O-14172
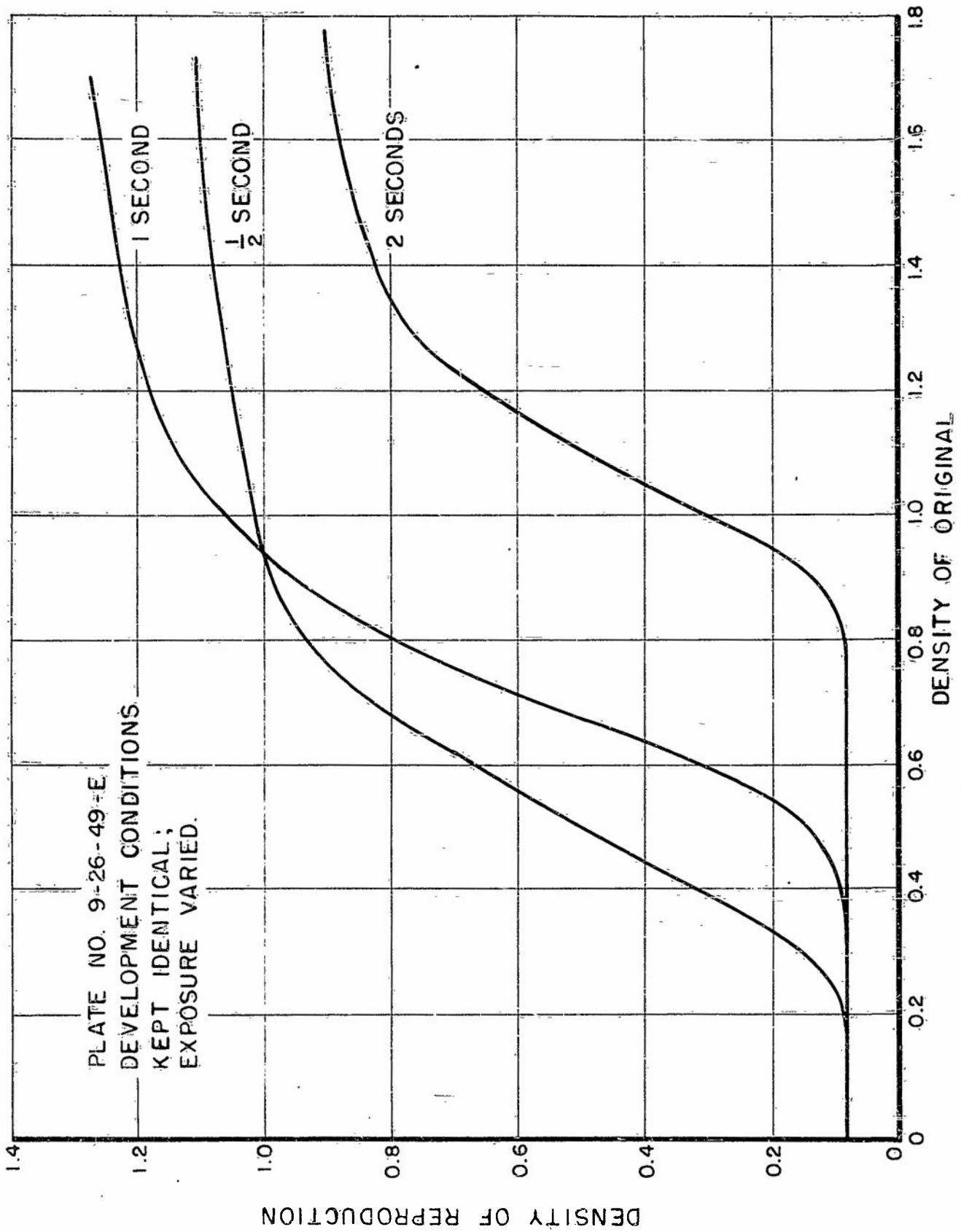


FIGURE 152. DENSITY CHARACTERISTICS OF CASCADE-DEVELOPMENT METHOD.
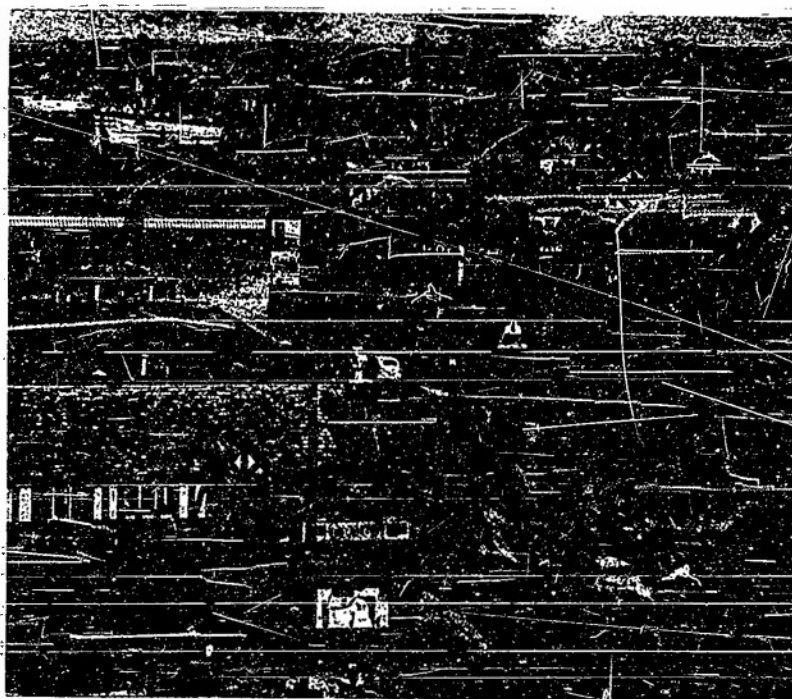
67120

PLATE NO: 9-26-49-E
DEVELOPMENT: POWDER-CARRIER CASCADE, NEGATIVE
DATE: 11-1-49

FIGURE 153. CASCADE-DEVELOPED OUTDOOR PICTURE

The experiments described above did not involve the use of a grounded metal electrode held just above the plate during development. For some reason, the negative developers are able to fill in large dark areas without the use of a grounded electrode. Furthermore, experiments using such an electrode showed that it had little effect on the quality of the picture produced, and seemed to decrease the effective photographic speed.

Because of the difficulty of controlling the development with an electrode, and the limited latitude of prints produced by powder-carrier development, work on this method has been discontinued.

## Spray Development

Methods of developing electrophotographic images using liquid sprays have been briefly studied and evaluated. This work has shown that spray development can produce electrophotographs as good as the best powder-cloud-developed pictures. However, the work has also shown that, with respect to a camera application, there are practical difficulties in spray-development methods which appear to be more serious than those of powder-cloud-development methods.

All of the spray-development methods tried in this work involved directing a fine liquid spray at a selenium electrophotographic plate that had been charged and exposed in the usual manner. An artists'-type airbrush (Type VL-1, Paasche Airbrush Company, Chicago, Illinois) was used to generate the spray. A variety of inks and pigment materials were sprayed.

In the first experiments with the spray method, the airbrush was charged with India Ink and the spray was directed at an exposed plate held about two feet in front of the airbrush. In this case, the spray deposited quite uniformly on the plate without developing out an image. However, when the spray was directed through a corona discharge, the ink produced a rough-textured image on the exposed plate. A similar, but better, image was obtained when the India Ink spray was directed through a small ring close to the airbrush nozzle and held at a high potential with respect to the nozzle. Placing a fine-wire grid just in front of the plate during development did not appreciably improve the quality of these images.

Microscopic examination of the ink deposit showed that the image itself was produced by very fine droplets. There was a high density of these fine droplets in the highly charged area of the plate, and none of the finer droplets in the highlight areas of the exposed plate. However, there was a fairly uniform scattering of larger droplets over all of the plate. Apparently, the larger droplets of the spray had enough momentum to be essentially unaffected by the electric field of the plate. In order to reduce this background of larger droplets, the plate was placed parallel to the direction of the ink spray during development. It was placed directly over the fine-wire grid in such a position that the frame of the fine-wire grid shielded the plate from the direct spray. The plate was then developed only by droplets carried near the plate by the turbulence around the grid frame. This arrangement eliminated most of the larger droplets, and also caused the plate to be developed very uniformly.

-499-

The final arrangement of the apparatus is sketched in Figure 154. Minor variations in this arrangement caused only minor changes in the resulting development. Thus, changing the distance between the plate and the airbrush changed the speed and sometimes the uniformity of development; changing the ink-feed rate also changed the time for development, without greatly affecting the droplet size, etc. In most cases, the charging ring was held at a potential of +1000 volts with respect to the nozzle. The airbrush was operated at a pressure of 30 pounds per square inch, and was adjusted to feed the ink at the maximum rate. In most cases, the spray was turned on for 20 seconds.

A variety of inks and pigment materials were used with the arrangement described above. With some materials, the charging ring charged the spray; with other materials, it had very little effect. In all cases, however, an image was produced. These images varied chiefly in texture, density, and their ability to be transferred and fixed. The results with the different materials are summarized below.

1. Water-base inks (undiluted): the spray was charged by the charging ring. The image developed on the plate appeared to be acceptable, but it was not possible to transfer the image to paper.

2. Oildag* (10 per cent solution in carbon tetrachloride): the charging ring had little effect on the polarity or quantity of charge on the droplets. A fine-grain picture was developed, which could be partly transferred to paper by pressure. The resulting print was much too light.

* Acheson Colloids Corporation, Port Huron, Michigan.

NOZZLE DETAIL
(4 TIMES ACTUAL SIZE)

INK FEED

AIR FEED

AIR BRUSH

CHARGING
RING

SPRAY
PATTERN

12"

$\frac{1}{3}$ ACTUAL SIZE.

PLATE

FINE-WIRE GRID
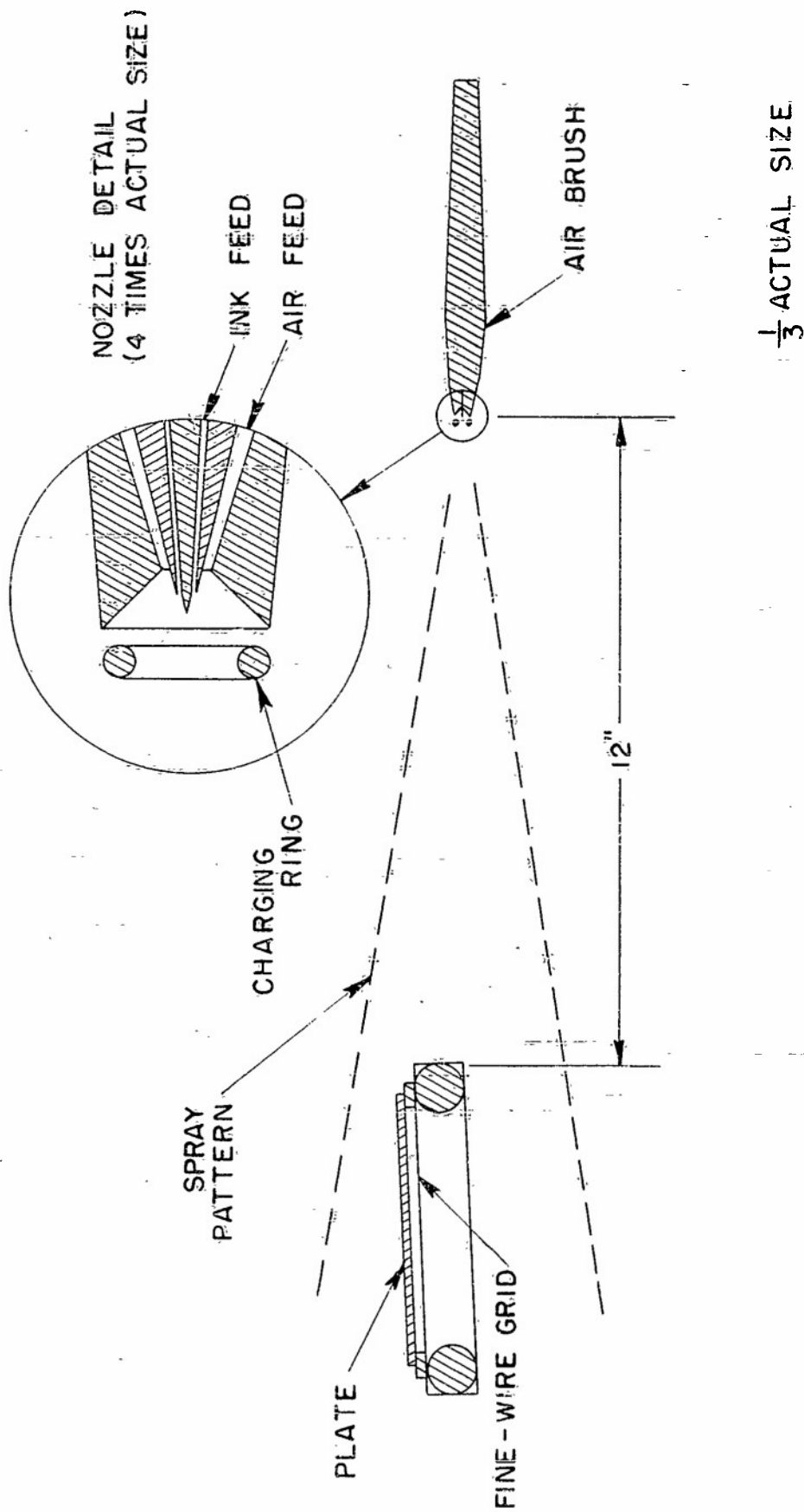
FIGURE 154. APPARATUS USED FOR SPRAY DEVELOPMENT OF
ELECTROPHOTOGRAPHIC PLATES.

3. Printer's ink (10 per cent solution in carbon tetrachloride): the charging ring had little effect on the charge of the droplets. A fine-grain image was obtained which could be transferred to paper by pressure alone, producing an acceptable print.

4. Dyes (5 per cent solution in ethanol): the spray was charged by the charging ring. Most of the alcohol of the solution evaporated before the spray reached the plate so that a dye-powder image was formed. This powder image could be partially transferred to paper by pressure, where the final print could be fixed and intensified by moistening with solvent.

5. Water-soluble mimeograph ink (20 per cent solution in water): the spray was charged by the charging ring. A somewhat rough-appearing image was developed on the plate. This image, though sticky to the touch, transferred poorly to paper under pressure.

6. Lampblack* (10 per cent dispersion in methanol): the spray was charged by the charging ring. The lampblack deposited dry and gave a fine-grain image on the plate. The image could be transferred electro-statically or by a pressure-sensitive adhesive, and the resulting print was of good quality.

Of all the materials used, the printer's ink and the lampblack gave the most acceptable results. The photographs obtained using the lampblack seemed a little better than those made with the printer's ink, but the process was simpler using the printer's ink. Figure 155 is a reproduction of a photograph produced by spraying a lampblack dispersion.

---

* No. 10 Lampblack, Monsanto Chemical Company, Camden, New Jersey.
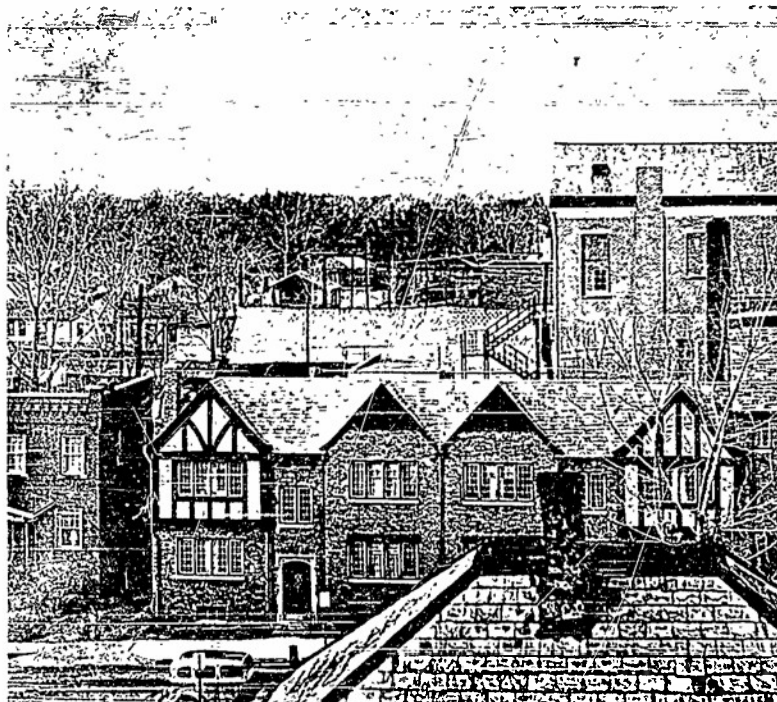
67121

PLATE : 9 -15 -49B
DEVELOPER : LAMPBLACK (10 PER CENT ) IN METHANOL
DATE : 11-16-49 , 1 P.M.
SPEED : A S A 4 (SLIGHTLY OVEREXPOSED )

FIGURE 155. LIQUID -SPRAY -DEVELOPED ELECTROPHOTOGRAPH

-501-

The photograph reproduced is one of the best electrophotographs developed by a liquid-spray method. It was transferred by pressing a moist gelatin-coated paper onto the plate after development. Although the lampblack images can be transferred electrostatically, the corona discharge sometimes disturbs, or "explodes", the thicker deposits.

In all of the liquid-spray methods, it was not possible to use granular material to clean the plate after transfer of the image. With the inks and dyes, the plates could be easily cleaned by an alcohol or carbon tetrachloride wash. However, a much more vigorous scrubbing was necessary to remove all traces of the lampblack. Often this scrubbing was sufficient to scratch the plate.

Following are the conclusions drawn from this work on liquid-spray development methods:

1. Liquid-spray development methods can produce photographs of quality equal to or better than that of photographs produced by powder-cloud-development methods.

2. None of the advantages or disadvantages of the liquid-spray methods appears to have outstanding importance. Included in the advantages of the process are: (a) a wide variety of inks and pigment materials may be used; (b) in many cases, the amount of charge on the spray may be easily controlled; and (c) with drying inks [such as printer's ink]; transfer and fixing problems are simplified.

Among the disadvantages are: (a) the liquid-spray methods do not seem to lend themselves to compact forms of developing equipment; (b) the plates are more difficult to clean; and (c) most of the

liquid-spray methods depend in part on solvent evaporation, which is a temperature-dependent process.

## Smoke-Cloud Development

In pictures taken by the use of phosphor plates, and also in experiments on the development-test plate, the powder deposit on the image is found to have a texture of considerably larger scale than the powder-particle size. It is reasonable to guess that this texture is caused by a tendency of the powder to "tree", due to induced dipole moments in the particles. If this guess is correct, a smaller powder particle will produce a finer texture in a photograph.

A series of experiments was made in the search for smaller developing particles than are available in present powders.

Vapor was first tried with limited success. Colored smokes were then tried and very promising results were obtained. Figure 156 shows a contact print developed by a colored smoke.

The colored smoke is generated by a chemical reaction that furnishes heat to vaporize a dye. Smokes of nearly any color can be produced. The smoke-producing material is placed in a capsule with an orifice at one end through which the smoke escapes on burning. The fine grain quality demonstrated in this print is attributed to small particle size. It may also be due to more desirable electrostatic properties than the currently used (Alj) electrophotographic powders have.

67112

FIGURE 156. CONTACT PRINT ON A SELENIUM PLATE (9-15-49 B)
USING A SMOKE CLOUD FOR DEVELOPMENT

-503-

## ADHESIVE FIXING AND TRANSFERRING

### P. G. Andrus

An investigation of the possibility of using pressure-sensitive adhesive tapes for fixing or transferring powder electrophotographic images has been started. The preliminary experiments carried out in this investigation have included fixing images by applying transparent adhesive tapes to powder images that had been electrostatically transferred to paper. Transfer of powder images has been accomplished by applying pressure-sensitive adhesive-coated film to developed electrophotographic plates. None of the methods or materials tested has been entirely satisfactory, but the general methods appear to be practical.

In experiments on fixing powder images using transparent tape, "Scotch" brand cellulose tape No. 600* and Stik-on No. 158** were pressed onto powder images on paper using a lithograph proof press. The gray areas of the print were satisfactorily fixed, but, in the black regions, the adhesive did not penetrate the entire thickness of the powder. When that happened, a loose powder pocket was formed. The "Scotch" brand tape retained more powder than did the Stick-on. The adhesive on "Scotch" brand plastic film tape No. 471 (which was not transparent) penetrated somewhat thicker layers of powder; with this material, the tape just barely adhered to the backing paper in the black areas.

---

\* Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

\*\* Eugene Dietzgen Company, Chicago, Illinois.

-504-

In experiments on transferring electrophotographic powder images, "Scotch" brand tapes and gelatin-coated paper were tested. Here again, the pressure-sensitive adhesive of the ordinary type of "Scotch" brand tape (No. 600) adhered to almost all of the powder in the gray areas, but did not transfer the powder from the thick areas. The No. 471 type of "Scotch" brand tape did remove black layers of powder from thick layers on the electrophotographic plate, as did wet gelatin-coated paper. The gelatin-coated paper consisted of photographic contact-printing paper which had been treated with a solution of sodium thiosulfate, washed, and left wet. All the adhesive materials used were applied to the electrophotographic plate using the lithograph proof press.

Except for the fact that the process required water and time for drying, the adhesive transfer using gelatin-coated paper was more satisfactory than the usual electrostatic method. Nearly all of the powder was transferred, and the black areas that transferred could be easily fixed by the application of transparent pressure-sensitive adhesive tape to the gelatin-coated paper.

The work on transferring and fixing, using pressure-sensitive adhesive tapes, will be continued by testing additional commercial tapes, and by searching for adhesive materials with the penetration, tack, permanence, and color (or transparency) properties required for satisfactory transfer or fixing operations.

BATTELLE MEMORIAL INSTITUTE

## SELENIUM PLATE-PREPARATION WORK

J. L. Stockdale and O. A. Ullrich

### Summary

In the preceding Quarterly Report (No. 5), data were given on
the effect of various cleaning treatments and various undercoating
materials on aluminum-backed electrophotographic plates. It was reported
that anodizing the aluminum plate before depositing the selenium resulted
in very slow dark-decay rates. This anodizing also caused the formation
of large circular powder-deficient areas in continuous-tone prints.

It has been found that, if brass is used as a backing-plate
material, not only will the dark-decay rates be slow, but print quality
will be good as well. Prints made using these brass-backed plates
exhibited considerable graininess, however. This occurrence of grain
and powder-deficient areas in prints has definitely been traced to over-
charging of the plate as the principal cause. Overcharging, undoubtedly,
is not the only cause of grain, but it is at present a most important one.

Using brass as a backing-plate material, electrophotographic
plates were prepared with various special treatments. The best prints
were made, however, from plates which had received no special treatment;
that is, they were prepared by cleaning with a polishing compound,
synthetic detergent, vapor degreasing, and depositing the selenium with
the plate maintained between 60 and 65°C. during vacuum evaporation.

-506-

## General Considerations on Plate Studies

Much work has been done in the past on the preparation of selenium electrophotographic plates using aluminum as the backing-plate material. The aluminum itself has been treated in a variety of ways. Many different undercoating materials have been applied to the aluminum before the selenium was deposited. Plates were subjected to various heat treatments, both during and after preparation. The results have been distinctive only in the difficulty of their evaluation. Certain valuable information has been obtained, however. This includes, in part, information concerning:

1. The dependence of potential-decay characteristics on plate-preparation temperature.

2. The dependence of spectral sensitivity on plate-preparation temperature.

3. The lack of dependence of potential-decay characterisitics on chamber pressure (up to 25 microns) during evaporation.

Another result, and equally important, is that plate character-istics are extremely dependent upon the character of the interface between the selenium and the backing plate.

The character of this interface is fully as important as the condition of the outer surface of the selenium. It can, apparently, give rise to fast dark-decay rates and a large difference between positive- and negative-potential characteristics. It can affect the magnitude of the potential accepted as well as other minor electrical properties. But, further, this interface plays a vital role in print-making quality.

-507-

Certain small, irregularly shaped blemishes in prints can be attributed to some discontinuous characteristics of the interface layer.

Blemishes in electrophotographic prints can be divided into five general groups as follows:

1. Small pin-point powder-deficient areas.

2. Large, circular, powder-deficient areas ranging around one millimeter in diameter.

3. Fairly large, irregularly shaped, powder-deficient areas, ranging from one to five millimeters in major dimension.

4. Long, narrow, powder-free, or powder-excess streaks, following scratch marks or rolling marks in the backing plate.

5. A grainy structure, apparently due to irregular deposition of the powder in clumps or ridges.

The direct cause of the powder-deficient blemish is a local potential irregularity of the plate. The graininess may be due either to local potential irregularities on the plate or a nonuniformity of the development cloud. The underlying cause of the potential irregularity is not understood. It could arise from nonuniformity of (1) charge acceptance, (2) dark-decay rate, or (3) light sensitivity over small areas of the plate. Any of these three possible nonuniformities could result from structural differences in the selenium, differences in selenium film thickness, or local interface-property variations. The structural differences could have developed during the deposition of the selenium as a result of local interface variation, or they could have developed later. Overcharging, with resultant breakdown of the selenium,

-508-

could change it from its insulating form to a more conducting form. Such breakdown might logically arise from a rough backing-plate surface or from the breakdown of a dielectric interface film. It might also arise from holes in the selenium caused by dirt on the backing plate while the selenium is depositing.

Four items of experimental evidence which bear directly on these questions involve (1) the use of a perfectly smooth backing-plate surface, (2) the use of a grid to control the potential to which the plate is charged, (3) the effect of anodizing aluminum backing plates, and (4) the comparison between the properties of brass and aluminum as backing-plate materials.

In the first experiment, involving the use of a smooth backing plate, selenium was deposited onto a glass plate. This plate was coated with a conducting layer (copper or aluminum) by vacuum evaporation in the same manner as that in which the selenium was deposited. The appearance of irregular powder-free areas and graininess was reduced but not eliminated. The tendency to form circular powder-deficient spots was increased. Remaining graininess can be attributed to potential irregularities in the selenium or to the developing process. It cannot, we believe, be due to surface roughness.

The second experiment involves the use of a potential-control grid. Here, the potential to which the plate is charged is limited so that the plate will not be subjected to breakdown voltages. When plates are charged using this grid, instead of open corona wires, a marked

-509-

reduction in the number and size of powder-deficient areas results. The graininess is also appreciably reduced, particularly in the denser regions of the print.

The third item of experimental evidence involves, as listed above, the effect of anodized aluminum backing plates. The effect of the aluminum oxide dielectric layer was to greatly increase the number, and, often, the size, of circular powder-deficient spots over those resulting from unanodized aluminum. In general, a thicker oxide layer gave larger and more numerous powder-free areas. The anodic layer had a very high leakage resistance before breakdown, as evidenced by the exceptionally slow dark-decay rates.

The fourth experimental result, this one also demonstrating the effect of interface layers, is the difference between brass and aluminum as backing-plate materials. The dark-decay rates and continuous-tone image quality are very much better for brass than for aluminum. This is apparently due entirely to an interface layer which has more beneficial properties in the case of the brass. An analysis of the chemical properties of selenium, aluminum, copper, and zinc indicates a much more intimate chemical bonding between selenium and brass than between selenium and aluminum. Differences in surface quality between the aluminum and the brass backing metals used cannot account, to any great extent, for the type of improvement noted.

In summation, it can be said that using a very smooth backing plate improves grain quality and reduces blemish appearance but does not eliminate either of these. Potential irregularities on the surface of

-510-

the selenium or in the selenium are the direct causes of the grain and blemishes. These irregularities may be due to structural variations in the selenium or may be due to discontinuous interface films. The evidence cited points strongly to the interface film as being the seat of the trouble, particularly since it undoubtedly can affect the selenium structure as well. Since it appears that plates which take a higher potential have faster effective speeds, it will be especially valuable to overcome the tendency to breakdown which is so dependent on interface layers.

Consequently, a continued study of the effect of interface films and backing plates should give the most fundamental information about plate properties.

Dark- and light-decay rates and fatigue in plates which are charged to potentials less than the maximum the plates can accept will be studied. Information resulting from such work is needed to establish charging-exposure and development-time sequences for the electrophotographic camera.

## Experimental Work on Selenium-Coated Plates

The principle defects in selenium-coated electrophotographic plates have been (1) excessively fast dark-decay rates, particularly for positive-potential charging; and (2) the lack of uniformity of potential characteristics over the plate surface. This lack of potential uniformity causes powder-deficient areas and, at least in part, grainy images. Various treatments of aluminum backing-plate material have been

-511-

previously reported. Table 41 summarizes recent experiments which have been directed toward improving potential and image-forming characteristics. The following sums up the important information given in the preceding table:

1. Anodized aluminum produces consistently slow dark-decay and fast light-decay rates, but, apparently, prevents the plate from accepting a high potential and definitely causes large powder-deficient spots in prints made from these plates.

2. Polished (photoengravers') brass as a backing-plate material is much superior to unanodized aluminum from both potential and image-forming standpoints. It is about equal to anodized aluminum in positive-potential dark-decay rates. It is much superior to anodized aluminum in image formation.

3. Copper has characteristics comparable with brass when the plate is first made. After several weeks, sufficient reaction between the selenium and the copper has taken place that the selenium film will very readily peel away from the copper. As yet, no such tendency has appeared with the brass-backed plates.

4. Zinc, chromium, and nickel do not appear to offer any advantages over brass. Prints made from selenium-coated plates of these metals are generally inferior in quality.

5. The cleaning technique for brass, which consists of polishing with Glass Wax*, washing with a synthetic detergent, rinsing with water, rinsing with isopropyl alcohol, and degreasing in isopropyl alcohol

---

* Glass Wax, manufactured by The Gold Seal Company, Bismarck, North Dakota. Composition - 75 per cent water, 15 per cent petroleum fraction (naphtha), 7.5 per cent abrasive, ammonia, emulsifier, and coloring agent.

TABLE 41. EFFECT OF VARIOUS TREATMENTS ON THE CHARACTERISTICS
OF SELENIUM ELECTROPHOTOGRAPHIC PLATES

| Item Number | Backing Material | Selenium Thickness, Microns | Treatment | Plate Appearance | Electrical Properties for Positive Potential Charging | Image Quality Using Open Corona Charging Wire |
|---|---|---|---|---|---|---|
| 1 | Aluminum | 10-20 | Anodize in trisodium phosphate (see quarterly report No. 5, pages 424-29) | Clear | Very slow dark-decay rate, positive - 10-20 per cent | Breakdown of anodic film causes prominent powder-deficient areas (potential-control grid not used in charging). |
| 2 | Aluminum | 10-20 | Standard - detergent wash and isopropyl vapor degrease | Clear | Generally acceptable but often excessively fast dark-decay rates | Generally good with cascade development. Generally poor with powder-cloud development because of powder-deficient areas. |
| 3 | Aluminum | 15 | Surface grained with sand until completely light-scattering at normal incidence. No further cleaning | Fine gray-appearing surface (not crystalline) | Slow dark-decay rates | Fine-grained print quality with powder-cloud development, but had unacceptable powder-deficient areas. |
| 4 | Aluminum | 15 | Surface grained with thirty-mesh carborundum | Ditto | Fast dark-decay rates greater than 40 per cent | Many large powder-deficient areas, but otherwise fine-grained texture. |
| 5 | Brass | 10-60 | Photoengravers polished surface -slightly rippled but very shiney. Cleaning standard as in 2 | Clear and Smooth | Slow dark-decay rates-generally 20 per cent or less | Fine textured unless overcharged, which develops coarse-grained texture and powder-deficient dots. |
| 6 | Brass | 1-60 | Rubbed with Glass-Wax (see text, page 511) before degreasing | Clear | Dark-decay rates generally slower than for standard-cleaned brass | More consistently fine textured than standard-cleaned brass. |
| 7 | Brass | 10-20 | Grained with sand until completely light-scattering at normal incidence | Fine gray surface as in 3 | Good - as in 5 | Good - as in 5 |
| 8 | Copper | 15 | Either grained with sand or standard cleaning as in 2 | Clear or as in 3 | Fairly slow dark-decay rates | About equal to brass as in 5. Adhesion between selenium and copper becomes extremely poor in one weeks time. |
| 9 | Nickel electroplated onto copper | 15 | Standard degrease, as in 2 | Clear | Will accept only 150-to 200-volts potential (brass takes 5-700) fair decay rates | Low density and contrast-grain quality nearly as good as standard-cleaned brass. |
| 10 | Chromium electroplated onto copper | 15 | Ditto | Clear | Ditto | Ditto |

TABLE 41. CONTINUED

| Item Number | Backing Material | Selenium Thickness, Microns | Treatment | Plate Appearance | Electrical Properties for Positive Potential Charging | Image Quality Using Open Corona Charging Wire |
|---|---|---|---|---|---|---|
| 11 | Zinc vacuum evaporated onto copper | 15 | Copper standard as in 2, zinc deposited prior to evaporating selenium | Clear | Will accept 350-400 volts potential, medium dark-decay rate | Great number of powder-free areas-spots. Good density. |
| 12 | Zinc | 15 | Photoengravers zinc standard cleaning as in 2 | Clear | Fast dark-decay rate. | Print quality fair but not so good as brass in 5. |
| 13 | Brass | 10 | Brass standard cleaned, copper evaporated, then copper and selenium simultaneously and, finally, just selenium | Clear | Dark-decay rate very fast, practically no light sensitivity | --- |
| 14 | Brass | 15 | Sulfuric acid (6 per cent) dip, then standard cleaned as in 2, coat with crystalline selenium by holding plate at 120°C, then deposit remaining selenium at 60°. | Clear | Dark-decay rate very slow. | Prints fairly good. |
| 15 | Aluminum | 15 | Ditto | Scattering and streaked | Fairly fast dark-decay rate | --- |
| 16 | Brass | 15 | Brass standard cleaned as in 2, then coated with organic film, then placed in vacuum system and selenium evaporated | Clear -but rough due to dust particles in resin | Take extremely high potential, have fairly good dark-decay rates, and have high residual potential | Print texture good. Dark background due to high residual charge. Non-uniform organic film thickness causes streaks in print. |
| 17 | Brass | 15 | Brass standard cleaned as in 2, Undercoats of germanium and tellurium deposited by evaporation in same evacuation as selenium | Clear | Fairly good positive dark decays. (negative dark decays very fast) | Prints full of small powder-deficient dots. Coarse grain texture. |
| 18 | Brass | 15 | Brass standard cleaned, selenium deposited, followed by an extremely thin coating of germanium in same evacuation | Clear | Very fast positive dark-decay rate, (very slow negative dark-decay rate) | Prints full of small, black, powder-excess spots. Texture grainy. |
| 19 | Brass | 15 | Standard cleaned, coated with arsenic by evaporation in same evacuation as the selenium which followed | -- | Takes low potential, fair decay rates, high residual charge | Very grainy. |

TABLE 41. CONTINUED

| Item Number | Backing Material | Selenium Thickness, Microns | Treatment | Plate Appearance | Electrical Properties for Positive Potential Charging | Image Quality Using Open Corona Charging Wire |
|---|---|---|---|---|---|---|
| 20 | Brass | 15 | Same as 19 only undercoat with arsenic pentoxide | — | Maximum accepted potential is 10 volts | — |
| 21 | Brass | 15 | Brass standard cleaned, coated with selenium, then with a 2-wavelength-thick layer of zinc sulfide | Zinc sulfide layer badly cracked | Fair decay rates, high residual potential | — |
| 22 | Brass | 25 | Same as 21 only use magnesium fluoride in place of zinc sulfide | Magnesium fluoride layer badly cracked | Very fast dark-decay rate, no light sensitivity | — |
| 23 | Glass | 15-20 | Conducting film of copper evaporated before depositing the selenium | Clear (except for scattered drops of selenium) | — | Finer texture than from standard-cleaned brass in 5, but still had definite grain. |

vapor (more or less taken as standard), gives good results. An acid dip does not have any noticeable effect. The effect of the Glass Wax treatment, which is actually just an abrasive cleaning process, is not noticeable in some cases. In others, it shows a definite improvement in the grain texture of the image.

6. Undercoatings of organic films, metallic films (Te, Ge, Cu, As, and gray selenium), and arsenic pentoxide did not bring about any improvement of decay or image-forming properties. The organic films appeared to give somewhat finer grain, but, due to their high resistance and dielectric strength, they caused a high residual potential. Uneven thicknesses caused uneven background densities, also.

7. A coating of zinc sulfide on top of the selenium did not seem to affect the plate. A similar coating of magnesium fluoride caused a fast positive-potential dark decay. Both of these dielectric films exhibited many fine irregular cracks.

The experiments in which germanium and tellurium were evaporated as undercoats and germanium as a topcoat are particularly interesting. With these materials as undercoatings, the plate had good charge acceptance and slow dark-decay rates for positive-potential charging. For negative-potential charging, the tellurium-coated plate had a very fast dark-decay rate and the germanium-coated plate showed no charge acceptance at all. On the other hand, when germanium was deposited in an extremely thin layer (invisible to the unaided eye) on the top surface of the selenium, the potential responses were just the reverse -- fast positive decay and relatively slow negative decay. A positive-hole donor

-514-

action is indicated here. This phenomenon might be very valuable in a more fundamental study of selenium and its properties.

Undercoatings of gray selenium were prepared in an effort to get a chemically and electrically homogeneous conducting surface upon which to deposit the vitreous selenium. The crystalline layer was formed by evaporating selenium onto a backing plate held at 125°C. This resultant layer was about three microns thick. The temperature of plate was then lowered to 60°-65°C., and the rest of the selenium deposited. Plates made in this manner had good positive-potential characteristics, but extremely fast negative decay characteristics. This may also indicate a positive-hole donor action.

A gray-selenium undercoating as described above was prepared in a run in which a brass and an aluminum plate were mounted side by side on the temperature-controlled platen. The positive dark-decay rate on the brass was 20 per cent, and on the aluminum it was 50 per cent. They both accepted the same initial potential. Again, the superiority of brass over aluminum, with regard to decay rates, is demonstrated.

The effect of firing rate was studied. The firing rate which has been used as standard since February of 1949 has been such as to evaporate 10 grams of selenium in 10-12 minutes. For these firing-rate tests, films about 15 microns thick were prepared in 5, 15, and 60 minutes. Some spattering occurred in the 5-minute test, but this is incidental to the results. The only difference in positive-and negative-potential decay characteristics between any of these plates and a normal-run plate appeared in the 60-minute plate. Here, the negative dark-decay

rate was abnormally fast. This can be accounted for by remembering that negative decays become abnormally fast as the temperature of the plate enters the 70-75°C. range. Since the selenium structure is dependent not only on temperature, but also the time interval for which any temperature is maintained, the fast negative decay is explained.

## Investigation of New Materials for Electrophotographic Plates

Twelve new materials were investigated for photoconductive properties. These materials were deposited in thin films on polished brass plates by vacuum evaporation. Materials tested were: germanium, tellurium, arsenic, copper oxide, calcium sulfide, lead sulfide, bismuth trisulfide, titanium dioxide, cadmium sulfide, barium titanate, tin diselenide, and arsenic pentoxide. Of this group, only the last two, tin diselenide and arsenic pentoxide, would accept a measurable potential; dark-decay rates for all materials tested were very fast and only the arsenic pentoxide showed any light sensitivity.

## PHOSPHOR-COATED ELECTROPHOTOGRAPHIC PLATES

### D. Reynolds

In the experiments reported in the last quarterly report, the experiment proposed by Kallmann was shown to be feasible. That is, a zinc sulfide phosphor in a suitable binder can be quenched (given a very high dark resistance) by heating, and then charged after light exposure to a potential that depends on the exposure. The charging process most

-516-

suitable was found to be the corona process. The potentials accepted after different exposure times were found to decrease with time between exposure and charging.

One of the main reasons for initiating the phosphor experiments was the hope that a plate could be found that would retain an image for a long period of time. Hence, it seemed desirable to try other phosphors before concluding that the Kallmann method -- charging after exposure -- was effectively the same with respect to image permanence as the Carlson method -- exposure after charging -- previously used.

### Electrical Characteristics of Phosphor Plates

#### Influence of Light on Decay Characterisitcs

Plates were made using a 2225 phosphor (manufactured by the New Jersey Zinc Company). The bulk materials of the phosphor are zinc sulfide and cadmium sulfide. The phosphor was mixed in a one-to-one ratio by volume, with DC-996 silicone resin, and the slurry sprayed onto aluminum backing plates.

The dark and light potential-decay characteristics of the plates were determined. Data from a representative plate are given in the Table 42.

It is evident from the table that there is a considerable differential in charge accepted by the 2225-phosphor plates depending on the wavelength of light to which the plate is exposed previous to charging.

TABLE 42.   POTENTIAL-DECAY DATA ON PHOSPHOR-COATED
ELECTROPHOTOGRAPHIC PLATES

| Charging Potential, Volts | Exposure to Infrared Light, Minutes | Exposure to Visible Light | Dark Decay | | Maximum Accepted Potential, Volts |
|---|---|---|---|---|---|
| | | | Volts | Minutes | |
| + 7000 | 10 | -- | 25 | $4\frac{1}{2}$ | 630 |
| + 7000 | -- | Saturated | 95 | 4 | 432 |
| - 7000 | 10 | -- | 20 | $4\frac{1}{2}$ | 708 |
| - 7000 | -- | Saturated | 188 | 3 | 559 |

-518-

The main aim of the experiment, however, was to find whether the dark decay, rather than charge accepted, was influenced by the wavelength of light to which the plate is exposed. The data show that there is little such effect, if any. Plates exposed to white light take less potential, but have decay characteristics very similar to plates exposed only to infrared light. Figure 157 shows this effect qualitatively. Plates exposed to either infrared or white light have fairly rapid dark-decay rates at first, leveling off to extremely slow decay rates in less than five minutes. The effect is the same for both positive and negative charging.

## Effect of Repeated Charging

The question may be asked what the origin of the photoelectric currents in the electrophotographic plate may be. If the current is due to carriers from the sensitizing impurity, it seems that they might possibly be "used up" by successive exposures after charging, followed by the usual discharge period. In such case, the speed of the plate ought to decrease and the residual voltage to increase with successive chargings.

A phosphor plate was repeatedly charged with the same polarity and allowed to discharge.

It was found that, for both positive and negative charging polarities, the initial accepted potential and the residual potential decreased with successive chargings. The initial and residual potentials were restored to their original values by regeneration, i.e., by one
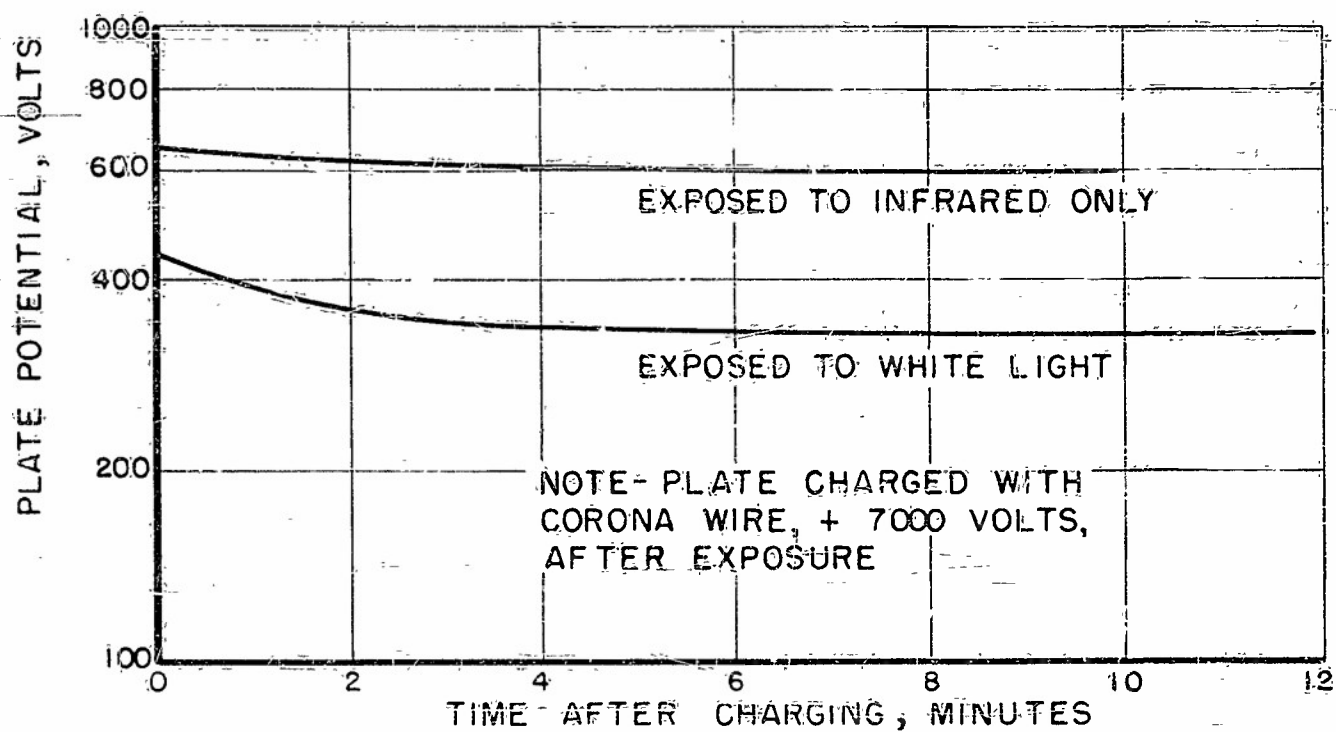
FIGURE 157. EFFECT OF INFRARED AND WHITE-LIGHT
EXPOSURE ON POTENTIAL-DECAY RATE
FOR 2225 PHOSPHOR PLATE.

-519-

charging with the opposite polarity before taking the next decay curve.

These results seem to show no exhaustion in the supply of carriers, if the number of carriers affects the plate speed.

These 2225 phosphor plates decay very rapidly in the light when used with the Carlson method —charge before exposure. They are faster than a selenium plate which has average speed. Electrometer data show the phosphor plates to be somewhat faster when charged negatively than when charged positively, as shown in Figure 158.

## Pictures Made with Phosphor Plates

Pictures made with these phosphor plates by the Carlson method have fair contrast but still have considerable grain. Out-door shots indicate an effective speed of ASA 25 or better. Pictures made using the Kallmann method were somewhat better in quality than by the Carlson method, but the speed was considerably less.

Pictures made using both methods with contact exposure are shown in Figure 159. A brush-type powder-cloud box was used, with the grid at ground potential.

## Effect of Pigment-to-Binder Ratios and Thickness of the Active Layer

Experiments were performed to determine the optimum thickness of the active layer and also the optimum pigment-to-binder ratio. These experiments were performed using a 2330 phosphor. The data obtained on the phosphor-to-binder ratio experiments are not entirely significant,
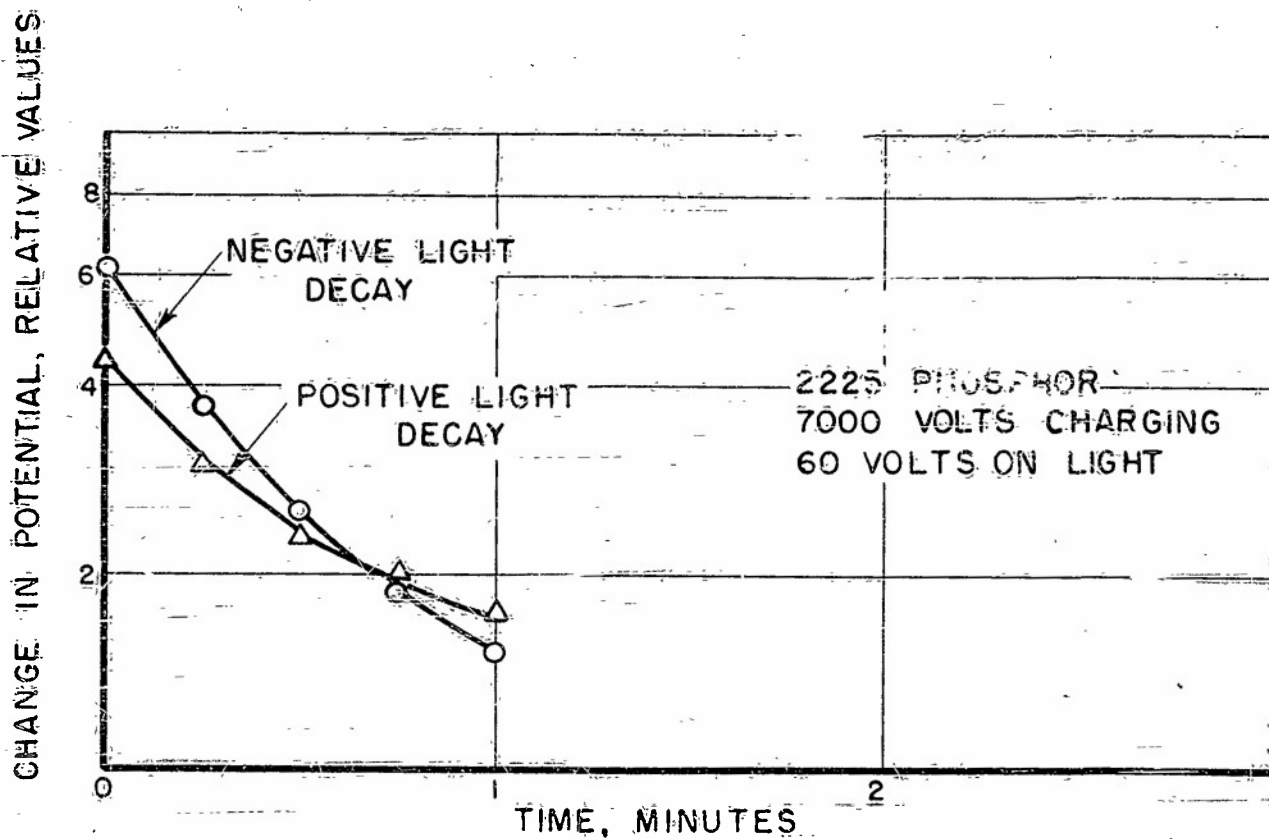
FIGURE 158. LIGHT-DECAY RATES FOR POSITIVE AND NEGATIVE
CHARGING OF A PHOSPHOR PLATE.

CARLSON METHOD
(CHARGE THEN EXPOSE)

A

KALLMAN METHOD
(EXPOSE THEN CHARGE)

B

NOTE: POSITIVE CHARGING, 6000 VOLTS. NO POTENTIAL-CONTROL GRID

FIGURE 159. COMPARISON OF THE CARLSON AND KALLMAN METHODS OF PRODUCING ELECTROPHOTOGRAPHIC PRINTS ON A 2225-PHOSPHOR PLATE

67114

as the thickness of the films was not uniform. More closely controlled experiments must be carried out before definite conclusions can be drawn, but it was found that the total potential accepted by the plate is greatest for a one-to-two phosphor-to-binder ratio. The light-decay rate was much faster for this ratio than for a one-to-one ratio.

Both the initial accepted potential and the light-decay half-time are roughly proportional to thickness.


## NEW APPARATUS

### P. G. Andrus

#### Point-Probe Electrometer

A refined point-probe type of electrometer as described on page 451 of Quarterly Progress Report No. 5 has been constructed. The general design of the electrometer is the same as described there. However, the basic electrometer used was a Lindemann Ryerson Electrometer manufactured by the Cambridge Instrument Company, New York, New York. The probe of this instrument was fitted with a 0.03-inch wire extension which projected into a 0.04-inch hole in a low-capacity shielding can. This combination was mounted on a microscope stage in such a way that the end of the probe wire was about 1/32 inch from the plate surface, the potential of which was to be measured. Under these circumstances, by proper adjustment of the sensitivity of the electrometer, it was possible to measure potentials to an accuracy of better than 5 volts. The plate

-521-

area "seen" by the electrometer under these conditions was circular and approximately 1/16 inch in diameter.

Data for this report are recorded in Laboratory Record Books:

No. 3903, pages 32 - 35, inclusive.
No. 3931, pages 85 - 100, inclusive.
No. 4388, pages 41 - 65, inclusive.
No. 4536, pages 77 - 83, inclusive.
No. 4700, pages 21 - 65, inclusive.
No. 4774, pages 1 - 100, inclusive.
No. 4872, pages 1 - 33, inclusive.
No. 4946, pages 1 - 18, inclusive.

RMS/DTW/LEW:swr
December 30, 1949

BATTELLE MEMORIAL INSTITUTE