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FINAL TECHNICAL REPORT

PRELIMINARY STUDY INTO THE PRINCIPLES OF CONTINUOUS TONE ELECTROPHOTOGRAPHY

June 15, 1962 - December 15, 1962

Contract No. DA-44-009-ENG-5100

Research and Development Procurement Office
U. S. Army Engineers
Research and Development Laboratories
Fort Belvoir, Virginia

American Zinc, Lead and Smelting Company
1515 Paul Brown Building, St. Louis 1, Missouri

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Preliminary Study into the Principles of
Continuous Tone Electrophotography

FINAL TECHNICAL REPORT
American Zinc, Lead and Smelting Company
Contract Nr DA-44-009-ENG-5100

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American Zinc, Lead and Smelting Company, Paul Brown Building, St. Louis 1, Missouri - PRELIMINARY STUDY INTO THE PRINCIPLES OF CONTINUOUS TONE ELECTROPHOTOGRAPHY - Otto C. Klein

Final Report, 15 December 1962.   61   pp. 20 illus., 9 tables.

This is a final report on a preliminary study made to determine the feasibility of extending the continuous tone range of prints made by electrophotography. Apparatus is described which can be used to make electrophotographic prints. The apparatus necessary for the electrical evaluation of electrophotographic coatings is also described. The effect of the following factors on continuous tone are examined: (a) zinc oxide particle size, (b) type of resin used, (c) light intensity, (d) pigment to vehicle ratio, (e) resistivity of the zinc oxide, (f) moisture in the zinc oxide, and (g) ambient humidity.
The report also discusses the effect of zinc oxide particle size on spectral response of the coating.

Erratum

Page 21, Item 9 should read 7.5, 15, 40, 60 and 100-watt lamps and reflector.

Page 48, paragraph 4, line 3 should read Bruning No. 32-155 Copytron paper.

Page 57, paragraph 2, line 2, last word should be desensitization.

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PRELIMINARY STUDY INTO THE PRINCIPLES OF
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PREFACE

Five scientists and technicians were directly involved in the work reported here. Messrs. G. E. Mason and Howard Armbruster were principally responsible for evaluation of the resins at the electrophotographic laboratory of the American Zinc Oxide Company in Columbus, Ohio. They also performed the bulk of the work on the study of the effect of additives to the coating slurry.

Messrs. Otto C. Klein, R. L. Bergman and G. P. Bollwerk worked in the electrophotographic testing laboratory in East St. Louis, located at the Fairmont City Plant of the American Zinc Company of Illinois. This facility is equipped in the same fashion as the Columbus laboratory, and the two groups frequently cross-checked results to insure accuracy of data.

Assisting this group and ready for immediate help when called upon were Mr. K. A. Phillips, Director of Research and Development of the American Zinc, Lead and Smelting Company, and Mr. J. H. Calbeck, recently retired from full time duties as Manager of Research for the American Zinc Oxide Company, a subsidiary.

The commercial plant for the manufacture of electrophotographic grade zinc oxide is located at Hillsboro, Illinois, a distance of about 60 miles from East St. Louis. At this plant we had the direct assistance and cooperation of Mr. H. R. Wampler, Plant Manager, and Mr. O. J. Hassel, Plant Superintendent. These men cooperated to the extent that their entire commercial facility and their collective years of manufacturing experience were at our disposal whenever needed. They assisted in the selection of different particle size oxides and in the design of a pilot furnace to produce doped zinc oxide.

On May 29, 1962 a major conference of all interested personnel was called by Mr. G. L. Spencer, Jr., Vice President, American Zinc, Lead and Smelting Company. At this time, he advised everyone of the major objectives and assigned areas of responsibility. The actual contract period was from June 15, 1962 to December 15, 1962, but work

was not terminated as of that date. Some of the data presented here was gathered as late as December 27.

TABLE OF CONTENTS

SUMMARY

This report describes all of the equipment necessary for the successful production and evaluation of electrophotographic prints.

The two basic ingredients of the electrophotographic coating, namely, zinc oxide and resinous binder, are examined and the effect of different types of binders are evaluated.

Using a Pliolite binder, the effect of change in particle size of the zinc oxide is studied. Change in particle size of the zinc oxide is used as a variable to show that higher charge acceptance is possible in an unsensitized system when small particle size zinc oxide is used. Particle size is also examined from the standpoint of its effect on spectral response of the coating, and spectrograms are presented showing that zinc oxide absorbs strongly in the ultra-violet and that changing the particle size does not shift this absorption curve.

The effect of various additives to the coating slurry are discussed and their usefulness in improving tonal range is evaluated.

INTRODUCTION

Electrostatic printing is no longer an unknown term in the graphic arts field. The production of readable office copy has already been successfully achieved by the American Photocopy Equipment Co., Evanston, Illinois, the Charles Bruning Co., Mount Prospect, Illinois, and the Microstatics Division of the Smith-Corona Marchant Co., Skokie, Illinois. These three companies have successful, operating machines and paper on the market, and we can expect a flood of competitors to announce their machines during the next twelve months.

All efforts by the above "Big Three" have been directed toward the design of a machine and a paper which will reproduce line copy. As a result, the resin manufacturer and the producer of zinc oxide have been called upon for samples of their product which, when mixed together, would yield a black and white copy with the fewest possible shades of gray.

The problems of the office copy group can be fully appreciated only by one who has worked in this field. Because it was and is a multi-million dollar market, all efforts have been directed toward the design and sale of a successful product, and the basic research which would give the answer to the many unknowns along the way simply has been neglected or is locked up in the company file marked "look at this when we have more time".

The U. S. Army Engineers Research and Development Laboratories, Fort Belvoir, Virginia, as the contracting agency, requested the American Zinc, Lead and Smelting Company to approach the problem of electrostatics from a less hurried and more theoretical standpoint. The investigation was to cover the effect of several major parameters upon the production of continuous tone prints. All efforts up to this point had been directed toward maximizing contrast. Now the problem shifted to black-and-white plus all the shades of gray possible between white and black.

One military need for electrostatics is in map printing and in the supplying of tactical maps on very short notice. The ability to reproduce as many shades of gray as possible

is most valuable when time is not available for the production of multi-color maps.

The usefulness of electrostatic printing for map reproduction using miniature film transparencies has been shown with the RCA Electrostatic Printer and more recently by the Harris-Intertype machine.

Our part of this total problem then was to study the feasibility of extending the tonal range of the electrophotographic coating, using any and all means at our disposal. This was to be literally a "stab in the dark", to see if it is possible to approach the tonal scale achieved with conventional bromide photography.

The problem quickly broke down into two parts when it was found that the resin binder used determined to a great extent the number of shades of gray possible. We therefore set our Columbus laboratory to work investigating all available resins, while the other investigators busied themselves with finding the answers to the effects of particle size of the zinc oxide, of pigment to resin ratio, of different wavelengths of light, and of other pertinent variables.

Investigation

A. Raw Materials

The zinc oxide used in this investigation was manufactured by the American Zinc, Lead and Smelting Company at their Hillsboro, Illinois facility. This plant has built a French oxide furnace specifically designed for the commercial manufacture of photoconductive zinc oxide, and the samples described below were made with this furnace.

Table 1

Standard Test Data on Zinc Oxide
Used in ERDL DA-44-009-ENG-5100

Grade	ZZZ-771	ZZZ-661	ZZZ-661	ZZZ-661	ZZZ-661
Lot No.	2-7863	2-5609	2-5686	2-5668	2-5678
% Pb	.0015	.0015	.0019	.0018	.0015
% Cd	.0020	.0020	.0020	.0015	.0016
Percent +325	.0245	.0090	.0026	.0036	.0040
Brightness	86.25	88.25	88.00	88.00	88.00
Grit	#3	#1	#1	#1	#1
Gardner oil	21.0	20.0	17.0	17.0	17.0
Rub-out oil	11.9	11.7	10.3	10.3	10.3
Specific surface (m^2/gm)	7.91	4.31	3.43	3.15	2.64
Specific surface diameter (μ)	0.136	0.250	0.314	0.342	0.408

All of the items on Table 1 are self-explanatory with the possible exception of the last two rows. The second to last item in the table is identified as specific surface (m^2/gm). Our routine measurement of specific surface (in square meters per gram) is carried out by dissolving a fixed weight of zinc oxide in a fixed quantity of 10 N tartaric acid in a calorimeter. A plot of time versus temperature gives an accurate measure of the rate of solution of the zinc oxide and its attendant liberation of heat. The procedure is standardized against nitrogen and helium absorption techniques and further checked by statistical counts on prints made with the electron microscope.

If we assume the zinc oxide particles to be spheres, it is possible to calculate a particle size figure which we show as the last item in Table 1 as specific surface diameter (μ). We know, of course, that French oxide consists not of spheres but of needles and platelets, but the assumption is necessary for the calculation. The "specific surface diameter" then refers to a sub-micron size which is the calculated average diameter of the zinc oxide particles.

Figures 1 through 5 show electron microscope enlargements (20,000X) of the five zinc oxides used in this project.

The binders used in this work were secured from a number of manufacturers. In most cases, the manufacturer was advised of the part his binder was to play in the program, and a number of samples were submitted. We present below the final list of binders chosen for the work, along with the name of the manufacturer.

Table 2

Resins Used in ERDL DA-44-009-ENG-5100

Type	Producer's Code	Producer
Pliolite	S5-B	Goodyear Chem. Co.
Pliolite	S-7	Goodyear Chem. Co.
Silicone	SR-82	General Electric Sil.Div.
Silicone	SR-111	General Electric Sil.Div.
Silicone	840	Dow Chemical Co.
Acrylic	B-82	Rohm and Haas
Vinyl Butryal Resin	XYHL	Union Carbide Plastics
Piccoflex-Styrene	120	Pennsylvania Ind. Chem.
75% Piccoflex)	1120	Pennsylvania Ind. Chem.
25% Acrylic)	B-82	Rohm and Haas
95% Styrene)	A-75	Pennsylvania Ind. Chem.
5% Acrylic)	B-82	Rohm and Haas
DeSoto	73-35A	DeSoto Chem. Coatings
DeSoto	73-35B	DeSoto Chem. Coatings
DeSoto	73-35C	DeSoto Chem. Coatings
DeSoto	73-35D	DeSoto Chem. Coatings
DeSoto	75-02	DeSoto Chem. Coatings
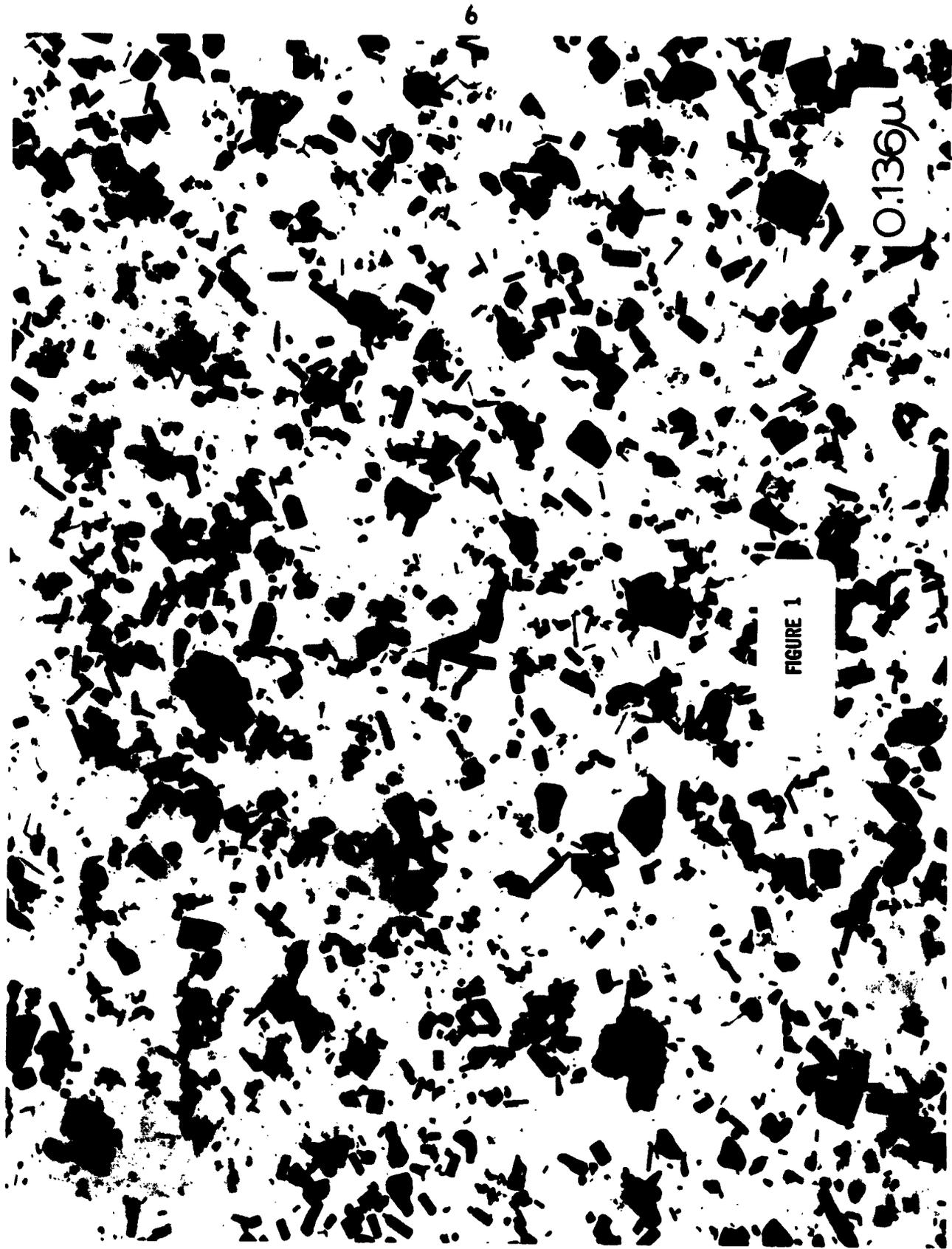
FIGURE 1

0.136μm
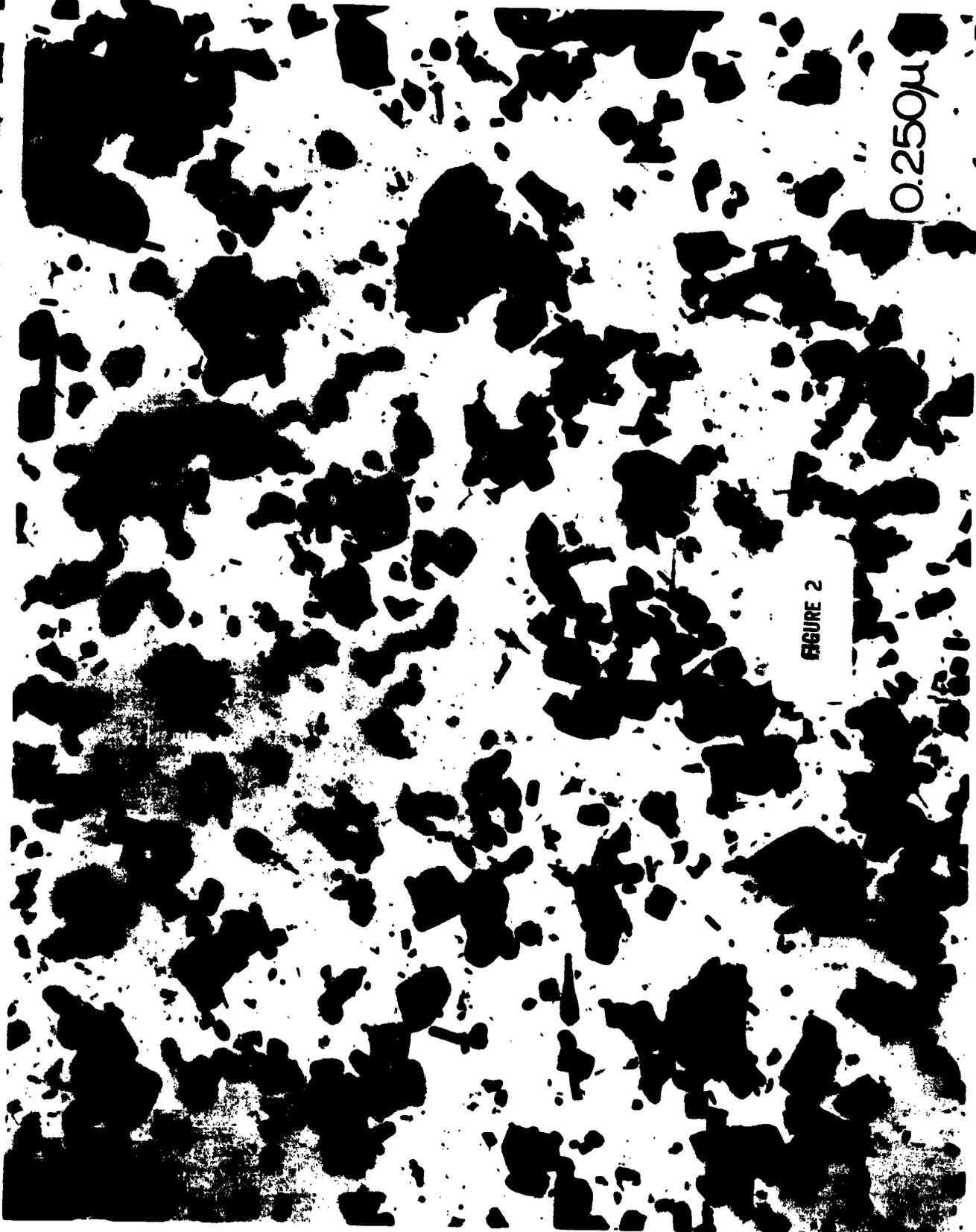
FIGURE 2

0.250μ

FIGURE 3

FIGURE 4

FIGURE 5

10

0.408μ

Table 2 (Cont'd)

Resins Used in ERDL DA-55-009-ENG-5100

Type	Producer's Code	Producer
DeSoto	75-648	DeSoto Chemical Coatings
Aroplaz-Alkyd	6006X50	Archer, Daniels, Midland
Lustrasol-Alkyd	13-075	Reichold Chemicals, Inc.
Styrenated-Alkyd	13-030	Reichold Chemicals, Inc.
Everflex	G	Dewey and Almy
25% Parez)	613	American Cyanamid
75% Everflex)	G	Dewey and Almy
25% Parez)	613	American Cyanamid
75% Gelva)	S-55	Shawinigan Resins Corp.
Parez	613	American Cyanamid
Water Soluble Alkyd	T.S1.0-619	Amoco Chemicals Co.
Dow	636	Dow Chemical Co.

B. Description of Equipment

1B. Humidity Chamber

The high cost of building temperature- and humidity-controlled rooms has deterred many investigators from making electrophotographic electrical measurements under standard conditions. We found it expedient to build a small chamber and to conduct all measurements in this chamber while keeping our instruments outside the cabinet.

Figure 6 shows the general construction details using two commercial standard-size aluminum storm windows for the front (entry) side of the cabinet. In Figure 7 is shown a schematic diagram of the control system and of the recirculated air.

All of the major items necessary to build this cabinet are given in the following list, and Figure 8 shows a photograph of the cabinet in use. The two front windows have been removed to show access to the working area.
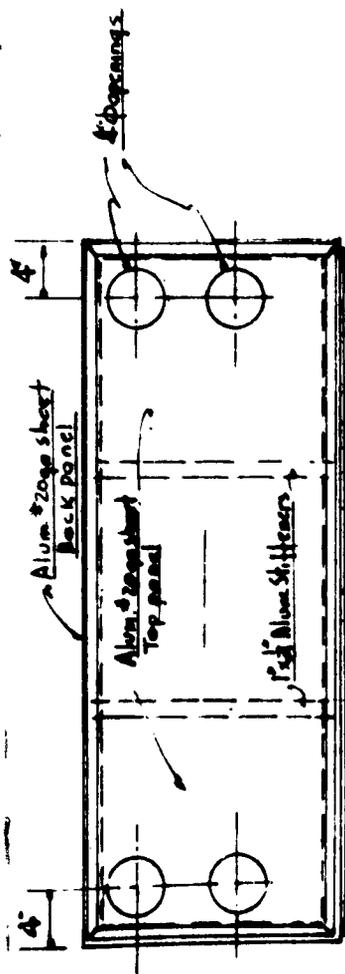
FIGURE 6

TOP
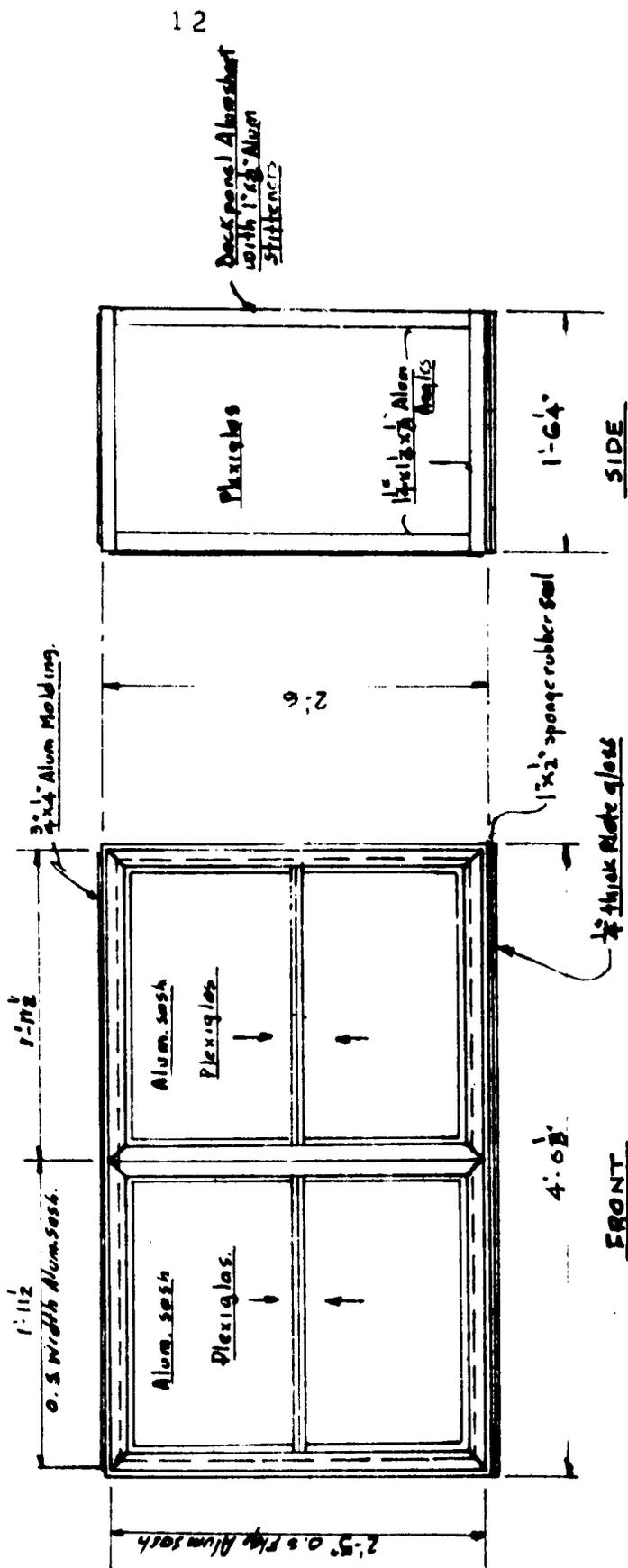
FRONT

SIDE

CONTROLLED HUMIDITY CABINET.
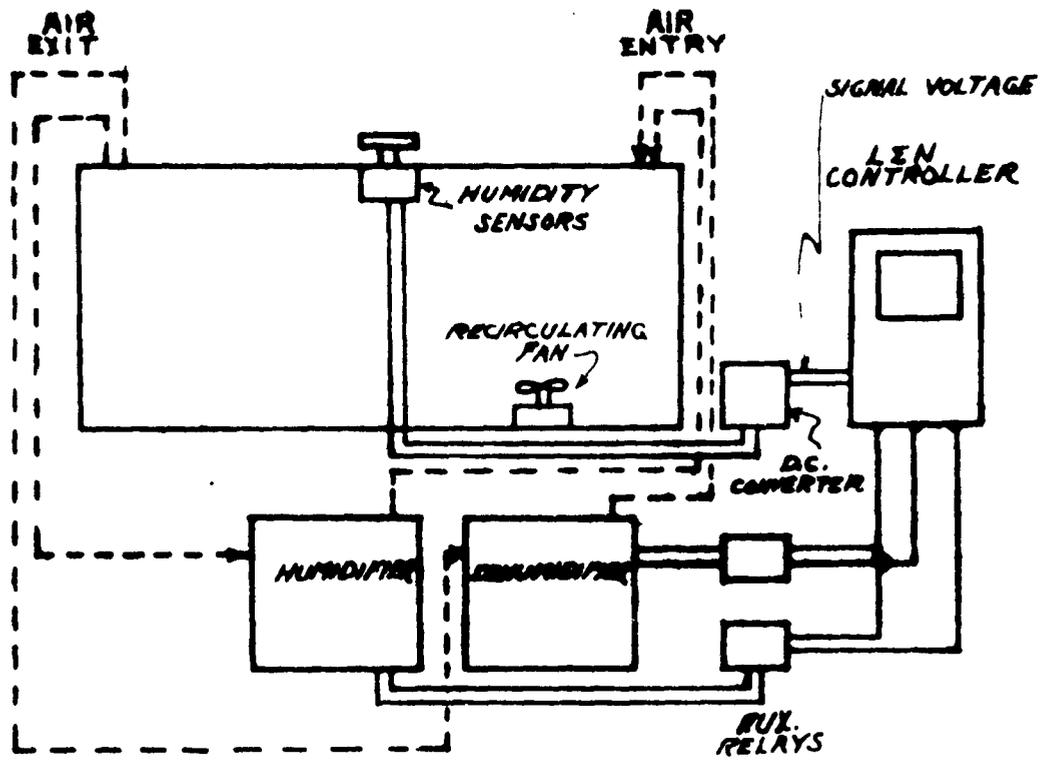
FIGURE 7

FIGURE 8

List of Materials

1. Bantam Duct Hose, 4", from J.P. Bushnell Co., 3436 Lindell Boulevard, St. Louis, Mo.

2. Humidity sensing elements, Cat. No. 4-4823 (see No. 4).

3. Converter to sense change in resistance of sensing elements and convert this to a d.c. signal, Cat. No. 15-6320, with 4-5014 cable.

4. Multiple mounting for sensing elements, Cat. No. 4-51⌐. Items 2,3, and 4 from Hygrodynamics, Inc., 949 Selin Road, Silver Springs, Maryland.

5. Room humidifier, Sears Roebuck & Co., Model 716A.

6. Room dehumidifier, Oasis Model SD-32.

7. Leeds and Northrup, Cat. No. 3-930-010-044-6-004-1-38, Model S, Speedomax-H indicating strip chart recorder controller with integral D.A.T. control unit.

8. Plexiglas and aluminum cabinet with standard household aluminum windows. Dimensions 18" deep, 30" high, 48" wide, built by local cabinet maker. Glass in windows replaced by 1/8" plexiglas.

9. Relays, Cat. No. 75P-603, Type PR7AY DPST, 115v., Allied Radio Co.

10. Harco Axial Fan, Cat. No. T-6802, Herbach and Rademann, 1204 Arch St., Philadelphia 7, Pennsylvania.

11. Plenum boxes for humidifier and dehumidifier and 4", 90 degrees elbows from local sheet-metal shop.

Figure 8 shows an overall view of the cabinet with the windows removed. In actual operations, the technician performs his manipulations through armholes cut into the plexiglas windows. The dehumidifier is shown on the lower right side below the cabinet and the humidifier

is on the left. The plenum boxes covering the inlets and outlets are clearly shown. Also shown is a small circulating fan in the chamber to insure thorough mixture of the air.

Humidity control is maintained by the Leeds and Northrup controller. This instrument is built with a neutral, a high and a low contactor. The humidifier is connected to the neutral and low points and the dehumidifier is connected between the neutral and high points. The desired humidity is set on the scale of the instrument and the humidifier or the dehumidifier goes into operation until the desired set point is reached. Both humidifier and dehumidifier have fans so that the conditioned air is blown into the chamber through the 4" bantam duct hose, and the emergent air is carried back to the same unit. This constitutes a closed system which makes for remarkably easy and uniform control. No temperature control is used. The large radiating surfaces of plexiglas and aluminum provide sufficient heat transfer so that the cabinet stays near the ambient room temperature. Humidity is currently being controlled $\pm1.0\%$ between 20 and 70% relative humidity at 80°F.

2B. Resistivity Measuring Equipment.

The measurement of surface resistivity of zinc oxide presents a problem not encountered in a bulk measurement. Zinc oxide is extremely active as a sorption-desorption agent and the surface resistivity reflects the ambient atmosphere. Tests in our chamber show a parallel series of curves in which the surface resistivity of zinc oxide exactly parallels the output from a set of Hygrodynamics humidity sensors. For this reason, this measurement must be made in a carefully controlled atmosphere.

A ten-gram sample of the oxide is compressed to 8,000 pounds in a standard Carver test cylinder and a silver contact paint (General Cement Co.) is applied to make a center contact of 8.0 mm diameter. A guard ring is next applied so as to give a spacing of 8.0 mm between the two contacts (see Figure 9). After a 30-minute drying interval at 110°F to remove the organic solvent used in

17
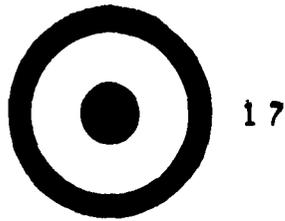
ZINC OXIDE RESISTIVITY SPECIMEN

TOTAL O.D. · 29 mm
CENTER DOT · 8 mm
SPACE · 8 mm
RING WIDTH · 2.5 mm

FIGURE 9

PROJECTION
LENSES

FILTER

CONDENSORS

FIRST
SURFACE
MIRRORS

FOCUSING LENS

OPTICAL SYSTEM FOR THE STUDY OF ZnO RESISTIVITY
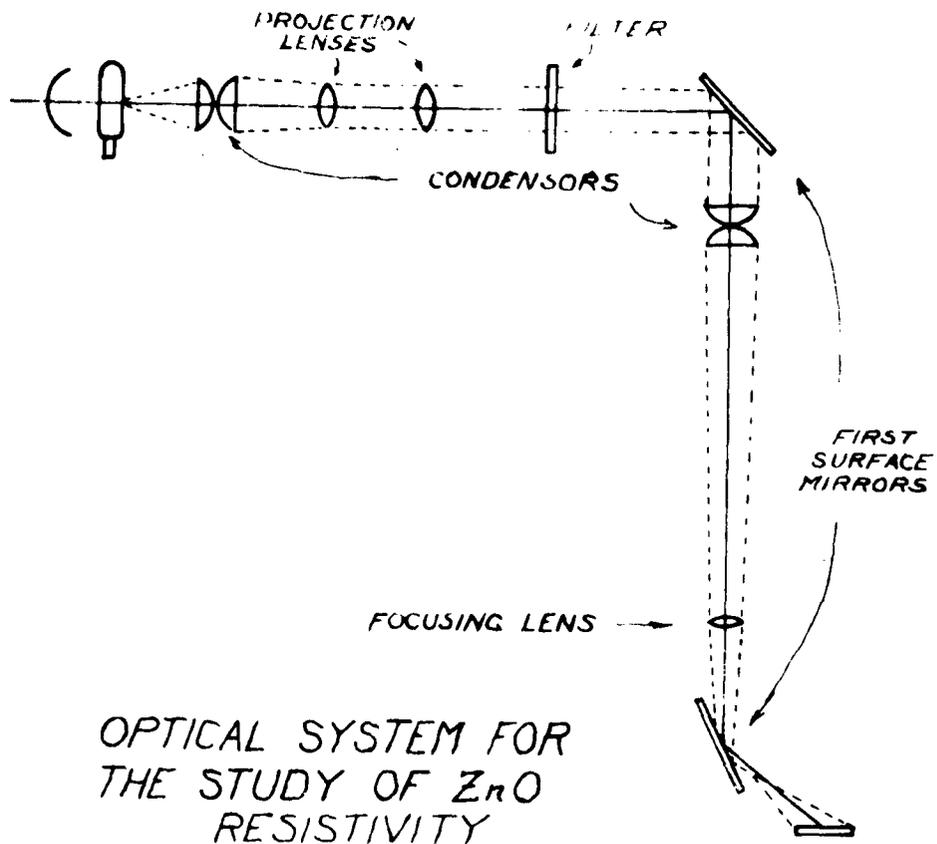
FIGURE 11

the silver paint, the compressed pill is held at the de-
sired humidity for two hours and then positioned in the
resistivity measuring jig. The weight-loaded, silver-
tipped contacts are lowered on the pill and the jig is
positioned in the dark box as shown in Figure 10.

The optical system consists of a 300-watt projector us-
ing a tungsten filament lamp, a plano-convex lens, and a
set of condensing lenses to insure a parallel beam to the
first mirror. This mirror is mounted in the top of the
dark box and is set at a 45 degree angle to reflect the
beam downward. Another set of condensers is used to col-
limate the beam and a final lens is used to focus the beam
on the lower mirror, which reflects the beam onto the
sample. The optical system is shown in Figure 11.

Provision has also been made in this system for the in-
sertion of interference filters in the light beam so
that we can study the photo-response of zinc oxide at
various wavelengths.

A General Radio electrometer type 1230-A is the measur-
ing instrument, and an Esterline Angus model AW, 0-1
milliampere meter monitors the output of the meter. The
electrical circuitry is arranged in such a way that the
sample can be subjected to repeated 10-second bursts of
light in order to study the fatigue effect as well as
using light saturation to determine the total change in
resistivity from light to dark environment. Photo-
current can be read by electrical switching of the cir-
cuits without disturbing the sample. The wiring diagram
for this operation is shown in Figure 12.

3B. Electrophotographic Equipment

Much of the equipment necessary for the successful gen-
eration of a static charge on a coated sheet is commer-
cially available from R. J. Paulus, Anken Chemical and
Film Corp., Newton, New Jersey (Items 1-5).

    1. Double corona power unit (8000-volt D.C. power
unit plus and minus, with two meters for use with double
corona discharge unit.) A 4000- to 6000-volt negative
D.C. power pack with no meter is available at lower cost.
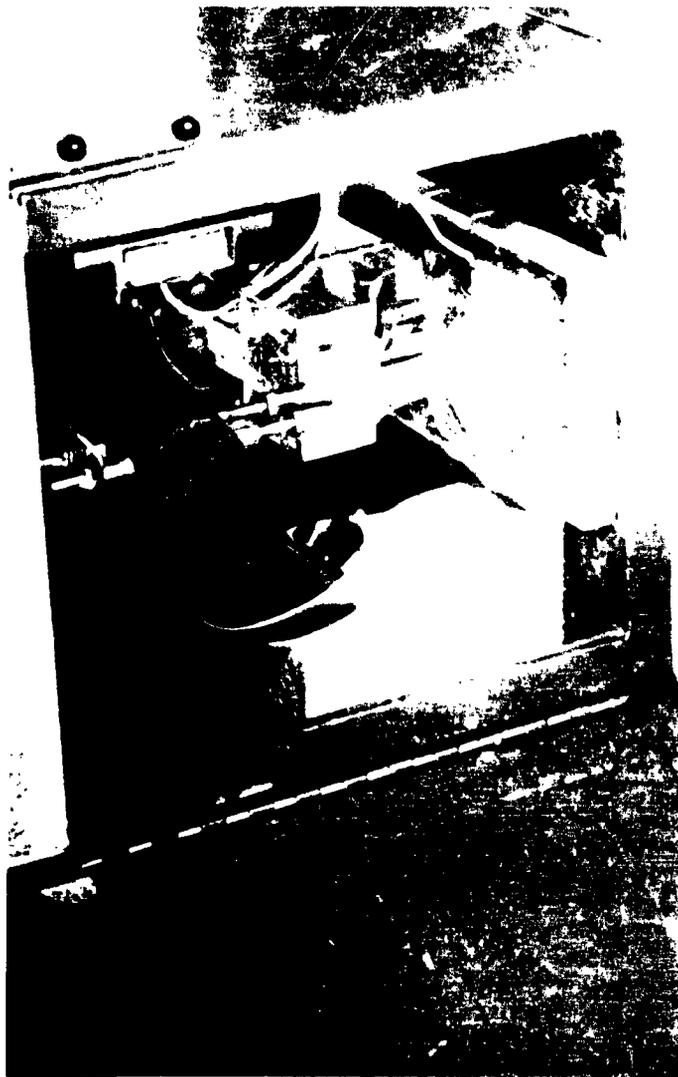
FIGURE
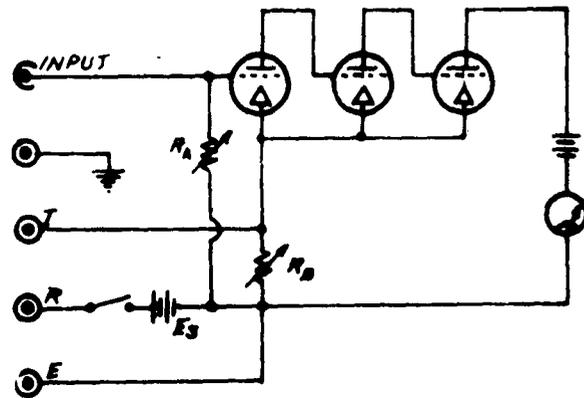
GUARD-POINT ARRANGEMENT
FOR RESISTANCE MEASUREMENT
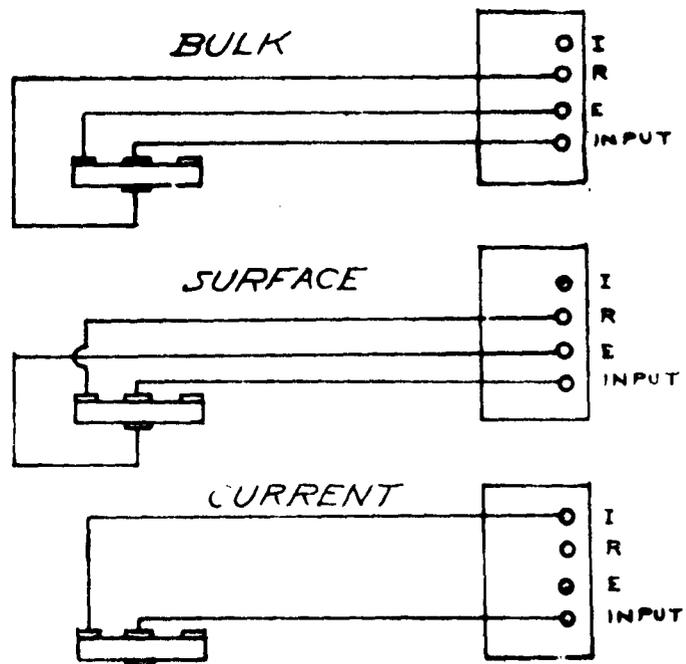
DIAGRAM FOR THE STUDY OF
FATIGUE, LIGHT-DARK RESISTIVITY
AND PHOTOCURRENT IN ZnO

FIGURE 12

2. Corona discharge unit (corona wand).

3. Special iron filings.

4. Alnico magnetic brush.

5. Low M.P. toner, Code 39-50, Philip W. Hunt Co., Palisades Park, New Jersey.

6. Brass (or aluminum) plate 1/8" x 12" x 18". This plate is used as a support for the coated sheet during corona charging. A good earth ground on this plate is essential.

7. Two sets of ball bearing drawer slides are used to mount the brass plate on a horizontal surface. This allows the plate to be moved left to right and front to back during corona charging with the wand held in a fixed position.

8. Photo timer (Time-o-Lite or equivalent).

9. 20, 40, 60, 100-watt lamps and reflector.

10. Standard laboratory drying oven capable of maintaining 100°C (for fusing the finished prints).

11. Osterizer or Waring blender.

12. Static Probe. This probe is made by cementing together four sheets, 1/8" x 4" x 8", of lucite or polystyrene. The sheets are cemented along their edges so as to form a rectangular box 4" square by 8" high with no top or bottom. Two holes are drilled on opposite sides of the box, 1/8" from the bottom edge, and a two-mil platinum wire is threaded into position. The interior of the box is lined with aluminum foil. Connection between the platinum wire and the electrometer is made by using Belden coaxial cable RG62U or equivalent. The aluminum foil interior in the probe is connected to the cable shield and is carried back to instrument ground.

The probe is calibrated by placing it on a metal plate maintained at some fixed and known D.C. potential. Moving

the platinum wire closer to or farther away from the D.C.
field above the plate allows a direct reading calibration
on the General Radio electrometer when the latter is set
to read voltage.

13. Wire applicator. This is a 1/4" steel or brass
rod wrapped with 22 or 24 thousandths nichrome wire.
Such an applicator is commonly used in the paint trade.

C. General Operating Procedure

Two general methods are commonly employed in the produc-
tion of laboratory-size electrophotographic coating
mixes. The Waring blender (or Osterizer) is rapid, usu-
ally requiring only a five-minute mix. The ball mill is
the second method. This is slow, requiring up to three
or four hours but usually giving better dispersions than
the high-speed mixer.

Our standard method of mixing and the one used to make
up the coatings for the prints displayed in this report
is as follows:

Resin Stock Solution

Dissolve 354 gm Pliolite S5-B resin (Goodyear)
in 1646 gm certified reagent xylene (17.7% dry
solids solution).

Weigh out 200 gm ZnO, add 141 gm resin solution (8:1
ratio dry solids ZnO:resin) and spatula mix in a poly-
ethylene beaker with a stainless steel spatula. Pour
into a high speed blender and mix at high speed for
five minutes. Pour the coating slurry into a glass jar
and allow to cool to room temperature. After cooling,
add 15 ml xylene and then coat treated paper sheets
using a No. 22 wire drawdown bar.

1C. Preparation of Paper for Coating

An A. B. Dick mimeograph bond 43-1210, 801/2" x 11",
Sub 16 is used. This is treated as follows:

a. Dissolve 15 gm paraffin in 400 gm
   toluene
b. Dissolve 6 gm ammonium acetate in
   200 gm 95% ethyl alcohol

Pour solutions (a) znd (b) together and warm until milkiness disappears.

The solution is placed in a photographic tray (glass) and kept warm while the mimeograph paper is passed through the solution (total immersion). The dipped paper is dried for a few minutes in a 100°C oven and is then ready for coating. The coated sheets are air dried and finally dried for 15 minutes in a 100°C oven. Before testing, the coated sheets are conditioned in a humidity chamber at 50% R.H. at 78°F for 16 hours.

The rest rf the equipment used in the project is of a specialized nature and will be discussed while we are describing the various phases of the work.

2C. Measurement of Electrical Resistivity of Zinc Oxide

The equipment used in this work was previously described on pages 16 and 18 under Resistivity Measuring Equipment. The purpose of this phase of the work was to point out the vital importance of keeping the entire electrophotographic system moisture-free. Since zinc oxide is an extremely fine particulate powder it is susceptible to moisture adsorption if it is improperly handled or stored prior to use. This work points out the deleterious effect of moisture and applies to entry of moisture at any stage of the manufacture of coated paper.

The resistivity specimens made on the Carver Press (Figures 9 and 10) were conditioned in the dark at the desired humidity for four hours before taking the dark surface resistivity measurement. All work was done in the humidity cabinet described earlier.

An examination of the curves shown in Figure 13 show the effect of humidity on the electrical resistivity of zinc oxide. All samples show a sharp decrease in resistivity as the humidity increases (see Figure 13). Furthermore,

EFFECT OF MOISTURE ON
ZINC OXIDE ON RESISTIVITY

FIGURE 13

Average particle diameter
of pigments

0.196 micron
0.250
0.314
0.342
0.408

RESISTIVITY IN OHM-CM

Percent Relative Humidity at 76°F
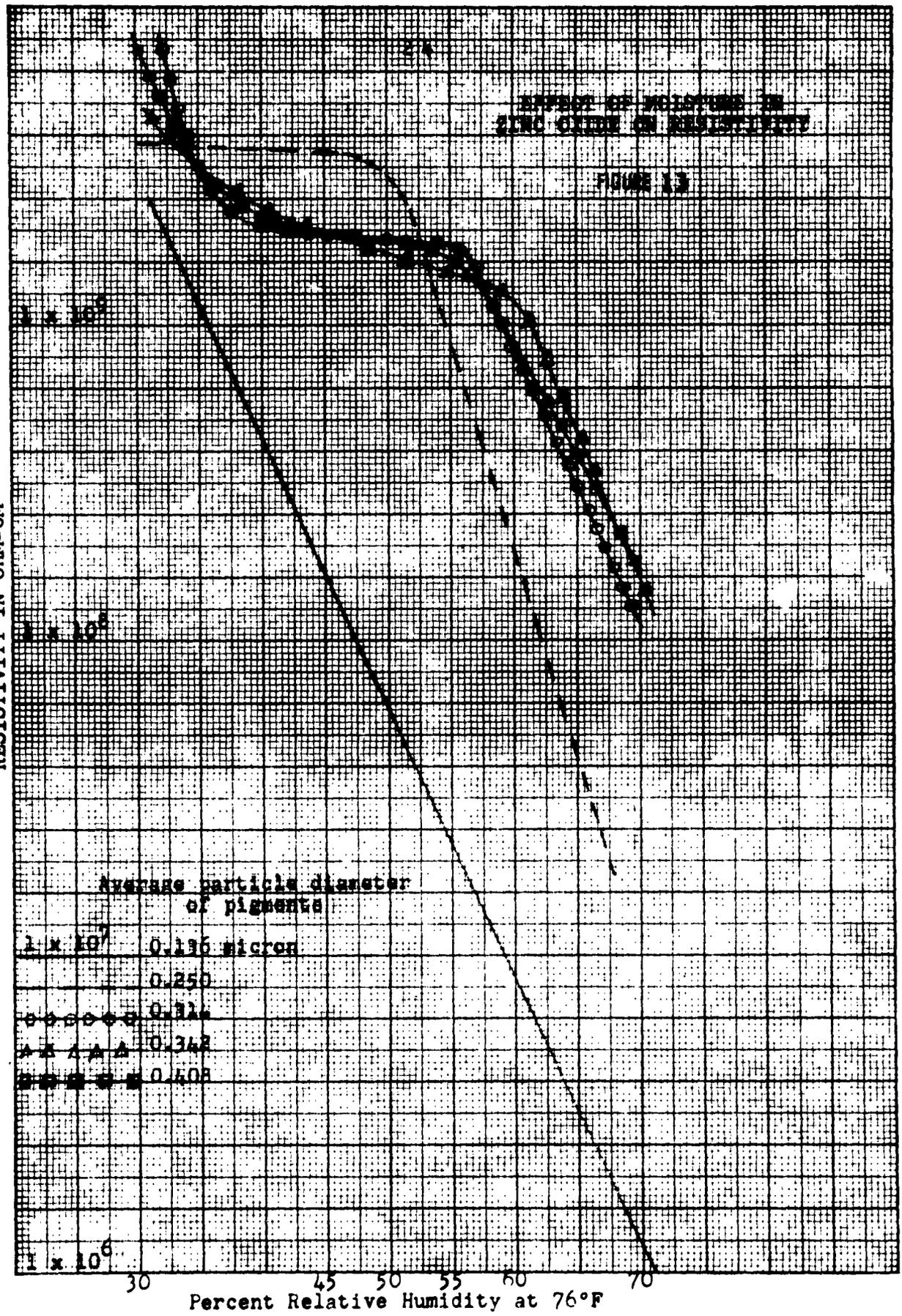
the smaller particle sizes are the most susceptible to change in humidity. This is extremely important because our measurements show that all of the samples tested fall to 1×10^6 ohm-cm resistivity under illumination. The 1×10^6 ohm-cm figure also holds true over the entire humidity range in which we worked from 30-70% R.H. at 76°F.

Maximum photoconductive response can be achieved only when the resistivity of the zinc oxide shows a sharp decrease under illumination. If an oxide such as the 0.136 micron sample is used at, for example, 55% R.H. the resistivity under illumination can drop from 1×10^7 to 1×10^6 (the lower limiting value under tungsten illumination at the light intensity level used in this experiment). A pigment having a particle diameter of .314, .342 or .408 microns under the same conditions (55% R.H.) will drop in resistivity from 2×10^9 to 1×10^6. Since drop in resistivity is a direct Ohm's Law function of conductivity, we can expect that higher humidities causing higher conductivity in the pigment will result in lower charge acceptance, and this we find to be true as will be shown later in this report.

It would appear therefore, that the best continuous tone prints made will be those in which the pigment-binder system has been freed of all traces of moisture.

Resistivity measurements of this type are useful because unless the bulk and surface resistivity of the zinc oxide is within certain limits it cannot function as a photoconductor. That is, the resistivity must be high enough so that current flow between adjacent particles is impeded sufficiently to enable the ZnO surface to take on and hold a static charge.

Recordings of the resistivity measurements under illumination followed by darkness confirms the work of Mollwo (Seitz, "Solid State Physics", Academic Press, N.Y., 1959, Vol. 8, p. 209) and others, and shows that the "recovery" of the zinc oxide is quite rapid. The curve showing the increase in resistivity of the

specimen after the light is extinguished, shows an extremely rapid recovery. The time interval necessary for recovery is less than one minute when using a tungsten filament lamp and at resistivity values of the order indicated previously.

3C. Measurement of Electrical Parameters of Electrophotographic Coatings (Under Wratten OA Safelight Conditions.

Using the equipment described previously we next proceed to the electrical measurements of the coated surfaces.

The coated sheet which has been conditioned at the desired humidity (described previously under heading C1) is placed, coated side up, on the metal plate under the corona wand. It is most convenient to suspend the wand at an adjustable distance over the metal plate. For normal electrostatic charging of paper using 2-mil platinum wires in the wand and working in a room at 50% R.H. at 78°F, this distance is about one-half inch. The high-voltage generator is turned on and the electrostatic charging is monitored by using a 0-100 microampere meter in the high-voltage line between the generator and the corona wand. We have found that results are much more reproducible when we maintain the same current flow on successive tests.

The metal plate (thoroughly grounded) is moved left to right and front to back on the drawer slides on which it is mounted. This movement continues throughout the charging cycle in order to assist in levelling out the electrostatic charge on the coated surface. The microampere meter is monitored and the current is held at 50-60 microamperes during the charging cycle, which may vary from 10 seconds to one minute at the discretion of the operator.

It will be noted that when a test is made on a conductive-base sheet it is necessary to move the corona wand a greater distance than 1/2 inch from the ground plate in order to maintain 50-60 microamperes of current. Similarly, when a test is made on a coating which has been applied to aluminum foil, it is necessary to

increase the wand-to-plate distance to nearly one inch
in order to maintain a 50-60 microampere current.

After charging, the General Radio electrometer and
Esterline Angus recorder, described under B2, are used.
The plastic 4" x 4" x 8" electrostatic probe is placed
on the charged sheet and the electrostatic voltage is
noted. After a standard time interval of about 10-20
seconds, during which time the loss of charge in the
dark is noted (dark decay or half-life), a light is
turned on and the static field collapses. The recorder
produces a record of this entire procedure and from the
chart it is possible to see the maximum charge which
the coated surface would accept, the rate at which the
static charge leaks off, the speed of discharge under
illumination and the residual voltage left after illu-
mination.

At this point it is customary to take a second coated
sheet which has had the same coating and humidity stor-
age as the one used above and to make an electrophoto-
graphic print. The electrical charging cycle is the
same as described. When it is complete, an image is
projected on the electrified surface (or made by contact
printing). The exposure must be controlled since over-
or under-exposure causes the same final effect as when
working with silver paper (except of course that the ef-
fects are opposite — over-exposure in conventional
electrophotography causing a weak image).

After exposure, the electrical image is made visible by
development. It is convenient to make the developer
using a 10-ml glass graduate. A volumetric measure of
10 ml of iron filing and 1-2 ml of Hunt 39-50 toner is
used. This is thoroughly mixed and applied to the
electrical image with a bar magnet (magnetic brush).
The areas which retain a negative charge will attract
the positively charged dye particles and the image
becomes visible. The image is made permanent by plac-
ing the picture in an oven at 100°C for a few minutes.
The Hunt toner contains a low melting resin, which
fuses and fixes the image to the paper.

Insert on Page 28 at end of Section 4C and before Section 5C.

4C-a.

Dielectric Constants of Various
Resins Used in Electrophotography

Resin	Frequency (Cycles per Second) at Which Determination was Made				
	60	1000	10^6	30×10^6	6×10^7
Acrylic B-82	4.7	4.1	3.3	2.9	-
Pliolite S5-B	-	2.5	-	-	2.5
Pliolite S-7	-	2.9	-	-	-
Vinyl Butral	3.61	3.58	3.33	-	-

Measurement of the dielectric constant of the resins used in electrophotography was considered because we felt that the dielectric constant would in large measure, determine the ability of the resin to accept and to hold a blanket negative electrostatic charge. While this was found to be true in a general sense, it was also found that other variables played a much more important part (oxide to N.V. resin ratio, type of solvent used, particle size of the ZnO) and we therefore concluded that the use of the dielectric constant was important only in a general sense in that when trying to develop absolute maximum charge acceptance it is best to use a resin with the highest possible dielectric constant.

4C. Effect of Resin Binder on Continuous Tone Behavior of Electrophotographic Surfaces.

Out of a total of approximately fifty resins tested we have selected the samples which showed the most promise in electrophotography and have tabulated the results of the tests in Table 3. The data is self-explanatory, and the tonal range shown in the right-hand column indicates the range of values obtained. That is, if a 13 were to be seen in this column it would represent 13 shades of gray from black-to-white.

As a further aid to future work and possible correlation of electrophotographic behavior and structure, we have indicated in Figure 14 the repeating portion of the structure of a number of the resins tested.

As an extension of this work we present in Table 4 a series of tests in which we have varied the ZnO to non-volatile resin ratio over a wide range and using two different resins. As can be seen from the tonal range values, this change in the solids ratio has little or no noticeable effect on the tonal range of the coating.

5C. Effect of Particle Size of Zinc Oxide on Spectral Response as Determined by Change in Electrical Resistivity.

As raw material suppliers we have been in a favorable position to see the strong demand for zinc oxide samples of every conceivable particle size for experimental use in electrophotography. The general impression in the trade is that particle size is very important. This has certainly been found to be true with respect to total charge acceptance (saturation voltage). One of the cloudy areas not yet reported on has been the effect of particle size on the panchromatic behavior of the electrophotographic layer.

Using the optical system described on Page 17 of this report, we prepared specimens using the electrophotographic grade zinc oxide set aside for this project. Sheets of West Virginia Paper Co. stock were coated as

TONAL RANGE OF VARIOUS RESINS IN ELECTROPHOTOGRAPHIC COATINGS

Resin	No.	Resin % Non-Volatile	Producer	Oxide to N.V. Resin Ratio	Oxide to Solvent Ratio	App. Max. Volts Charge Accept.	Tonal Range 1-13 Beads
Pliolite	S-5B	100	Goodyear Chemical Div.	8 -1	1.75-1(1)	385	7
Pliolite	S-7	35	Goodyear Chemical Div.	8 -1	1.25-1(1)	300	7
Silicone	SR-82	60	General Electric Sil. Div.	2.56-1	2.0 -1(2)	525	5
Silicone	SR-111	60	General Electric Co.	2.56-1	1.15-1(2)	600	2
Silicone	840	-	Dow Chemical Co.	2.56-1	2 -1(2)	450	3
Acrylic	B-82	100	Rohm & Haas	10 -1	1.43-1(3)	320	5
Vinyl Butyral	XYHL	100	Union Carbide Plastics Co.	10 -1	1.15-1(4)	425	6
Piccoflex-Styrene	120	100	Pennsylvania Industrial Chem.	8 -1	1.45-1(1)	300	3
75% Piccoflex} 25% Acrylic}	1120	100	Indicated above	8 -1	1.43-1(1)	690	3
95% Styrene} 5% Acrylic}	A-75 B-82	100	Pennsylvania Industrial Chem. Rohm & Haas	2.56-1	1.54-1(1)	550	5
DeSoto	73-35A	64.0	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	630	2
DeSoto	73-35B	65.6	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	630	2
DeSoto	73-35C	64.8	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	560	2
DeSoto	73-35D	63.9	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	560	2
DeSoto	75-02	65.0	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	430	5
DeSoto	72-648	63.6	DeSoto Chem. Coatings, Inc.	8 -1	4 -1(2)	460	5
Aroplaz-Alkyd	6006450	50	Archer, Daniels, Midland Co.	8 -1	4 -1(2)	660	2
Lustrasol-Alkyd	13-075	48-52	Reichold Chemicals, Inc.	8 -1	2.2 -1(1)	560	2
Styrenated-Alkyd	13-030	45	Reichold Chemicals, Inc.	8 -1	2.2 -1(1)	570	2
Everflex (6)	G	50	Dewey & Almy	2 -1	.5 -1(5)	450	5
25% Pares} 75% Everflex}	613 G	80 50	American Cyanamid Dewey & Almy	2.2 -1	1 -1(5)	440	5
25% Pares} 75% Gelva}	613 S-55	80 50	American Cyanamid Sharinigan Resins Corp.	2.5 -1	.9 -1(5)	390	5
Pares (7)	613	80	American Cyanamid Co.	2.5 -1	1.2 -1(5)	750	5
Water Sol. Alkyd (8)	T.Sl.0-619	40	Amoco Chemicals Co.	8 -1	2.5 -1(5)	1000	3
Dow (9)	636	48.1	Dow Chemical Co.	5 -1	1.4 -1(5)	420	4

(1) Solvent - Xylene
(2) Solvent - Toluene
(3) Solvent - p-dioxane
(4) Solvent - 95% Ethyl Alcohol
(5) Solvent - Water
(6) Polyvinyl Acetate Emulsion. Oxide predispersed in H_2O and made into filter cake.
(7) Urea formaldehyde resin plasticized with dehydrated castor oil and maleic anhydride. Small amount of adipic acid and 30% hydrogen peroxide used to increase charge acceptance.
(8) Tri-mellitic neopentyl glycol. Experimental water soluble alkyd. At present the resin gives high residual voltage.
(9) Oxide predispersed in 1% gelatin and 1,4 butanediol-later added to predispersed oxide.

TABLE 3

1) DeSoto Resins 72-35A, 72-35B, 72-35C, 72-35D, and 75-02.
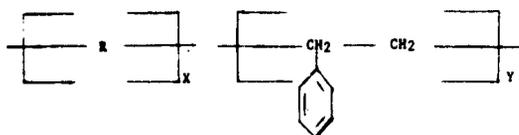
X = 40-20 Mole %
Y = 60-80 Mole %
R = Alkyl Ester

Differences between resins are variation in
molecular weight and ratio of X to Y.

2) DeSoto Resin 72-64B.
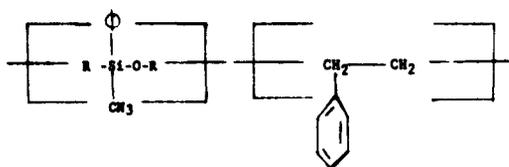
R = Alkyl Ester

3) Pliolite S-5B & S7.
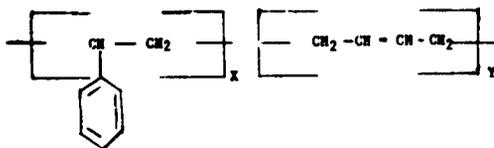
Pliolite S-5B - X = 67 Mole %
Y = 33 Mole %

Pliolite S7 - X = 58 Mole %
Y = 42 Mole %

4) General Electric SR-82.
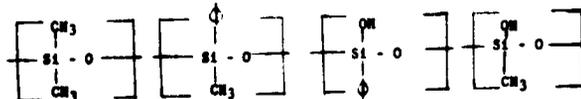
The exact ratio of these units is not known.

5) Polyvinyl Acetate.
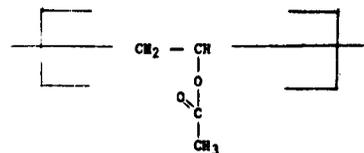
6) Polyvinyl Butyral (Butvar B-72A).
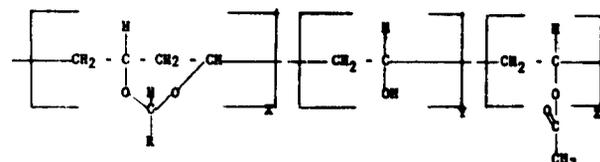
X = 78 Mole %
Y = 20 Mole %
Z = 2 Mole %
R = Alkyl

7) Acryloid B-82.
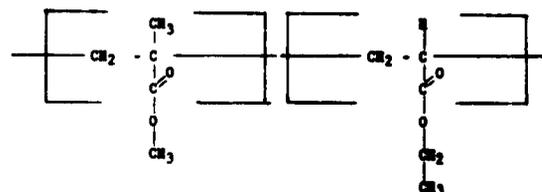
FIGURE 14

STRUCTURE OF VARIOUS
RESINS BEING EXAMINED
FOR USE IN
ELECTROPHOTOGRAPHY

TABLE 4

EFFECT OF ZINC OXIDE DISTRIBUTION UPON THE CONTINUOUS TONE
CHARACTERISTICS OF AN ELECTROPHOTOGRAPHIC COATING

Resin Type	No.	Oxide to N.V. Resin	Oxide to N.V. Ratio	Oxide to Sol.	Oxide to Ratio	Electrical Characteristics						Exp. Sec. 150 Ft.Cd.	Tonal Range 1-13 Basis
						Max. Volts	V. End Dark Decay	Volts 1-Sec.	Volts 2-Sec.	Volts Res.	Time to Pass. Sec.		
Pliolite	S-5B	2.7	1.0	.9	1.0	405	350	120	70	10	10.0	1/2	7
Pliolite	S-5B	2.9	1.0	1.0	1.0	450	425	200	130	50	9.0	1/2	7
Pliolite	S-5B	3.3	1.0	1.1	1.0	480	445	160	110	50	6.5	1/2	7
Pliolite	S-5B	4.0	1.0	1.25	1.0	440	410	140	75	20	7.5	3/8	7
Pliolite	S-5B	5.0	1.0	1.37	1.0	520	460	160	90	40	7.5	3/8	7
Pliolite	S-5B	5.7	1.0	1.5	1.0	540	480	180	100	40	7.5	3/8	7
Pliolite	S-5B	6.6	1.0	1.6	1.0	545	470	170	100	35	6.5	3/8	7
Pliolite	S-5B	8.0	1.0	1.7	1.0	440	400	110	60	20	6.5	3/8	7
Silicone	SR-82	1.4	1.0	1.7	1.0	-	-	-	-	-	-	-	5
Silicone	SR-82	1.8	1.0	1.7	1.0	-	-	-	-	-	-	-	5
Silicone	SR-82	2.2	1.0	1.7	1.0	-	-	-	-	-	-	-	5
Silicone	SR-82	2.4	1.0	1.7	1.0	-	-	-	-	-	-	-	5
Silicone	SR-82	2.5	1.0	1.7	1.0	-	-	-	-	-	-	-	5

described on Page 22 in this report, and silver contacts were painted on the coated sheets. The sheets were conditioned for 16 hours at 50% R.H. at 78°F and were then placed in the resistivity measuring equipment.

The optical system consists principally of a tungsten lamp and an interference filter (Bausch and Lomb No. 42-47-55-01, set of 5). Light intensity at the measuring surface is standardized, using a 3/8" diameter, 8-junction bismuth-silver Eppley thermopile, and the tungsten filament bulb is moved away from the condensing lens of the projector until an illumination level of 0.00036 watts/cm² is reached. This same level of illumination in watts per square centimeter is then maintained using the 450, 500, 550, 600 and 650 mm interference filters by moving the bulb closer to the projector condenser lens.

The electrical surface resistivity of the zinc oxide-resin surface was measured first in the dark and then under standard illumination. The results are shown in Table 5.

6C. Effect of Particle Size of Zinc Oxide on Spectral Response as Determined Using a Grating Spectrograph.

The five zinc oxide samples set aside for this project were mixed in our standard coating formula preparatory to coating.

A Central Scientific Co. Cat. No. 87102 grating spectrograph is used to make the spectrograms. The film holder and slotted masks are removed and a piece of clear film is taped over the film holder opening. A mercury lamp (for example, Cenco Cat. No. 87268 high pressure mercury arc light source) is used as a calibrating light source and the prominent mercury lines at 5790, 5460, 4358, 4046 and 3650 A.U. are marked on the film. This film is then inscribed at these points with the proper wavelength values and the calibrated film is then permanently taped in place on the spectrograph. A light source such as Cenco 86605-1 optical bench illuminator, is satisfactory, and it is well to use a light shield such as Cenco 87118.

TABLE 5

Electrical Sensitometry of ZnO-Resin Photoconductive Coatings

Particle Size of ZnO Used in Coating Slurry (Microns)	0.136	0.250	0.314	0.342	0.408
Tungsten filament lamp with no filter	100×10^8 D* 175×10^6 L*	65×10^8 D 225×10^6 L	45×10^8 D 160×10^6 L	20×10^8 D 275×10^6 L	200×10^8 D 300×10^6 L
Tungsten filament lamp with 650 mm filter (red)	50×10^8 D 125×10^6 L	150×10^8 D 70×10^6 L	150×10^8 D 60×10^6 L	60×10^8 D 85×10^6 L	125×10^8 D 90×10^6 L
Tungsten filament lamp with 600 mm filter (orange)	175×10^8 D 140×10^6 L	75×10^8 D 150×10^6 L	90×10^8 D 160×10^6 L	110×10^8 D 150×10^6 L	150×10^8 D 225×10^6 L
Tungsten filament lamp with 550 mm filter (green)	40×10^8 D 150×10^6 L	125×10^8 D 160×10^6 L	65×10^8 D 240×10^6 L	140×10^8 D 200×10^6 L	45×10^8 D 225×10^6 L
Tungsten filament lamp with 500 mm filter (greenish-blue)	125×10^8 D 70×10^6 L	100×10^8 D 105×10^6 L	110×10^8 D 85×10^6 L	100×10^8 D 80×10^6 L	70×10^8 D 80×10^6 L
Tungsten filament lamp with 450 mm filter (blue)	90×10^8 D 65×10^6 L	30×10^8 D 55×10^6 L	85×10^8 D 45×10^6 L	250×10^8 D 50×10^6 L	65×10^8 D 60×10^6 L

*D - Resistivity in ohm cm in the dark.
L - Resistivity in ohm cm in the light.

Note: 1. All light measurements at 0.00036 watts/cm² illumination.
2. All measurements at 50% R.H. at 78°F.
3. All filters are 20 mm maximum half-width.

The sensitometric measurement is made by first corona-charging a coated sheet. The charged sheet is placed against the calibrated film on the spectrograph and the shutter is opened. An exposure time of 30 seconds is usually sufficient to produce a good density print on development after the exposure. The calibrated film prints the wavelength scale directly on the sensitized sheet, thus making the determination extremely rapid.

A Cenco 87123 logarithmic sector disc can be added to the optical system to make the determinations quantitative.

Figure 15 shows the sensitometric sheets prepared by using zinc oxide samples ranging from 0.134 to 0.408 micron average particle diameter.

Evidence presented both by electrical change in resistance and by direct photographs on the spectrograph show quite clearly that, regardless of the particle size of the zinc oxide (within the limits here chosen), the sensitivity of the undyed coating does not respond to a change in particle size of the zinc oxide.

7C. Effect of Particle Size of Zinc Oxide on Total Charge Acceptance.

In the previous section we demonstrated the lack of dependence of spectral response on particle size of the zinc oxide in the binder coat. We have pursued this facet of the work to its ultimate conclusion and now present data which indicates that particle size does indeed play an important role when we attempt to increase or decrease the electrostatic field on the coated sheet. Furthermore, the speed of electrical discharge appears to be a function of particle size in an unsensitized ZnO-binder system. Table 6 shows the numerical results of measuring a family of curves obtained by electrometer tests on various particle size zinc oxide-binder coating mixes. Charge acceptance is highest in the case of the smaller particle size oxide and charge acceptance decreases as the particle size increases. Figure 16 shows a single electrometer tracing and the points usually selected for evaluation, namely, (1) total charge acceptance,

Spectrograms Showing the Effect of
Zinc Oxide Particle Size on Spectral Response
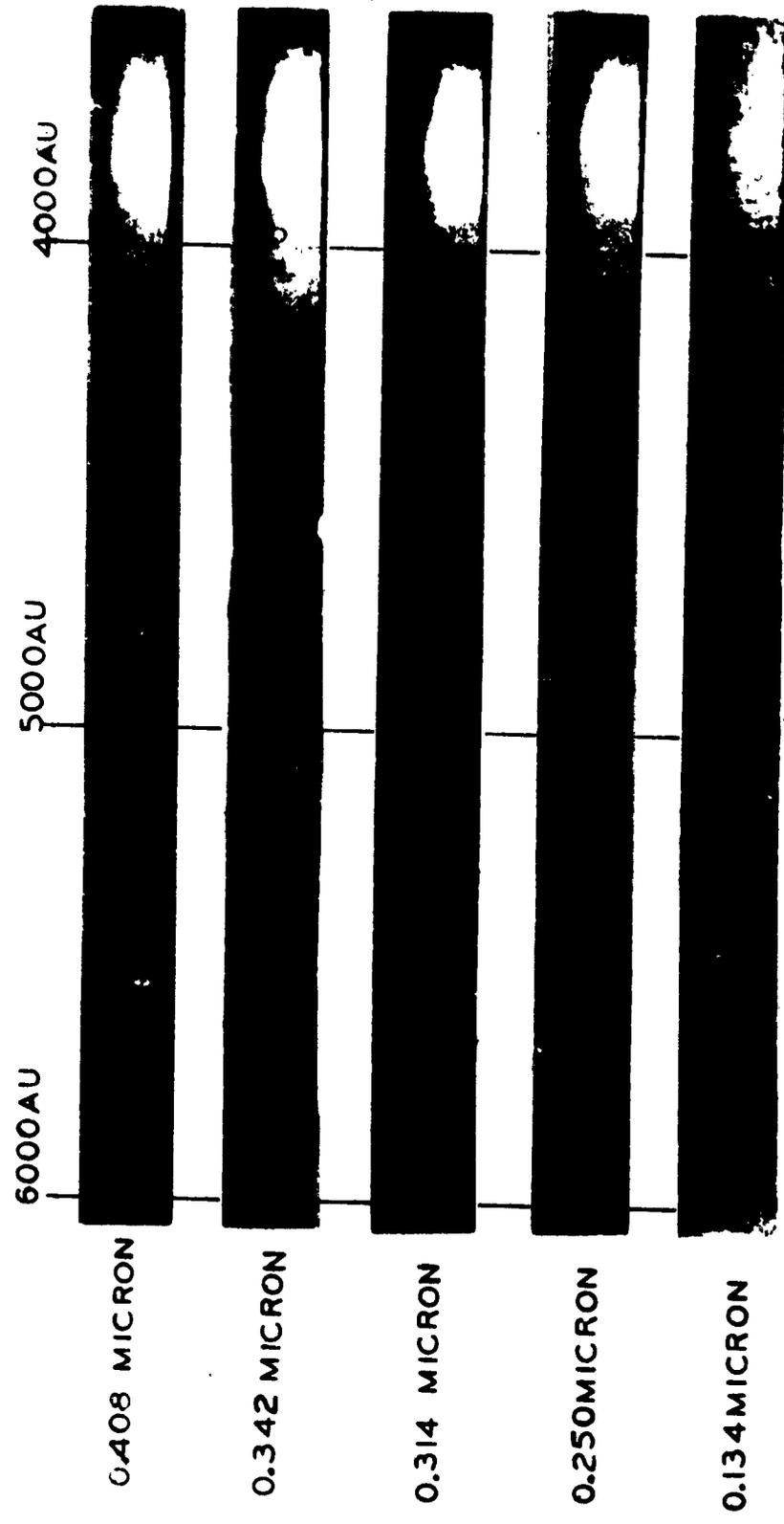
FIGURE 15

Pliolite S5-B Coating on Treated Paper
Using Copytron No. 32-405 Developer Mix

36

TYPICAL ELECTROMETER TRACE

FIGURE 16

← electrometer drift 20 v.

← probe lifted from surface

← residual voltage 50 v.

to reach residual 8.75 sec.

2.50 sec.

1.25 sec.

light on

dark decay voltage 460 v.

← total charge acceptance 480 v.
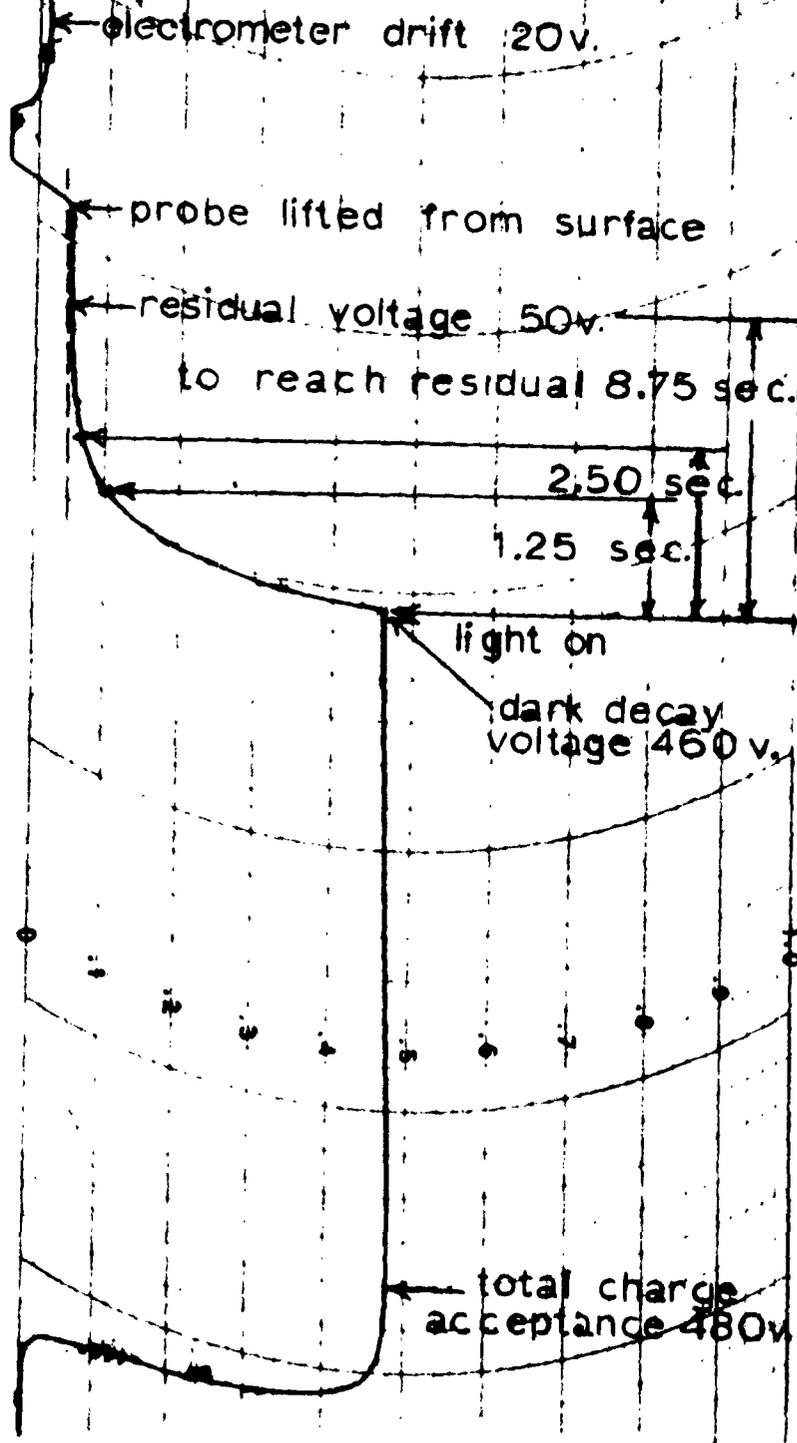
(2) charge level at the end of the dark-decay (called half-life by some investigators)interval, (3) voltage 1.25 seconds after illumination begins, (4) voltage 2.50 seconds after illumination begins, (5) residual voltage (when voltage drop approaches a linear function), and (6) number of seconds to reach residual voltage. Table 6 shows how this data is tabulated for evaluation purposes. The data is "neat" in the respect that it leaves no doubt regarding (1) total charge acceptance is highest in the case of the smaller particle size oxides, (2) residual voltage is also the highest in the case of the small particle size oxides, and (3) the time to reach residual voltage is the longest in the case of the small particle size oxides. A photographic reproduction of a family of curves is shown in Figure 17.

The work was repeated at two humidities (Table 6) and the results are exactly as expected.

1. Charge acceptance is highest in the case of the lower humidity.

2. Speed of discharge is slowest in the lower humidity test coating.

3. Residual voltage is highest in the case of the lower humidity test coating.
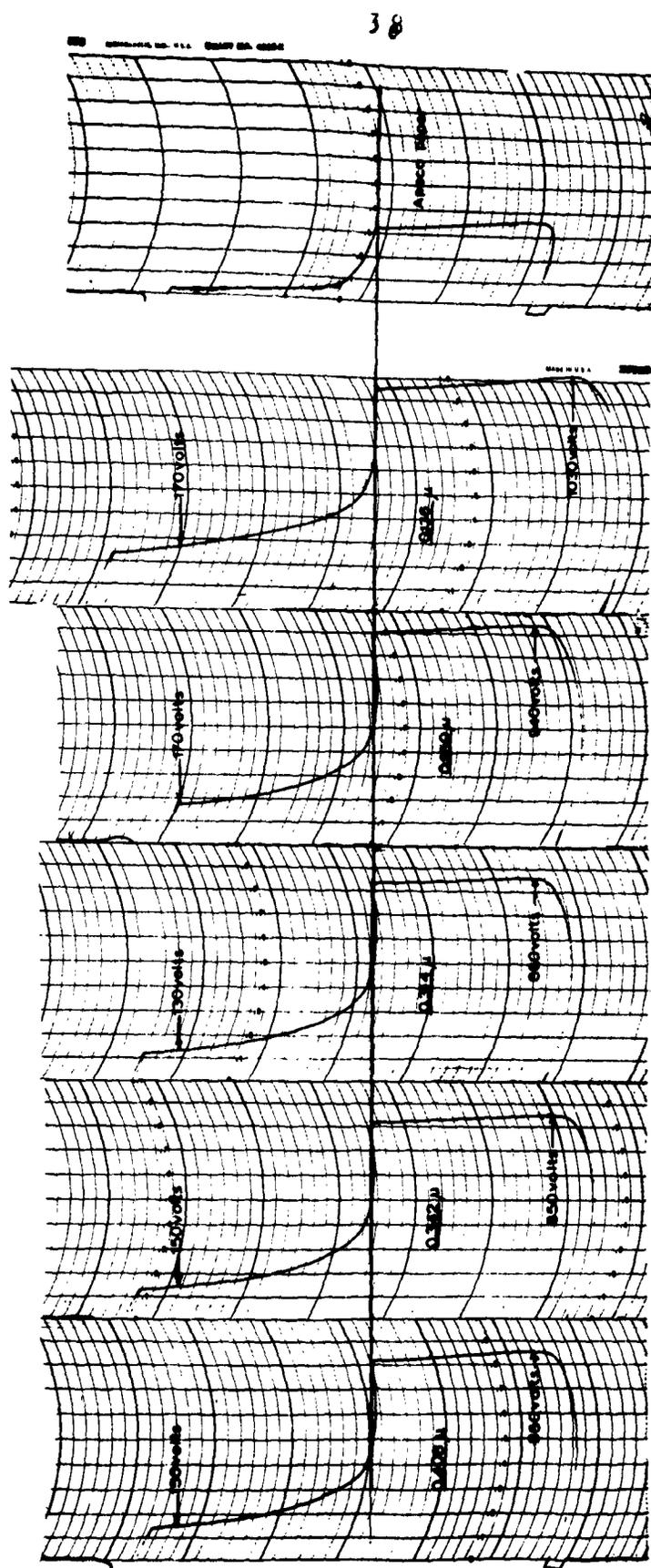
FIGURE 17

EFFECT OF ZINC OXIDE PARTICLE –
SIZE ON TOTAL CHARGE ACCEPTANCE

SR-82 Binder
T-96°F RH 30%

Table 6

Effect of Particle Size of Zinc Oxide on Electrophotographic Electrical Parameters at Various Humidities*

A. At 92°F and 50% R.H.

Sample	In Darkness		Under 140 F.C. Illumination			
	Total Charge Accept.	Dark Decay Volt.	After 1.25 Second	After 2.50 Second	Resid- ual Volt.	Seconds to Reach Residual
APECO Standard	340	330	50	4	0	4.00
0.136 micron sample	780	780	610	460	180	17.25
0.250 micron sample	740	740	440	320	159	16.00
0.314 micron sample	660	660	350	250	100	14.00
0.342 micron sample	660	660	340	250	100	14.00
0.408 micron sample	640	640	330	250	90	10.00

B. At 96°F and 30% R.H.

Sample	In Darkness		Under 140 F.C. Illumination			
	Total Charge Accept.	Dark Decay Volt.	After 1.25 Second	After 2.50 Second	Resid- ual Volt.	Seconds to Reach Residual
APECO Standard	360	320	80	60	40	5.00
0.136 micron sample	1000	950	780	600	270	16.00
0.250 micron sample	940	900	640	420	180	15.00
0.314 micron sample	860	830	620	400	140	14.00
0.342 micron sample	850	8-5	500	350	140	14.00
0.408 micron sample	850	815	460	340	150	14.00

*Coated sheets conditioned for 16 hours at indicated temperature and humidity.

Insert on Page 40 at end of Section 7C and before Section 8C.

7C-a. Effect of Zinc Oxide Particle Size on Dielectric Break-
down Voltages of Coated Sheets at Various Humidities.

Some of the coated sheets prepared for charge acceptance tests
and made as described on Page 22 were used in this work. We
coated both paper and aluminum foil using a wire drawdown bar
and coating weight of twenty pounds. All voltages were deter-
mined using the ASTM Standard Dielectric Strength Procedure
and a 10-second approach to actual breakdown. It should be
noted that in this test, a D.C. potential was applied, whereas
the regular ASTM test utilizes 60 cycle A.C.

An analysis of the breakdown voltages showed the following:

        1. Particle size of the zinc oxide used in the coating
has very little effect on electrical breakdown of the coating.
This was found to be true both on paper and aluminum foil sub-
strates.

        2. Breakdown voltages varied from 1750 volts D.C. at 30%
R.H. to 600 volts D.C. at 70% R.H. using the same pigment
(0.136 micron size). Intermediate humidities have intermed-
iate breakdown voltages pretty much as expected.

From this we conclude that particle size has little effect on
electrical breakdown and that the breakdown voltage is much
more dependent on the type of resin used and on the total
moisture present in the system when the test is made.

It would appear that the particle size of the zinc oxide used in an electrophotographic coating would be dictated by the ultimate speed desired in the coating. While larger particle size oxides do not accept as high a charge as the smaller particle size oxides, they discharge more rapidly and in effect produce a "faster" (higher emulsion speed) coating. This is true, of course, only in an unsensitized system.

Dye sensitization as currently practiced in the industry today changes the particle-size picture. Since the organic dye is adscrbed on the surface, the smaller-particle oxides present a larger specific surface with resultant higher dye-adsorbing capacity. When the correct sensitizer dye is chosen, the junction between zinc oxide and binder becomes more conducting in the ZnO $\longrightarrow$ binder direction under illumination and the smaller-size oxide then shows a significant increase in speed over the larger-size zinc oxide. This increased conduction of the dye-sensitized zinc oxide is used to further advantage because lower total charge acceptance figures are obtained on a sensitized oxide. This also contributes toward the faster coating.

8C. Effect of Additives on the Continuous Tone Characteristics of an Electrophotographic Coating.

The effects of a number of additives or combinations of additives on the continuous tone of electrophotographic coatings are illustrated in Table 7. These additives are only a few of many that have been tried, but since additives fall in several different categories we assume that all or most additives chosen from a specific category would have similar effects on continuous tone characteristics. In general, additives for electrophotographic coatings fall into the following categories: (1) additives to improve the charge acceptance of a coating — usually oxidants or oxygen-containing materials, (2) additives to increase the speed of the coating, (3) additives which decrease the dark decay rate — usually waxes or high molecular weight aliphatic materials, (4) additives which increase sensitivity of a coating to all colors of light — dyes or combination of dyes, (5) additives which change the mechanical surface properties of a coating — for better adherence of

EFFECT OF ADDITIVES ON THE CONTINUOUS TONE
OF AN ELECTROPHOTOGRAPHIC COATING

Resin Type	No.	Additives Type & Percent	Max. Volts	V. End Dark Decay	Volts 1-Sec	Volts 2-Sec	Volts Res.	Time to Res.-Secs.	Exp. Secs. 150 Ft. Cd.	Tonal Range 1-13 Basis
				Electrical Characteristics						
Pliolite	S-5B	None	420	340	120	80	50	4.5	0.4	7
Pliolite	S-5B	0.3 SbCl3 (2)	345	305	120	105	40	5.0	0.5	8
Pliolite	S-5B	0.3 Nopcogen 14L	260	210	70	50	25	7.0	0.4	7
Pliolite(1)	S-5B	None	225	195	90	70	35	5.5	0.5	7
Pliolite(1)	S-5B	0.1 KMnO4	390	355	170	130	40	9.0	0.7	5
Pliolite(1)	S-5B	0.2 KMnO4	420	375	190	140	45	10.0	1.5	4
Pliolite(1)	S-5B	1.5 Hydroso Wax	240	225	110	75	35	5.5	0.5	7
Pliolite	S-5B	0.2 Na2S2O3	320	290	130	80	30	6.0	0.4	5
Pliolite	S-5B	0.3 SbCl3(2)	365	345	150	105	35	6.0	0.4	8
Pliolite	S-5B	0.3 Nopcogen 14L / 0.3 SbCl3 (2) / 2.5 ML. Dye Sol.	210	115	50	40	30	2.5	0.1	8
Pliolite	S-5B	0.3 SbCl3 (2) / 0.3 Nopcogen 14L / 0.1 KMnO4 / 2.5 ML. Dye Sol.	260	180	60	50	35	2.0	0.2	8
Pliolite	S-5B	.1% KMnO4 / 2.5 ML. Dye Sol. (5)	530	465	100	60	30	3.0	0.1	6
Pliolite	S-5B	.1% d-araboscorbic / 2.5 ML. Dye Sol. (3)	285	160	30	15	15	2.5	0.1	3
Pliolite	S-5B	Eosine (6)	565	320	50	30	20	3.5	0.1	7
Pliolite	S-5B	.3% Nopcogen 14L Dye (7)	360	270	85	75	75	1.7	0.1	8
Pliolite	S-7	None	430	390	160	95	30	6.5	0.4	7
Pliolite	S-7	2.0 Paraffin	420	390	170	115	40	6.0	0.4	7
Pliolite	S-7	2.0 Paraffin / 2.5 ML. Dye Sol. (3) / 10 gms. p-dioxane	240	180	55	45	25	3.5	0.2	6
DeSoto	73-35A	None	630	595	300	220	80	9.	0.8	2
DeSoto	73-35A	2.0 ML. Dye Sol. (3)	560	460	70	50	25	3.7	0.2	6
DeSoto	73-35A	0.05 KMnO4	670	590	?	260	60	12.5	0.8	4
DeSoto	73-35A	.3 Nopcogen 14L / 2.5 ML. Dye Sol. (3)	495	330	65	50	30	2.2	0.1	4
A.D.M.	6006	None	670	630	380	330	70	13.5	1.0	2
A.D.M.	6006	.3 Nopcogen 14L / 2.5 ML. Dye Sol (3)	635	480	100	65	30	3.0	0.2	4
95 Styrene 5% Acrylic	A-75 B-82	.4 Nopcogen 14L / .1 Ascorbic Acid / 2.0 ML. Dye Sol. (3)	420	340	105	105	105	1.3	0.1	6

TABLE 7

(1) Zinc oxide aged nine months in open container.
(2) .3% SbCl3 dissolved in water and surface treated on oxide.
(3) Dye solution: .135 g. brom phenol blue, .045 g. eosine dissolved in 30 ml amyl alcohol.
(4) Potassium permanganate dissolved in 10 ml acetone.
(5) Dye solution same as (3) but also containing .1 g brom cresol green.
(6) Eosine surface treated on oxide and dried before incorporating in the coating.
(7) Dye solution of brom phenol blue surface treated on oxide.

toner or to produce adherence of the toner at lower voltages, and (6) additives to produce desirable rheological properties, used for the most part in aqueous systems as thickening agents, viscosity stabilizers, pH controllers, etc.

The charge acceptance of French process zinc oxide, such as AZO-ZZZ-661, either produced fresh or partially carbonated when aged in the presence of moisture, can be increased materially by the addition of small amounts of benzyl peroxide, 30% hydrogen peroxide, potassium permanganate or other oxidants. When potassium permanganate in .1% and .2% additions, based on the weight of zinc oxide, was added to an aged oxide (Table 7) in a Pliolite S-5B coating, it was found that the tonal range was reduced from 7 to 4 or 5 by this addition. The tonal ranges were determined by using a No. 3 Kodak 21-step tablet and Hunt 39-50 toner. In general, all our results to date indicate that addition agents of this type reduce the tonal range with the presently available toners.

Small quantities of other additives, such as cationic agent Nopcogen 14L, p-dioxane solvent, ascorbic acid, etc., the selection of which depends on the solvent and other materials of the coating mix, can increase the speed of the coating materially. These additives have been found to be particularly desirable when coating speed is essential with a minimum amount of dyes to obtain a whiter coating. In most cases where the charge acceptance is not materially reduced, agents to increase coating speed reduce the tonal range. The exception to the rule is 14L. This agent decreases charge acceptance while increasing the tonal range.

Materials such as paraffin amd hydrozo wax, which have high electrical resistance, can be incorporated in solvent systems at 1 to 4%, based on weight of zinc oxide, to decrease dark decay. However, it was found that agents of this type (Table 7) have little or no effect on the continuous tone quality of the electrophotographic coating.

Specific dyes or combinations of two or more dyes have been found to increase coating speed and to increase the sensitivity of the coating to all colors.

There is some evidence to indicate that the physical characteristics of the coated surface play an important role in the development of an electrical image. Thus, a number of electrophotographic coatings have been produced in which the mechanical surface properties have made it impossible to produce quality prints. This is usually apparent in coatings which are extremely smooth; the toner that adhers originally is rapidly displaced on further brushing.

An example of a coating of this type is one produced with the water-soluble alkyd, tri-metallic neopentyl glycol. It is possible with this material to develop an image and then, by further work, to completely remove the image. (The experiment described here was done on a coating having good dark-decay characteristics and the image removed was not due to loss of static charge by dark decay.)

With some acrylic resins the addition of paraffin to the coating has changed the mechanical surface properties to give uniform deposition of the toner but this does not increase the tonal range.

Rheological characteristics of coatings are controlled in solvent systems by the resinous binder while in aqueous-base systems agents such as Daxad 11 and 1,4 butanediol are effective. In aqueous systems additives such as Daxad did not affect the continuous tone characteristics of the print. In solvent-based systems, high solids content, high pigment to resin ratios, and low viscosity are the desired combination of properties. For example, the DeSoto resin 72-64B had a relatively low viscosity at high non-volatile content and high pigment to resin ratio (750 centipoise viscosity at a pigment-resin ratio of 12:1 at 80% non-volatile).

9C. Effect of Light Intensity on Tonal Quality.

The procedure used in testing light intensity was to print a step tablet using different wattage lamp bulbs for different time intervals. Obviously, it would not be wise to use a single bulb and control the intensity with a powerstat because of the wide color shift which would be encountered, with strong reds predominating when the bulb was operated at low voltage.

Insert on Page 44 at end of Section 9C and before Section 10C.

9C-a. Correlation Between Electrophotographic Charge Density
and the Resultant Print Image Density.

It was our feeling at the beginning of this work that in order
to achieve a good dynamic range consisting of perhaps twelve to
fourteen shades of gray it would be first necessary to develop
a high total charge acceptance. This procedure would then al-
low, for example, fourteen steps between white and black in 50
volt increments. Work with a commercially available black toner
(Hunt 39-50) showed that by our test method, black toner part-
icles were capable of "seeing" 10 volt increments and could per-
haps be made to "see" even smaller increments by a more refined
test technique. Armed with this data we then proceeded to test
a number of toners and carriers submitted to us by the Philip
W. Hunt Company, Palisades Park, New Jersey,   hoping that a
better combination of developer and carrier could be found.

Our results showed that with Hunt Carr⁻ ⁻ No. 1 and No. 2, and
Hunt 39-50 toner powder, almost no toner adherence was observed
on a step tablet carrying voltages ranging from 450 volts to 10
volts and made by exposure of a charged sheet through a nega-
tive prepared expressly for this purpose. The experiment was
repeated using a special "low charge toner" prepared by Hunt
and the results were the same. The Hunt Carrier No. 1 and No.
2 (iron filings) carried no designation other than No. 1 and
No. 2.

Next, we used Belmont iron carrier and compared Hunt 39-50
toner with Hunt low charge toner. On a step tablet carrying
voltages ranging from 500 volts to 30 volts, the best reflec-
tion density which would develop was only 0.75. The two step
tablets were nearly identical in appearance.

A final test was made using Hunt 39-50 toner and Cormack iron
carrier (now currently supplied by Anken Chemical Co.,
Newton, New Jersey, and designated as #100-200 mesh iron fil-
ings). On a step tablet carrying voltages ranging from 675
to 10 volts we were able to distinguish eight distinct steps
with the reflectio density ranging up to 1.65. With this
overall dynamic range it should be possible to develop many
intermediate shades of gray.

After the work on tonal scales had advanced to the point where
we had standardized on the use of a Pliolite binder (rather
than SR-82 as was used in the above work) we found that high-
charge acceptance was not a necessary requirement to the de-
velopment of good black print density. A step tablet with

9C-a (continued)

voltages ranging from 150 volts to 10 volts and made with
Pliolite S5-B or S-7 binder gave a black density and dynamic
range equal to the one produced with SR-82.

We therefore conclude that the combination of Hunt 39-50 toner
and the iron filings from Anken Chemical Company, is the best
possible combination which we can use at this time for an ex-
panded dynamic range. These materials could certainly be im-
proved but they represent commercially available products at
the present time.

We also conclude from this that high charge acceptance is not
a primary requisite to the production of an extended gray
scale. If the toner powder can "see" differences of only ten
volts, a fourteen step tablet could be made on a sheet having
only 140-150 volts total charge acceptance.

We used standard formula of Pliolite S5-B and the 0.342 micron oxide. Light conditions were as follows:

Watt Rating of Bulb Used in Printing	Light Intensity as Measured on G.E. Foot-Candle Meter	Exposure Time (Seconds)	Foot Candle Seconds
100	600	0.1	60
60	300	0.2	60
40	150	0.4	60
15	50	1.2	60
7.5	25	2.4	60

The five step tablets were all equally exposed (within allowable experimental error) and despite the slight extra red which one would expect from a 7.5-watt bulb versus a 100-watt bulb, the 7.5-watt light source gave the same tonal scale as the 100-watt lamp, and residual voltages after exposure through a step tablet were all within the limits of experimental error.

These residual voltages were measured by using a simple hand probe (as is used with a conventional VOM). A piece of insulating spaghetti is slipped over the metal end of the probe to keep the metal probe from making contact with the sheet under test. The probe can be calibrated in the same way as the 4" x 4" x 8" probe, that is, by using a metal plate held at a fixed D.C. potential. The insulation spaghetti over the metal end of the probe is lengthened or shortened until the electrometer reads the actual voltage on the D.C. test plate. This is a very useful hand probe for the exploration of small areas. In this work we note no departure from the reciprocity law, and we can expect no improvement in quality by using stronger or weaker light sources within the ranges tried in this experiment.

## 10C. Effect of Alternate Charge-Discharge Cycles on Tonal Quality.

The procedure was to charge a sheet to saturation voltage and then to expose it under a step tablet at 60-foot candle seconds. Residual voltage was then measured with

the small hand probe described under 9C. After 70 seconds for dark adaption the sheet was recharged and a second exposure and measurement was taken. The procedure was then repeated a third time. The voltages observed seemed to be a little lower on the second cycle but recovered to their full value on the third cycle. In other words, we observed no shrinkage or expansion of the gray scale by alternate charge-discharge cycles. The fact that we were using the fairly conductive binder S5-B (as contrasted with a silicone) accounts for the fact that we were able to, in a large extent, eliminate fatigue. High conducting resins relax (dark adapt) more rapidly. If we had been using a less conductive resin the system would have had a tendency to reach saturation at a lower voltage.

11C. Effect of Doping Zinc Oxide During Manufacture on its Continuous Tone Properties.

A comprehensive survey of all types of zinc oxide which are commercially available (both American and French process) shows that all zinc oxide is photoconductive. The degree of photoconductivity, however, varies widely with the past thermal history and origin of the zinc oxide.

American process oxide is manufactured by burning zinc vapor in the presence of CO and CO_2 formed by the reactions

$$C + O_2 \longrightarrow CO_2$$
$$C + CO_2 \longrightarrow 2CO$$
$$CO + ZnO \longrightarrow Zn + CO_2$$
$$Zn + CO_2 \longrightarrow ZnO + CO$$
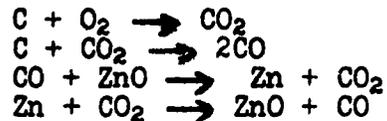
Here the zinciferous material, such as roasted zinc sulfide (converted by the prior roasting to crude ZnO), is mixed with coal or coke, and the mixture is laid on a steel hearth where it is ignited. The above reactions represent only a part of the mechanism. The crude ZnO used, having had no prior refining other than mechanical concentration, carries portions of the associated minerals such as copper, cadmium, magnesium, calcium and other impurities. All of the metals present show

a sufficient partial pressure at the boiling point of zinc to cause their volatilization in part or in total. As a result, American process zinc oxide contains numerous impurities in variable amounts. The chemical analysis of a typical American process lead-free zinc oxide is shown in Table 8 below.

Table 8

Analysis of Typical American Process Zinc Oxide*

Zinc oxide	99.0% minimum
Zinc sulfate	0.20-0.35%
Lead	0.01-0.03%
Cadmium	0.05-0.10%
Sulfur	0.02-0.04%
Acidity (SO_3)	0.02-0.10%
Water soluble	0.20-0.40%
Insoluble in HCl	0.05-0.20%
Ignition loss (91 hr/760°C)	0.05-0.20%
Loss at 110°C	0.05-0.15%
Moisture	0.01-0.06%
Chlorine	0.01-0.03%
Copper	0.01-0.03%
Iron	0.01-0.03%

*Mathewson, C.H., "Zinc", ACS Monograph, Reinhold Pub. Co., N.Y., 1959, p. 350.

General speaking, American process oxide shows very poor photoresponse despite the fact that its bulk and surface resistivity does not differ greatly from the French process oxide.

French process oxide is made by simply burning metallic zinc. Pure zinc metal is manufactured by distillation or by electrolysis. This metal is remelted, raised to the boiling point, and allowed to burn under carefully controlled conditions. If the burning is conducted in a deficiency of air the final product assumes a gray color characteristic of its content of metallic (unburned) zinc. If the burning is conducted in a large

chamber held at high temperature, the zinc oxide parti-
cles will grow to larger size. Thus by careful control
of the amount of air used and by the design of the burn-
ing furnace, it is possible to produce a wide variety of
zinc oxide types with respect to particle size and shape
and to chemical, physical and electrical behavior.

Table 9

Analysis of Typical French
Process Zinc Oxide

Lead	.002%
Cadmium	.0003%
Iron	.0006%
Copper	.00005%
Silver	.00010%
Chromium	.0001%
Tin	.003%
Calcium	Trace
Magnesium	Trace
Silicon	Trace
Boron	Trace
Fluorine	Trace
Arsenic	Trace

Doping of the zinc oxide produced by either of the above
processes can be done by moistening the oxide with a
solution of the desired doping agent. For the doping
to be effective, however, the treated oxide should be
heated to a temperature sufficiently high to allow mi-
gration of the doping agent into the ZnO lattice. For
zinc oxide, the temperature at which ionic migration be-
gins is also the temperature (about 450°C) at which part-
icle growth begins. Therefore, when the treated oxide
has been heated to a sufficiently high temperature to
cause ionic migration, the particle size distribution
has been radically shifted due to the growth of the large
particles at the expense of the fine particles. Electron
microscope pictures show quite clearly that "pirating" of
the small crystallites takes place, and after a heating
period of 2-3 hours at 500°C nearly all of the smaller
particles have disappeared.

Doping by this technique when using large single crystals is, of course, an entirely satisfactory procedure, but doping a particulate powder consisting of crystallites ranging from 0.02-0.6 micron diameter results in two separate simultaneous phenomena (doping and shift in particle size distribution).

Being aware of this problem, we decided to do all of our doping by introduction of the foreign element directly into the crystal via thermal treatment during burning of the metallic zinc.

We have constructed a furnace in which a 15-liter quartz flask is heated by a gas flame inside a brick muffle. The top of the flask is closed with a quartz plate in which is drilled a 1.25-inch opening. The neck of the flask is surrounded by a heavy ceramic shield which can be sealed to prevent entry of outside air. The top of the ceramic shield is connected to a fan and the exit from the fan is connected to a baghouse. When the zinc metal in the flask is heated, the vapors escape through the opening in the lid and burn inside the ceramic chamber. Air is admitted in an amount sufficient to burn the zinc vapor. The zinc oxide goes through the fan and is collected in the baghouse. Using this system we can produce about one kilo of oxide per hour. Usually after one hour of operation under normal conditions we add the doping element directly to the molten zinc in the quartz flask and then continue to run until enough sample is collected. Using this scheme we have begun our doping experiments using antimony and arsenic. The antimony addition produced nothing of merit, but the use of enough arsenic to produce 0.12% As in the zinc oxide gave a product which had a slightly extended gray scale (see Figure 18).

Figure 18 is self-explanatory but it is worth while to point out the short tonal range of a paper which is now commercially available, Bruning No. 32-155 Coptron paper. All efforts have been directed toward the production of a "short-scale" step tablet. Other commercially-available papers designed for office copy work are similar in their behavior.

FIGURE 18

Comparison of Tonal Ranges

ARSENIC-DOPED ZnO

KODABROMIDE E 2

BRUNING NO. 32-155
COPYTRON PAPER

12c. Effect of Larger Particle Size on Tonal Scale

Because previous work indicated that arsenic doping was
beneficial in the extension of the tonal range we exam-
ined this pigment in greater detail. We normally make
three products from a run. The first product is undoped
French oxide, and this is used as the control sample.
Then, without interrupting the operation in any way we
introduce the doping element into the molten zinc pool.
The run is then continued until sufficient doped product
is produced. A third product is collected when we dis-
assemble the furnace, and this represents the oxide
which has settled out in the flues. An analysis of
these three products showed the following:

	% As	% SO₃	% Pb	% Cd	Average Particle Size (Microns)
Undoped oxide	.001-	.046	.0034	.0028	0.280
Doped oxide	0.16	.023	.100	.250	0.230
Flue cleanings	0.12	.032	.066	.191	0.325

Prints made from the above oxides showed the flue clean-
ings to give a slightly better tonal range than the
doped oxide. Since these two oxides are almost identical
in analysis we suspected that the larger particle size
might be responsible for the better print. A number of
runs were then made in which larger particle size oxide
was produced. It was found that when we produced a large
particle size we could get a less mottled print with an
extended tonal range. This oxide was made using no ar-
senic dope and containing only the normal amounts of lead
and cadmium encountered in commercial French oxide. A
routine analysis of the zinc oxide made on this experi-
mental run resulted in the following data.

Table 9

Chemical and Physical Test Data
on Large Particle Size ZnO

Sample	% Pb	% Cd	% SO$_3$	Spec. Surf. (m^2/gm)	Part. Diam. (μ)
Normal product	.0045	.0030	.084	3.48	0.309
Flue cleanings	.0045	.0038	.050	2.23	0.484
Combustion chamber cleanings	.0065	.0053	.012	0.604	1.79

When the large particle size oxide was run through the routine electrophotographic tests we found that its total charge acceptance was considerably below that which we have heretofore considered necessary to produce a good quality print. The measurements were as follows:

Sample	Total Charge Accept.	Dark Decay Volt.	After 1.25 Second	After 2.50 Second	Resid-ual Volt.	Sec. to Reach Residual
Normal prod.	140	130	55	40	20	8.0
Flue clngs.	130	120	40	20	0	7.5
Comb. chbr. cleanings	50	40	20	15	10	7.5

As can be seen from Figure 19, a fairly good tonal scale can be achieved simply by increasing the particle size of the zinc oxide. A word of caution must be expressed here. We speak of an increase in particle size as being responsible for the better quality print. This increased size may be only a side-effect. To produce the larger size we must operate the furnace at a higher temperature, and the air to zinc vapor ratio is increased. The thermal history of the oxide changes because the crystallites stay in the "growing" portion of the combustion chamber for a longer time and the collection system is hotter, resulting in longer storage of the oxide at elevated temperature. Any or all of these or additional unknown factors could be responsible for the better oxide. We simply refer to it as large-particle zinc

FIGURE 19

oxide because this is one of the measurable parameters. Proper doping could possibly further enhance the advantage gained by the larger particle size.

The direction of future work is certainly clearly pointed out in Figure 20. Here we have presented a graph in which we plotted the Kodak step tablet number versus the actual reflection density. Two step tablets were made similar to those shown in Figure 18. Using a Welch Densichron densitometer with a direct reading optical density scale and a reflection unit No. 3832A it is possible to read the step tablets and determine the reflection density. As a closing portion on this report we point out the direction for future work by showing a comparison between the results of silver photography and electrophotography. When the density values are compared we see that our whites are not pure enough and that the black densities begin to fall off at about one-half the value realized in conventional silver photography.
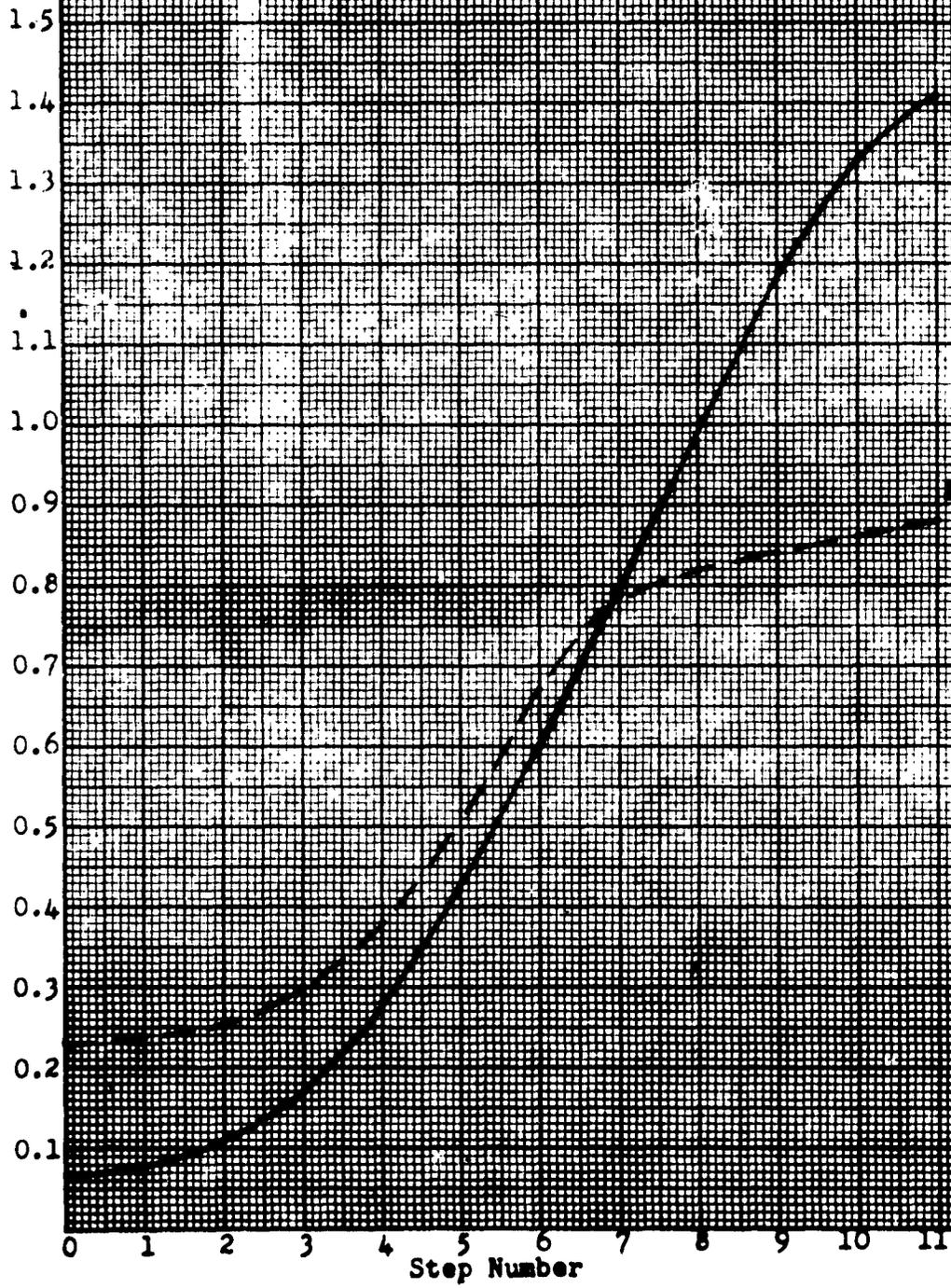
FIGURE 20

Discussion

Electrical Resistivity of Zinc Oxide

The data presented in Figure 13 shows the deleterious
effect of moisture on photoconductive response. As the
moisture content of the zinc oxide increases its elec-
trical resistivity decreases due to an enhanced elec-
trical path between adjacent zinc oxide crystals. The
moisture need not necessarily originate in the zinc
oxide. We have seen numerous resins which contained
more than enough moisture to seriously injure photocon-
ductive response. Moisture can also enter via addition
agents, coating machinery or even if the coating mixes
are made in a room where both the temperature and humid-
ity have reached a high figure.

Zinc oxide is also susceptible to moisture during stor-
age. If it is stored in an unprotected condition in a
humid atmosphere it will adsorb carbon dioxide and
slowly begin a conversion to zinc carbonate. This does
not cause any significant change in the electrical re-
sistivity of the oxide (in the dark) but its photore-
sponse diminishes, and the resistivity under illumina-
tion is not as low as an uncarbonated sample. Oxide
which has begun this conversion can be restored to its
original condition by careful heating to decompose the
carbonate.

Another effect of moisture should be mentioned. Photo-
conductive zinc oxide can be slurried in water, fil-
tered, dried and reground. Oxide which has had this
treatment does not lose its photoconductivity; if it
is thoroughly dried it is as active after the slurry-
ing as before. If, however, tap water is used which
is heavy in mineral salts, it will be found that the
calcium and magnesium salts have been injurious to the
photoconductive response.

The sensitivity of zinc oxide to moisture changes with
the particle size as was shown in Figure 13. Very small
particle size is extremely susceptible to moisture ad-
sorption. Since photoconductive response dimishes with
increase in moisture in a given system we might be led

to believe that the smaller particle size zinc oxide
gave a shorter tonal scale. A careful check for mois-
ture content will usually show the smaller particle size
zinc oxide to carry the highest moisture and this higher
moisture is responsible for the shorter gray scale.

One final word on electrical resistivity of zinc oxide.
The resistivity results reported in the literature for
zinc oxide range from 1×10^{-1} to nearly infinite re-
sistance. After making many measurements with and with-
out interference filters, we believe that all of the re-
sults reported are correct. Almost any value obtained
can be varied through several orders of magnitude by the
measuring technique. For example, a large single cry-
stal (2.5 x 2.5 x 10 mm) produced accidently in our
Hillsboro furnace combustion chamber was examined and
found to have a resistivity of about 50 ohm-cm. This
crystal was then carefully pulverized and reduced to a
size which was roughly comparable to our larger parti-
cle size photoconductive zinc oxide. The resistivity
was almost an exact match of the French oxide. We can
only conclude that the resistivity is in the grain
boundaries between crystals.

Measurement of Electrical Parameters of Electrophoto-graphic Coatings.

The so-called "static" method of testing a photoconduc-
tive coating presents a number of advantages and disad-
vantages as opposed to the "dynamic" test. Using a
probe and a recorder it is possible to develop a rou-
tine technique which gives extremely reproducible re-
sults (±15 volts on a 350-volt test). Also, the charts
drawn by the recorder (Figure 16) lend themselves to
careful examination and study.

The obvious disadvantage of the "static" test is its in-
ability to show the rate at which the charge is accepted
by the coating. A complete and thorough test should
therefore probably include both methods utilizing the
attendant advantages of each method.

One of the interesting experiments, for example, which
we have been able to perform with the static test and
which does not readily lend itself to duplication with

the "dynamic" test involves the strange behavior of a
zinc oxide coated sheet which has been corona charged,
exposed and then simply stored until no electrical
charge can be detected with our instruments. The ap-
plication of a good developer causes the appearance of
an image where no measurable static charge was to be
found. Some strange condition, possibly internal po-
larization, causes the developer particles to adhere
in areas where we cannot detect an electrostatic field.

Pre-exposure to cause fatigue is a well recognized phe-
nomena, but pre-exposure to cause complete densitiza-
tion can also be performed and checked by the "static"
method of measurement. If zinc oxide is mixed with a
high resistivity resin and coated on a sheet and this
sheet is charged to saturation (for example, 1000 volts)
we would next, in the logical course of events, expose
the sheet to the image. If, however, the sheet is given
a very short exposure so that the voltage is decreased
to perhaps 900 volts before exposure to the image, it
will be found that no image will develop regardless of
the exposure used to project the image. A very short
pre-exposure has caused some unknown phenomena to oc-
cur in the coating so that it becomes insensitive to
the subsequent light which carries the image. We can-
not explain this, but it is possible that the dipoles
formed during corona charging are sensitive to light
and collapse during the pre-exposure. The current
which passes through the sheet during charging estab-
lishes these dipoles (oxygen) and the static field
normally maintains this warped condition. When light
strikes the surface the zinc oxide becomes sufficiently
conductive to allow current flow, and electron-hole
recombination occurs. We are inclindd to be.ieve that
two separate and distinct phenomena occur during expo-
sure to light; (a) return of the dipole to its normal
state, and (b) collapse of the static field due to the
lowered electrical resistivity of the zinc oxide.
Only further work on this problem will furnish the
answer. The first line of attack would be to learn
how to detect the dipole in the presence of the static
field.

Effect of Resin Binder on Continuous Tone

Binders which are relatively non-conductive, such as
alkyds and silicones, produce coatings which have the
highest charge acceptance. It is natural to expect
that a highly charged surface would be more effective
in holding toner than a surface with a low charge. We
have not found this to be true. Experiments with
coated surfaces charged to high voltage have shown that
the ability to attract and hold toner has very little
relationship to total voltage on the surface. This can
be demonstrated very quickly by running a comparison
between an alkyd resin and Pliolite S5-B using the same
oxide. The alkyd will accept a charge of 600 volts or
more while the Pliolite will accept no more than per-
haps 250 volts. Despite this, the Pliolite will show
seven or eight steps of gray while the alkyd shows only
five or six at the most. We have no explanation. We
can only suggest again that perhaps internal polariza-
tion is responsible and that static charge is simply an
accompanying condition which has been established dur-
ing the charging cycle. The developer then sees only
differences in polarization instead of differences in
potential.

Effect of Doping Zinc Oxide

Prior work in this field has been done almost exclu-
sively on single crystals of zinc oxide. Unfortunately,
the results of this work are not generally applicable to
a particulate powder. The electrical resistivity of a
sample of zinc oxide, both surface and bulk values, re-
sides in the grain boundaries between crystals, and the
effect of any doping is very likely to be obscured by
the very high resistivity values of the zinc oxide
powder.

Numerous attempts have been made to produce a more "con-
ductive" oxide by doping and/or by heat treatment. It
is true that the resistivity can be changed, but whether
the oxide becomes "conductive" or not depends on the de-
finition of the work "conductive".

Our doping experiments were inconclusive, and not enough
experimental work was performed to really accumulate
data which would set a pattern. We hope to be able to
run the pilot furnace on a routine basis in the near
future and thereby try enough doping agents to enable
us to set a pattern for their behavior. We have learned,
however, that any "dope" will have to be added in gross
amounts and that our long-studied technique of doping
germanium melts will be of little value in predicting the
results which might be expected from doping zinc oxide.

CONCLUSIONS

An analysis of the factual data leads to the following conclusions:

1. In a zinc oxide-resin system, the strongest photoconductive response will be attained when moisture is carefully excluded from the coating mix.

2. In an unsensitized system, photoconductive response is slightly more rapid when using larger particle size zinc oxide.

3. The use of a smaller particle size zinc oxide allows the development of a higher electrostatic charge on a coated sheet.

4. Less conductive resins, such as silicone, in conjunction with small particle size zinc oxide give the highest possible electrostatic charge on the coated sheet.

5. Particle size of the zinc oxide has no noticeable effect on spectral response within the limits specified in the above work.

6. The development of a high electrostatic charge on a coated surface is not a guarantee of an extended tonal scale.

7. Shortest tonal ranges are observed with the alkyd resins and longest tonal ranges are attained when using Pliolite resins.

8. Experiments on doping of zinc oxide have been inconclusive, but there is some evidence to indicate that arsenic might be beneficial. This is clouded by the introduction of a second variable, namely, large particle size.

RECOMM

Future work in this field ⟨c⟩ ...
ful if the doping experime⟨t⟩ we⟨r⟩e con⟨...⟩
more work should be carrie⟨d⟩ ⟨at⟩ u⟨si⟩n⟨g⟩ ⟨...⟩
coating mix. From a theor⟨⟩t⟨i⟩c⟨a⟩l st⟨an⟩d⟨po⟩⟨...⟩
be helpful if a workable t⟨⟩e⟨o⟩ry ⟨c⟩o⟨u⟩l⟨d⟩ ⟨be⟩ ⟨...⟩
along the same lines as i⟨s⟩ n⟨o⟩w i⟨n⟩ ⟨pro⟩⟨g⟩⟨r⟩⟨...⟩
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