

FOREWORD

This report describes the progress made from 1 February 1961 to 1 October 1961 on a research and development program for an electrochemical light modulator. The electrochemical work was performed by the Applied Physics Research Group of the Basic Science and Technology Department of the Philco Research Division, Blue Bell, Pennsylvania. The associated electronic circuitry was designed by the Engineering Department of the Government and Industrial Group of the Philco Communications and Weapons Systems Division, Philadelphia, Pennsylvania. Captain L. R. Loper, USAF, of the Vision Section, Protection Branch, Life Support Systems Laboratory, monitored the program under Contract No. AF 33(616)-7928, Project No. 6301, "Aerospace Systems Personnel Protection," Task No. 630103, "Vision Enhancement and Protection in Aerospace Environment." Dr. Marvin E. Lasser and Dr. P. H. Cholet, of the Philco Research Division, were responsible for the over-all technical direction of the program.

The author of the electrochemical section of this report, Dr. Solomon Zaromb, Research Specialist of the Applied Physics Research Group, was the scientist in charge of the electrochemical research and development work. He was assisted by Dr. Joseph Y. Chang, Project Scientist, and Mr. Edward Kostyk, Technician. Mr. Ralph E. Husband of the Engineering Department was the author of the circuit work section of this report. Other personnel of the Engineering Department who contributed significantly to the circuit work were Mr. Donald A. Bixler, Mr. Harold J. Churchill, and Mr. John W. Hayward. Thanks are due also to Mr. Fred Johnson, who, being "on loan" to the Applied Physics Research Group, performed most of the cell tests. Acknowledgment is made of the invaluable assistance lent Dr. Zaromb by Dr. John O'Mara Bockris, Mr. Vincent de Maria, and Mr. Robert R. Kegg, Consultants, and also by Mr. Boris D. Cahan of the Surface Studies Group of the Philco Research Division.

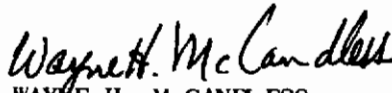
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ABSTRACT

An electrochemical device was developed to automatically provide vision protection for aircraft personnel during nuclear flashes. The requirements were that it have an optical density of 4 within 50 μ secs, clear in one second, and have an open-state transmission of 33% for visible light. In the original cell design, difficulties were encountered with the fabrication of conducting glass plates, contact resistances, and heavily loaded parallel circuits. To eliminate these difficulties, design changes were made. However, completed cells are not entirely satisfactory. All of the specifications, therefore, could not be met. Improvements are still possible in the size and weight of the electronic package, and in the lens plating time. It is concluded that, by placing 5 cells (with series-connected subelements) back-to-back, fabrication difficulties will be reduced and specifications met.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.



WAYNE H. McCANNILLESS
Chief, Life Support Systems Laboratory

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SECTION 1

CELL RESEARCH AND DEVELOPMENT

Dr. Solomon Zaromb

I. INTRODUCTION

The reversible electroplating light shutter originally proposed was to achieve an optical density of 2 within 500 μ sec. However, according to subsequent specifications, an optical density of 4 within 50 μ sec was to be aimed for, although the possibility of achieving this within the scope of the present contract was clearly declared to be doubtful. Of the other requirements, only the following need to be discussed in the electrochemical section of this report:

- a. The shutter area was to be 4-1/2" x 1-1/2".
- b. The open state transmission was to be at least 33% for visible light wavelengths (between 3,750 and 7,500 \AA).
- c. The cell was to clear within 1 sec, following manual operation of a switch.

II. THEORETICAL CONCLUSIONS AND THEIR APPLICATION TO THE PRESENT LIGHT SHUTTER

To achieve an essentially uniform plating charge density over a large area A , the shutter must be composed of a number n_s of adjacent, narrow-band subelements of minimal width b and any desired length L . Each subelement should be composed of two rectangular, transparent (tin-oxide-coated glass) electrodes g'_1 and g'_2 both having the dimensions $b \times L$ and a nearly uniform surface resistivity ρ_g' . The electrical connections to the electrodes g'_1 and g'_2 of the various subelements can be arranged in eight different ways, as shown in Fig 1. However, only the arrangements 6 and 7 are worth considering. The experimental work was done with arrangement 6. Arrangement 7 was discovered too near the end of the present contract to be fully investigated.

The spacing \underline{a} between the anode and cathode should be within the range

$$b^2/(2k) \leq a \leq 2k/5 \quad (1)$$

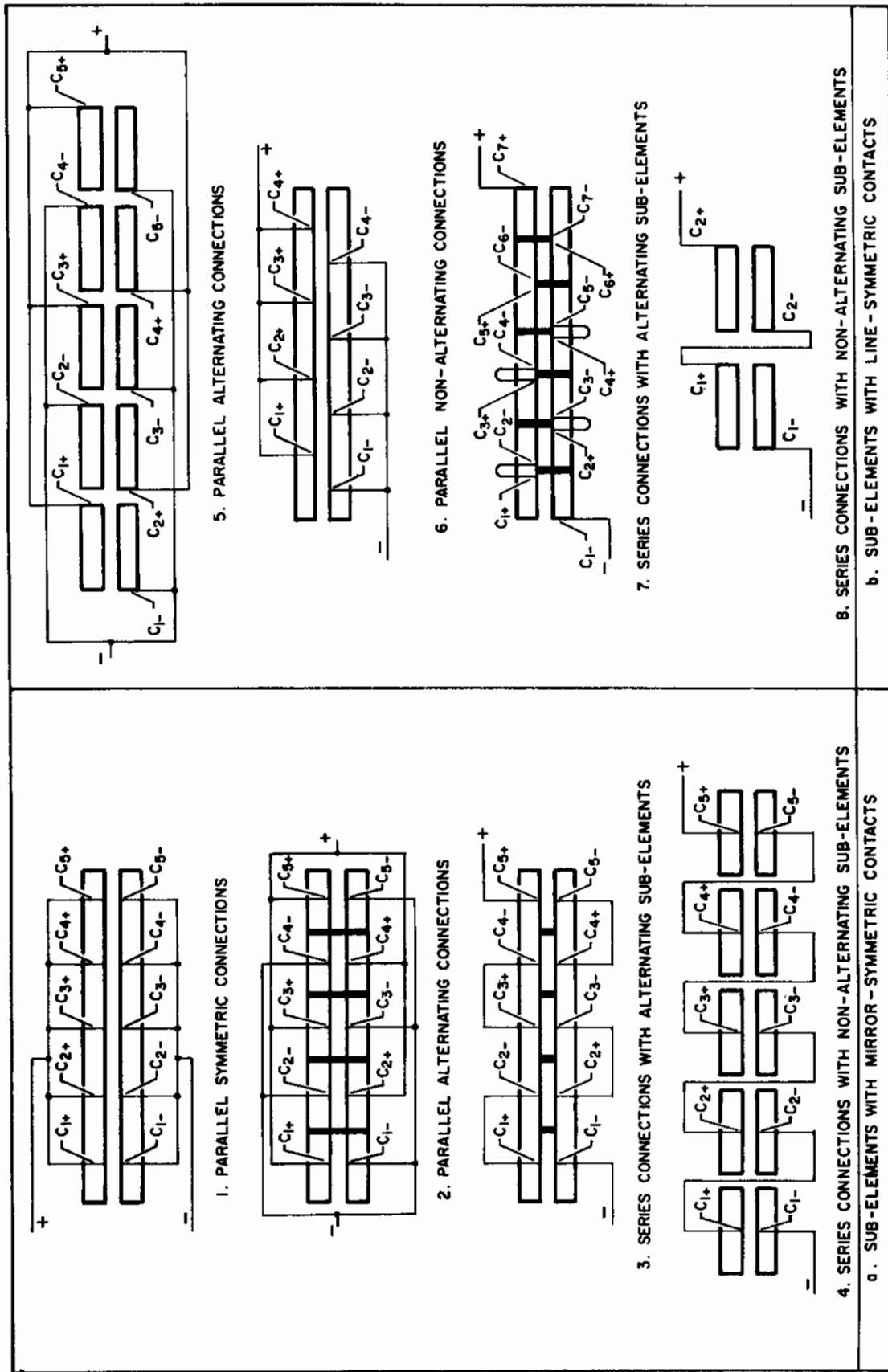


FIGURE 1 POSSIBLE CONTACT ARRANGEMENTS FOR A LARGE-AREA LIGHT SHUTTER

where

$$k = \rho_e / \rho_g \quad (2)$$

and ρ_e is the resistivity of the electrolyte solution. Thus, for $\rho_e = 10$ ohm-cm, $\rho_g = 10$ ohms/square, and $b = 0.3$ cm, one obtains $k = 1$ cm and $0.045 \text{ cm} \leq a \leq 0.4 \text{ cm}$ or $0.018'' \leq a \leq 0.16''$, whereas for $\rho_g = 5$ ohms/square and $b = 0.2$ cm, k becomes 2 cm and $0.01 \text{ cm} \leq a \leq 0.8 \text{ cm}$ or $0.004'' \leq a \leq 0.32''$.

The requirements for an optical density of 4 in the closed state and an open state transmission of 33% (corresponding to an optical density of 0.5) in the open state (see "Introduction") amount to a net optical density change δ of 3.5. On the other hand, according to Fig 2, the minimum ratio of δ to the plating charge density q_d in the visible wavelengths region is $(\delta/q_d)_{\min} = 36 \text{ coul/cm}^2$. Hence, the required charge density is $q_d = 3.5/36 = 0.097 \text{ coul/cm}^2$. Thus, for an area A of $4\text{-}1/2'' \times 1\text{-}1/2''$ or $11.4 \text{ cm} \times 3.8 \text{ cm} = 43 \text{ cm}^2$, the total required plating charge Q_p becomes

$$Q_p = q_d A \quad (3)$$

which is 0.097×43 or 4.2 couls. This value may be reduced by the approximate fraction of the shutter area occupied by the opaque and non-plateable contacts described below, i.e., by 5%. The total plating charge required is, therefore, 4.0 couls.

The resistance r_{sl} of each subelement is

$$r_{sl} = \frac{\rho_g}{L} \left[\frac{b}{2} + \frac{2}{\delta} \coth \frac{\delta b}{2} \right] \quad (4)$$

where

$$\delta = (ak/2)^{-1/2} \quad (5)$$

Eq 4 can be simplified for $\delta b < 1$ (e.g., $a = 0.03 \text{ cm}$, $k = 2 \text{ cm}$, and $b = 0.3 \text{ cm}$) to

$$r_{sl} \approx \frac{\rho_g b}{2L} + \frac{2 a \rho_e}{bL} \quad (6)$$

For n_s subelements connected in parallel, Eq 6 would yield an over-all resistance

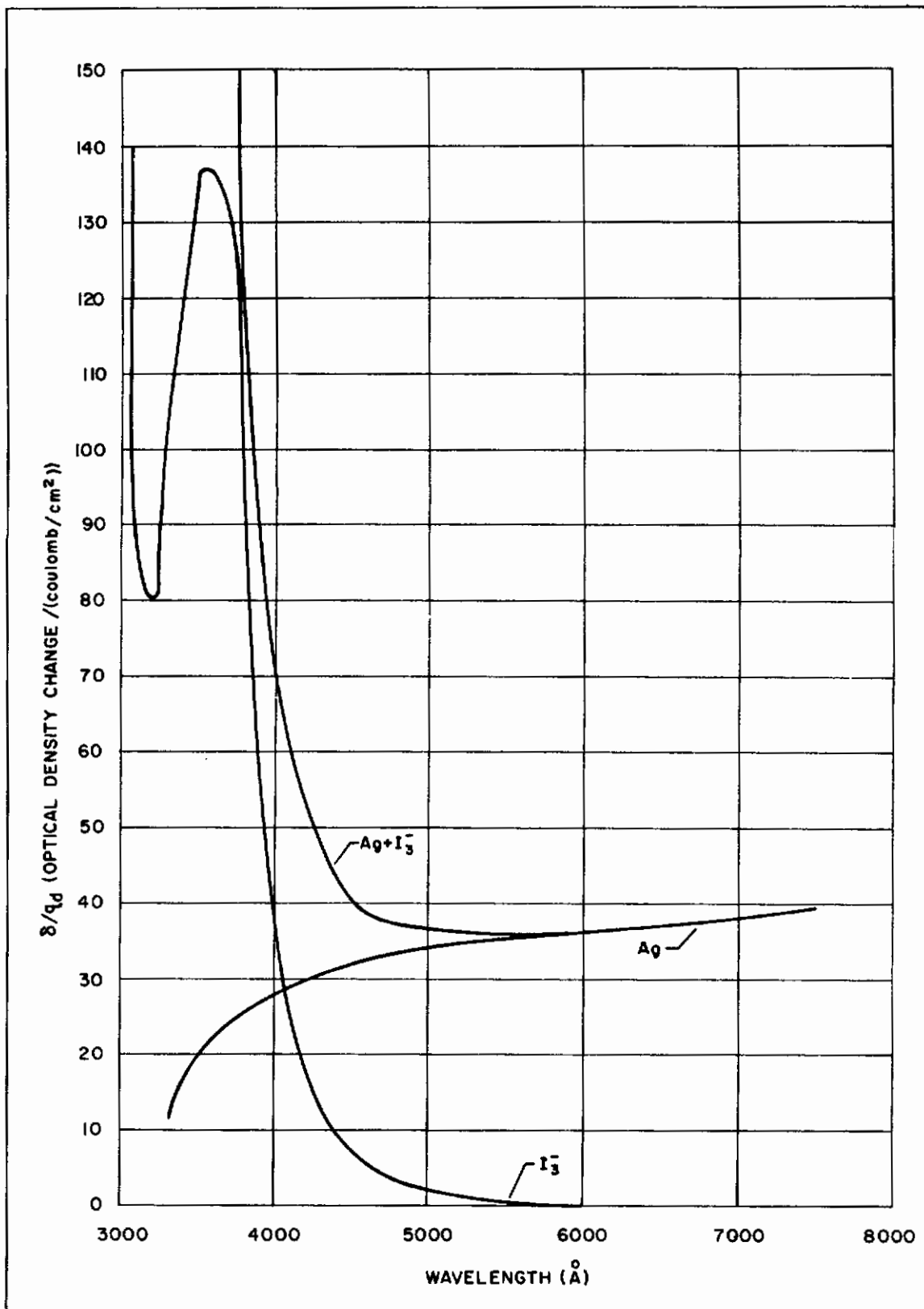


FIGURE 2 OPTICAL DENSITY CHANGE PER PLATING CHARGE DENSITY FOR $Ag\ddagger$ SOLUTIONS

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$$R_p \simeq \left[2a\rho_e + 0.5 \rho_g b^2 \right] / A \quad (7)$$

if the contact resistance could be neglected. However, the contact resistance of the actually produced cells was far from negligible, as discussed below.

Even under the nearly ideal conditions when Eq 7 is approximately valid, the heat H generated in the electrolyte by a plating charge density q_d passed at a uniform rate (square wave pulse) within a time period τ_p must be

$$H \geq 2a\rho_e q_d^2 A / \tau_p \quad (8)$$

Since the instantaneous temperature rise in the electrolyte must not exceed 100°C , Eq 8 results in a definite limitation of the maximum possible plating speed

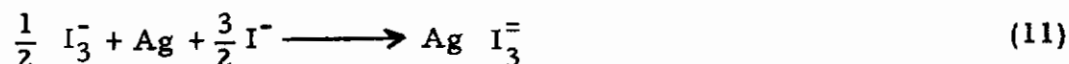
$$1/\tau_p \leq 200 / \left(\rho_e q_d^2 \right) \quad (9)$$

Thus, for $\rho_e = 10 \text{ ohm} \cdot \text{cm}$ and $q_d = 0.1 \text{ coul/cm}^2$, τ_p must exceed $5 \times 10^{-4} \text{ sec}$ or $500 \mu\text{sec}$. Eq 9 shows that it would be impossible to attain the desired optical density of 4 within $50 \mu\text{sec}$ with a single-layer shutter. However, by placing 5 shutters back-to-back, one could reduce q_d to 0.02 coul/cm^2 , which would lead to a minimum τ_p of $20 \mu\text{sec}$.

Another plating speed limitation (considered in the original contract proposal) may arise from a depletion of plateable ions at the electrode-electrolyte interface. This leads to a minimum plating time

$$\tau_{\min} \simeq 5 \times 10^{-6} q_d^2 / c_p^2 \quad (10)$$

where c_p is the concentration of plateable ions in moles/cc. However, there is an uncertainty associated with the proper value of the numerical coefficient of Eq 10 which makes this limitation less absolute than that imposed by Eq 9, especially under conditions where most of the cations in the electrolyte are plateable and where the H_3O^+ concentration is extremely low, i.e., in solutions with neutral or basic pH values. The best known way of clearing the light shutter is via a chemical reaction of the type



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where the I_3^- is introduced by an unplating (reversed polarity) pulse of charge density q'_d such that

$$q'_d/q_d \simeq \left[2 + e^{-r^2 Dt'_p/4a^2} \right] / 3 \quad (12)$$

where D is the diffusion coefficient of I_3^- ions and t'_p is the length of time for which the opacity was maintained following the initial plating pulse. To maintain the desired opacity it will have been necessary to pass a continuous plating current density i_p following the initial plating pulse

$$i_p = 2D(q_d + Fac_i)/a^2 \quad (13)$$

$$\simeq 2Dq_d/a^2 \quad (14)$$

where F is a Faraday (96,000 couls) and c_i is the initial concentration of I_3^- ions (in moles/cc) in the electrolyte before the passage of any charge pulse. Thus, for $D \simeq 10^{-5}$ cm²/sec, $q_d = 0.1$ coul/cm², and $a \simeq 0.03$ cm, i_p should be approximately 2×10^{-3} amp/cm² (i.e., a constant current of about 0.1 amp for a 43-cm² area).

The unplating charge Aq'_d specified by Eq 12 may be supplied from two capacitors, one having a permanent charge $Q'' = 2/3 Aq_d$, and one having a capacitance C_f and an initial charge $Q''' = Aq_d/3$ immediately following the pulse (i.e., for $t'_p = 0$) and a parallel leakage resistance R_f such that

$$C_f R_f = r^2 D/4a^2 \quad (15)$$

Following passage of the unplating charge Aq'_d , the shutter should revert to 90% of its original transmission within a maximum time $t_u \leq 3a^2 / r^2 D$. Thus for $D \simeq 10^{-5}$ cm²/sec, a maximum clearing time t_u of 1 sec, as required by the contract specifications (see the "Introduction"), would be obtained for an electrode spacing $a \simeq 6 \times 10^{-3}$ cm. With larger electrode spacings, reversion to 90% of the original transmission would occur within a maximum time $t_u \leq 3 \times 10^4 a^2$ sec, i.e., within 3 sec for $a \simeq 0.01$ cm, 30 sec for $a \simeq 0.03$ cm, and 75 sec for $a \simeq 0.05$ cm. For $a \simeq 0.01$ cm, the degree of clearing at $t_u \simeq 1$ sec should correspond to at least 90% of the plating removed (cf Eq 16) or a residual δ of 0.35, i.e., to 78% of the original transmission, which may still be acceptable for the sponsor's purpose.

$$f_r(t_u) \simeq \left[1 - (8/\pi^2) e^{-\pi^2 Dt_u/a^2} \right] (q_d + ac_i F)/q_d \quad (16)$$

Finally, the most suitable plating solution meeting the requirements of low toxicity, good plating uniformity, minimum charge requirements, and maximum plating and unplating speeds appears to be 3.0 to 3.5 M AgI plus 6 to 8 (preferably 6.9) M NaI at neutral or slightly alkaline pH values.

III. PLATING CELL DESIGN

As discussed in the paragraph before last, the electrode spacing a should be 0.01 cm or less in order to allow for satisfactory clearing within 1 sec. On the other hand, Eq 1 requires that $a \geq b^2/2k$. A low value of $b^2/2k$ is also desirable for minimum power requirements, as seen from Eqs 4 and 7. However, because of the contact requirements discussed below, the minimum practical subelement width b in a shutter based on the contact arrangement 6 of Fig 1 is 0.2 to 0.3 cm. Furthermore, the lowest practical value of ρ_g for tin-oxide-coated glass is about 5 to 10 ohms/square, which leads to a maximum value of 2 cm for k for an electrolyte resistivity ρ_e of 10 to 21 ohm - cm. Hence, the minimum feasible value of $b^2/2k$ is 0.01 cm. Thus, the requirements for both uniform plating (Eq 1) and fast clearing can be just met by using an electrode spacing of 0.01 cm or 0.004". This was the spacing proposed in the original cell design.

The minimum b value of 0.2 to 0.3 cm was arrived at by considering the practical requirements for forming satisfactory electrical contacts to each subelement. The best way of achieving such contacts is by sawing parallel, narrow grooves in each of the flat glass plates with a distance $2b$ between adjacent grooves, applying a conductive tin oxide coating over the entire grooved surface, introducing metal leads into the grooves and forming good electrical contacts between the leads and the conductive coating within the grooves. The minimum required groove width proved to be 0.005" to 0.010", partly for mechanical reasons (the thinnest saw blades available being at least 0.004" thick), partly due to difficulties in rendering the groove surface conducting, and partly because of the requirements for good lead conductivity, as discussed below. Furthermore, the required heavy tin oxide was bound to render the over-all light transmission dangerously close, if not below, the specified minimum of 33%. Hence, the fraction of the shutter area occupied by the opaque grooves could not be allowed to exceed 5 to 10% of the clear area, i. e., the ratio of b to groove width should be 10 to 20. Hence, the widths b were set at either 0.078" or 0.118", i. e., 0.2 cm or 0.3 cm.

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The metal leads were designed to be capable of supplying the total required plating charge within 50 μ sec. The current I_l carried by each lead would be

$$I_l = q_d bL/\tau_p \quad (17)$$

Setting $q_d = 0.1$ coul/cm², $b = 0.3$ cm, $L = 3.8$ cm, and $\tau_p = 5 \times 10^{-5}$ sec, one obtains a maximum $I_l \approx 2,000$ amps. The heat developed in the lead can be expressed in terms of both the $I_l^2 \rho_l$ power loss ($\rho_l =$ lead resistivity) and in terms of the resulting temperature rise Δt , as follows

$$I_l^2 \rho_l \tau_p / S = 4.18 \Delta t c_p S d \quad (18)$$

where S is the cross section, c_p the specific heat, and d the density of the metal lead. Hence,

$$S_{\min} = \left[I_l^2 \rho_l \tau_p / (4.18 \Delta t_{\max} c_p d) \right]^{1/2} \quad (19)$$

Setting Δt_{\max} equal to the melting point of the metal to be used, one finds that the lowest value of S_{\min} can be obtained with Cu leads with $S_{\min} \approx 5 \times 10^{-4}$ cm². The next lowest value is $S_{\min} \approx 6 \times 10^{-4}$ cm² with Ag leads.

In order for leads of 500×10^{-6} cm² or 80 square mils in cross section to fit easily into 6- to 10-mil wide grooves, they were made in the form of ribbons 4 mils thick and 20 mils wide. Furthermore, to allow for differential thermal expansion during subsequent high temperature treatments, these ribbons were made by compressing fine tubes of 2 mils wall thickness and 40 mils circumference to a thickness of 4 to 5 mils. In view of the ready availability of Cu tubes and of the slightly smaller required cross section area, Cu was used in preference to Ag. This proved to be an unfortunate choice, as some of the Cu leads were embrittled and broken in partial oxidation during the subsequent high temperature treatments, which reduced the yield of usable plating cells.

The high temperature treatments following the insertion of the Cu leads were required to form a sufficiently protective inert insulating layer between the leads and the electrolyte, as shown schematically in Fig 3. The arrangement of the grooves and leads in the individual plates and the assembled light shutter is shown in Figs 4 and 5.

As seen from Fig 3, the contact resistance r_c between a Cu lead and the conductive film layer near the top of the groove may be written as

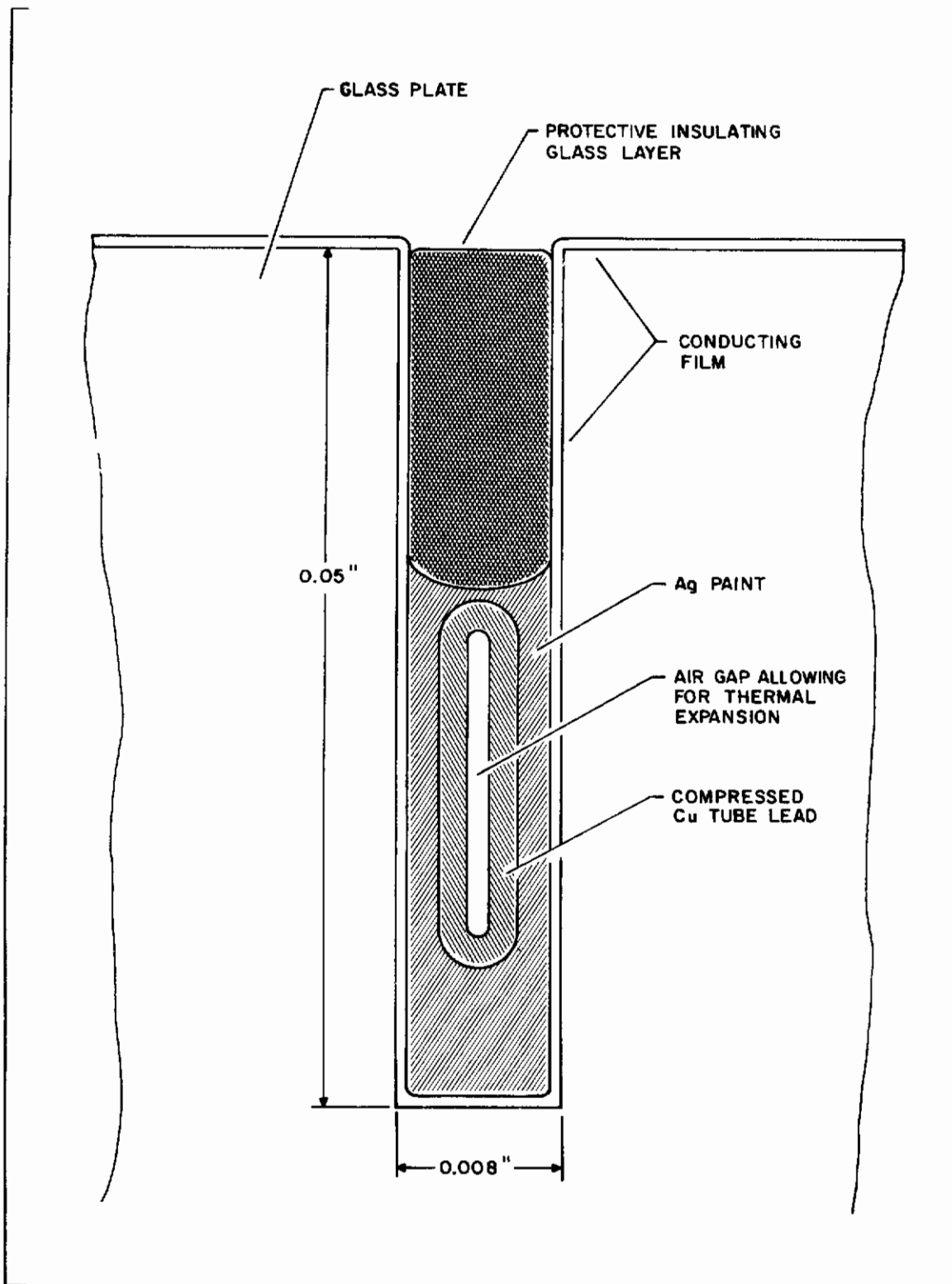


FIGURE 3 SCHEMATIC CROSS SECTIONAL DRAWING OF GROOVE, CONTACTING LEAD, AND PROTECTIVE LAYER

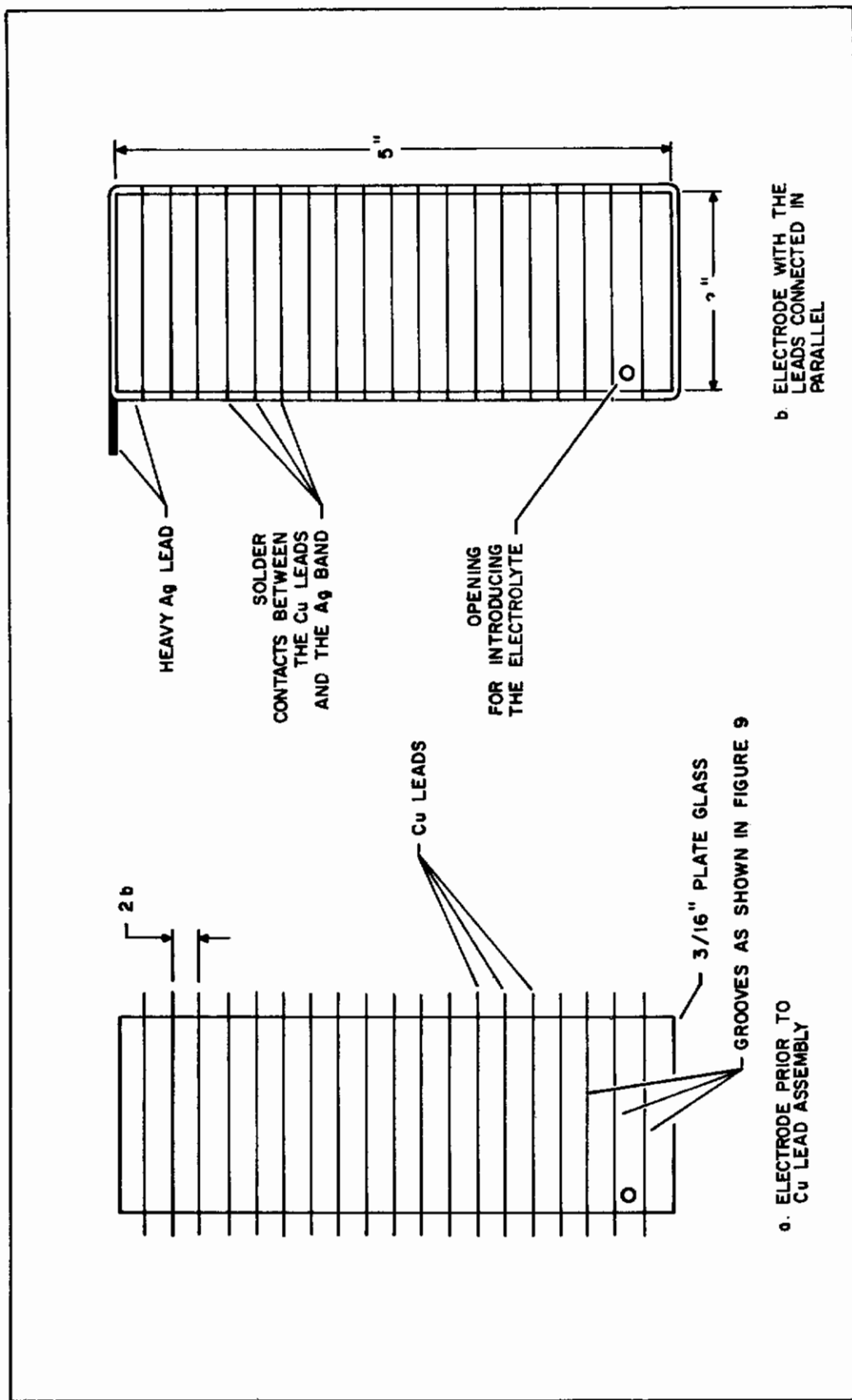


FIGURE 4 CONSTRUCTION OF THE TRANSPARENT ELECTRODES

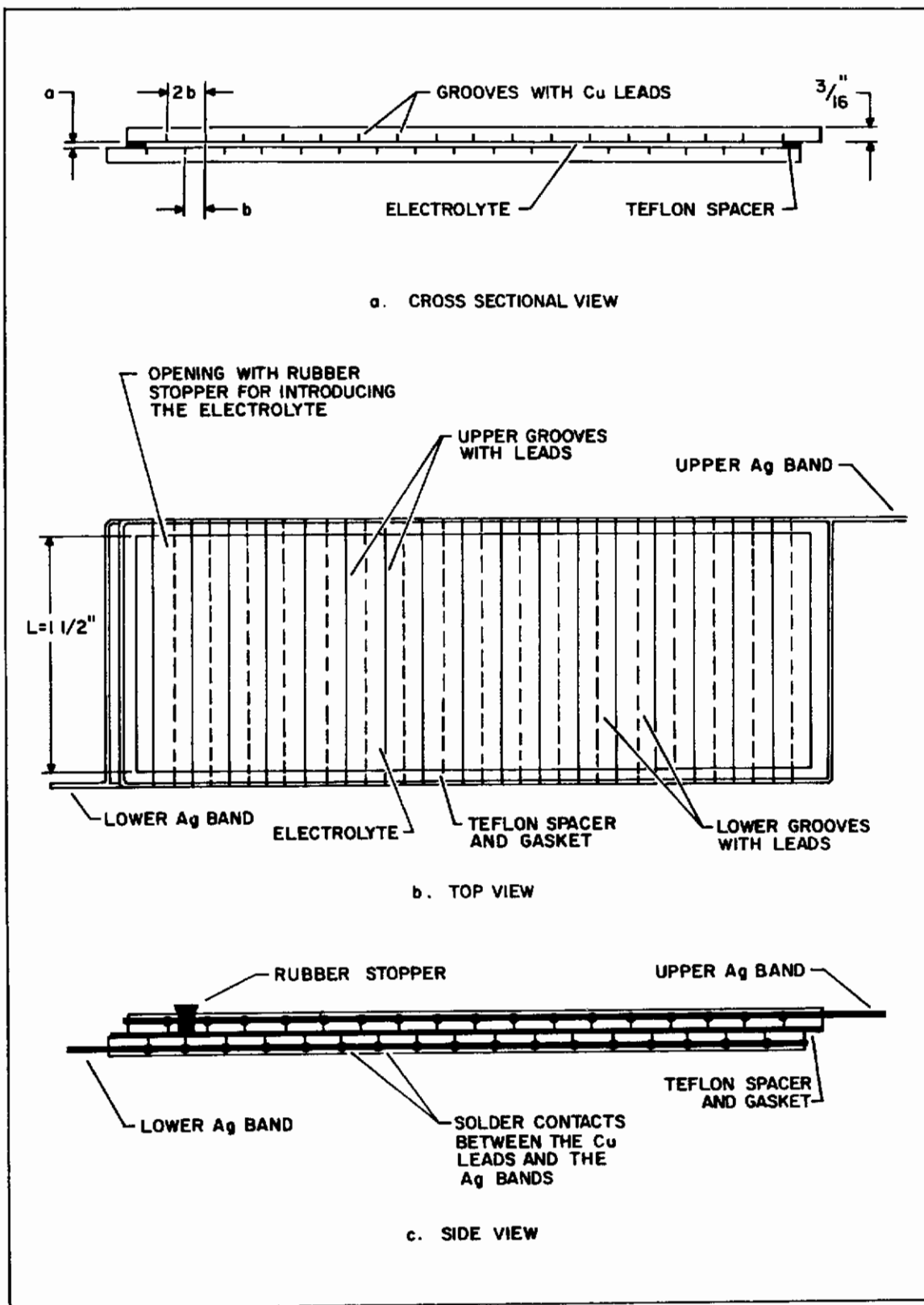


FIGURE 5 ASSEMBLED REVERSIBLE ELECTROPLATING LIGHT SHUTTER

$$r_c = r_{Ag} + r_{tg} \quad (20)$$

where r_{Ag} is the resistance of the Ag paint layer, and r_{tg} is that of the conductive film in the upper half of the groove. If ρ_G is the surface resistivity of the latter film, then

$$r_{tg} \simeq \rho_G \times 0.02''/2'' \simeq 0.01 \rho_G \quad (21)$$

where the factor $0.02''/2''$ corresponds to the approximate width and length of the top half of the groove wall. Considering that the resistance of each subelement must be at least

$$\rho_{g'} b/2L \simeq 0.03 \rho_{g'} \quad (22)$$

(cf. Eq 6), and that there are two contacts per subelement (cf. Fig 5(a)), then the total resistance due to the r_{tg} component would be less than $2/3$ of the theoretical cell resistance given by Eq 7, if ρ_G were not larger than $\rho_{g'}$. On the other hand, the r_{Ag} component should be negligible if no serious cracks, air gaps, or other sources of spurious resistance are present between the Cu lead, the Ag paint, and the conductive film at the lower half of the groove surface. Furthermore, the resistance of a Cu lead 2 cm long and $500 \times 10^{-6} \text{ cm}^2$ in cross section is less than 0.01 ohm; i.e., less than 10% of $\rho_{g'} b/2L$, which can be considered negligible. Hence, according to the design of Fig 3, the total resistance due to contacts should be nearly half the theoretical value of R_p of Eq 7.

IV. CELL CONSTRUCTION

A. Conducting Glass Plates

Polished plate (lime) glass pieces (softening temperature $\sim 690^\circ\text{C}$), $1/8''$ or $3/16''$ thick, and $5'' \times 2''$ in area, with grooves 6 to 10 mils wide and 50 mils deep sawed over one surface parallel to the $2''$ edges and spaced $1/4''$ or $1/6''$ apart (center to center) and a $3/16''$ diameter hole located between the first and second grooves from one edge were cleaned with laboratory detergent (Alconox or Calgonite), rinsed with alcohol, air dried, etched for at least 1 minute with a solution of 1.5 volumes concentrated HF to 3 volumes concentrated H_2SO_4 and 0.9 volume H_2O , rinsed with distilled water, and placed on graphite holders. The holders with plates were heated in a muffle furnace from room temperature to 1200°F , and then placed in front of several, hot, propane burners (temperature $\gg 1400^\circ\text{F}$) within a firebrick enclosure arranged so as to yield fairly uniform and intense heating of the entire glass plate and holder. Within 10 to 20 minutes, dull-red heat was reached (corresponding to the softening temperature of the

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glass), at which time a fine spray of SnCl_4 solution was immediately directed at the grooved glass surface.

The spraying solution was made up by slowly adding anhydrous SnCl_4 to 9 parts of a solution of 100 gm $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 50 gm distilled water plus 10 gm concentrated HCl and 1.0 or 1.5 gm SbCl_3 until a slight super-saturation was observed, and then adding a tenth part of the same solution to render the solution slightly undersaturated. The spray gun was constructed entirely of Pyrex glass. The spray was triggered by the passage of compressed O_2 through a gas inlet tube. The spray nozzle was held at a distance of 4" from the glass plate and the spray applied for 10- to 15-second periods with a continuous horizontal and/or vertical motion of the nozzle aimed at obtaining a uniformly conductive coating. After allowing a few minutes for the glass to regain its softening temperature, the spraying was resumed, and this was repeated 4 to 10 times depending on the desired conductivity and light transmission. The plates were then placed in an annealing furnace and allowed to cool slowly (in > 2 hours) to room temperature.

Whereas there was no difficulty in obtaining smooth, flat plates with a surface resistivity of 5 to 10 ohms/square and a light transmission of approximately 60%, the formation of a satisfactory, conducting film in grooved plates proved to be a major obstacle, the conductivity of the film in the grooves being usually much lower than on the flat, outer surface. Two approaches were then attempted, involving application of an extra heavy, initial coating, resulting in a satisfactory groove conductivity, followed by removal of the opaque coating from the outer surface and a second application of a lighter conductive coating on that surface. However, these approaches involved the following difficulties:

1. The heavy coating tended to peel off in various spots, which sometimes caused breaks in the film inside the grooves.
2. Removal of the heavy film on the outer surface by chemical reduction of the SnO_2 to Sn (using nascent H formed by adding concentrated HCl to Zn dust) invariably entailed partial removal of the film inside the grooves, although the grooves were masked with various materials (beeswax, Ag paint, etc.).
3. Removal of the initial heavy film by mechanical polishing was very time-consuming, and entailed frequent breakage of plates during the various handling and processing operations, resulting in an over-all yield of only 10%, about half of which showed unsatisfactory, non-uniform conductivity; the non-uniformity and irreproducibility being attributed to contamination of the glass surface by the polishing grit.

A less-objectionable approach, consisting of preliminary selective spraying into the grooves through a graphite mask followed by a

spraying over the flat outer surface, yielded a satisfactory resistivity in the grooves (5 to 30 ohms/square). However, the double-spraying operation was still rather time consuming and also resulted in frequent plate breakage.

The best plates were obtained with a single-spraying treatment and either wider (10 mil) grooves or a high O₂ pressure (50 to 80 psi) spray directed mainly along the grooves and sprayed at various angles. However, even then the breakage and other types of damage resulting from subsequent treatments, handling, and miscellaneous plating-deplating experiments reduced the final yields of truly satisfactory plates to zero.

The spraying treatment usually caused a warping of the plates, resulting in an unevenness of 5 to 20 mils (as compared with 3 mils before heating). Since the electrode spacing was designed to be only 4 mils (cf. the preceding Section), the observed warping was definitely unacceptable. Of a number of methods tried to reduce the warping, involving flattening by heat and weights, or graphite holders specially designed to minimize warping during spraying, the simplest one consisting of placing the hot plates in the hot annealing furnace on flat supports for 1 hour and allowing them to cool overnight, proved the most effective, but the unevenness still remained as high as 4 to 8 mils, making it impractical to use average cell spacings of less than 15 mils.

B. Estimates of the Average Resistivity in the Grooves

Let r be the ratio of the surface resistivities ρ_g and ρ_G of the conductive film inside and outside the grooves respectively,

$$r = \rho_G / \rho_g \quad (23)$$

n the number of grooves or conductive strips between grooves, W_g and W_G the respective perimeters of a strip and groove cross section, l_g and l_G the length of each groove or strip. Then the resistances R_{gl} and R_{Gl} between the long edges of each strip and groove, respectively, are

$$R_{gl} = \rho_g W_g / l_g \quad (24)$$

and

$$R_{Gl} = \rho_G W_G / l_g \quad (25)$$

whereas the respective resistances R_{gs} and R_{Gs} between the shorter edges are

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$$R_{gs} = \rho_g \ell_g / W_g \quad (26)$$

and

$$R_{Gs} = \rho_G \ell_g / W_G \quad (27)$$

The total series resistance R_l between n_g alternating resistors (R_{gl} and R_{Gl}) is

$$\begin{aligned} R_l &= n_g (R_{gl} + R_{Gl}) \\ &= (\rho_g W_g + \rho_G W_G) n_g / \ell_g \end{aligned} \quad (28)$$

whereas the total conductance ($1/R_s$) of n_g conductors ($1/R_{gs} + 1/R_{Gs}$) connected in parallel is

$$\begin{aligned} 1/R_s &= \frac{n_g}{R_{gs}} + \frac{n_g}{R_{Gs}} \\ &= \frac{n_g}{\ell_g} \left(\frac{W_g}{\rho_g} + \frac{W_G}{\rho_G} \right) \end{aligned} \quad (29)$$

The ratio

$$\frac{R_l}{R_s} = \frac{n_g^2}{\ell_g^2} \frac{(\rho_g W_g \rho_G W_G) (\rho_G W_g + \rho_g W_G)}{\rho_g \rho_G} \quad (30)$$

was measured readily by clamping two, parallel, soft-copper contacting lines first along the shorter and then along the longer edges of each conductive plate. Setting $W_G \simeq 2 \times 0.06'' \simeq 0.12''$, and $W_g = 2b$, one obtains

$$R_l/R_s \simeq n_g^2 W_g^2 (1 + 0.5 r) (r + 0.5) / r \ell_g^2 \quad (31)$$

$$\simeq W^2 (1 + 0.5 r) (r + 0.5) / r \ell_g^2 \text{ for } b \simeq 0.12'' \quad (32)$$

where

$$W \simeq n_g W_g \quad (33)$$

is the total length (or width) of the plate along the direction perpendicular to the grooves, and for $b \simeq 0.08''$

$$R_f/R_s \simeq W^2 (1 + 0.75r) (r + 0.75) / r l_g^2 \quad (34)$$

The values of R_f/R_s corresponding to various resistivity ratios r are shown in Table I for $w^2/l_g^2 = 1$ (square plates). Multiplication of the actually measured ratios R_f/R_s by the dimensional correction factor l_g^2 and comparison with the values of Table I gave a direct estimate of r . Furthermore, since usually $W_g/\rho_G/\rho_G$, the value of R_s gave an approximate estimate of ρ_g

$$R_s \simeq \rho_g W/l_g \quad (35)$$

TABLE I

EXPECTED RESISTANCE RATIOS R_f/R_s FOR VARIOUS RESISTIVITY RATIOS r AND SQUARE PLATES

	b = 0.12"	b = 0.08"
r	R_f/R_s	R_f/R_s
1	2.25	3.1
2	2.5	3.4
3	2.9	4.1
4	3.4	4.75
5	3.85	5.5
6	4.3	6.2
7	4.8	6.9
8	5.3	7.7
9	5.8	8.4
10	6.3	9.1

By this method, as well as by more accurate but more elaborate methods, the lowest measured values of ρ_G were approximately 20 ohms/square as compared with usual values of 5 to 10 ohms/square for ρ_g . Furthermore, in most plates ρ_G exceeded 30 or even 50 ohms/square. This proved to be a major cause of failure in the resulting cells.

C. Forming Electrical Contacts to the Glass

The cooled plates were cleaned with soap and water and degreased with acetone. After filling the grooves with Hanovia Liquid Silver, the Cu ribbons (4.5 to 5 mils x 20 to 25 mils) were forced down into the grooves,

and the plates were baked at 100°C to harden the Ag paint. The excess of Ag near the top of the grooves was then carefully and thoroughly removed with acetone, and the top of the grooves was filled with CV137 nonconductive solder glass frit (made by the Kimble Glass Co.) carried by Vehicle NCAA (1.5% nitrocellulose in amyl acetate). The plates were then placed in a muffle furnace and their temperature was increased at a rate of approximately 10°C/min up to 425°C, maintained at 425°C for 1 hr, and finally lowered to room temperature at a rate of less than 5°C/min. Since the first firing of the solder glass resulted in incomplete filling of the grooves and numerous pinholes, at least one or two more firings with additional solder glass were necessary to yield an acceptable insulating coating over the metal leads. Unfortunately, this multiple firing occasionally resulted in a partial oxidation of the Cu leads with ensuing embrittlement and introduction of additional undesirable contact resistances contributing further to an otherwise high failure rate.

Following the sintering operations, the Cu leads were carefully polished to remove the CuO film, the resistance between the leads were occasionally measured, and the leads were soldered onto the surrounding Ag band shown in Figs 4 and 5.

D. Resistances Between the Cu Leads Prior to Their Connection in Parallel

With the Cu leads and Ag paint imbedded in the lower part of the groove, the resistance R_{Cu} between two neighboring Cu leads was

$$R_{Cu} = 2 r_c + R_{gl} \quad (36)$$

$$\simeq 2 r_{tg} + \rho_g W_g / l_g \text{ (cf. Eqs 20 and 21)} \quad (37)$$

$$\simeq 0.02 \rho_G + 0.12 \rho_g \text{ for } b \simeq 0.012'' \quad (38)$$

$$(\simeq 0.02 \rho_G + 0.08 \rho_g \text{ for } b \simeq 0.008'') \quad (39)$$

Thus, for $b \simeq 0.12''$, $\rho_g \simeq 5$ ohms/square and $\rho_G \simeq 20$ ohms/square, one obtains $R_{Cu} \simeq 1.0$ ohm. The actual values of R_{Cu} measured in most of the plates were usually higher than 1.0 ohm, which was another indication of those plates being unsatisfactory. On the other hand, those plates which yielded the best experimental cells actually showed R_{Cu} values of 0.4 to 0.9 ohm suggesting higher conductivities or values of ρ_G even lower than 20 ohms/square in the upper parts of the grooves.

E. Other Materials Used in the Cells

The insulating glass solder mentioned previously had the disadvantage of:

1. Requiring tedious and time-consuming, repeated sintering operations; and
2. apparently dissolving, at least partially, when in prolonged contact with the electrolyte (this being unfortunately noticed only after completion of the experimental work).

Other insulating materials have, therefore, been tested both for protection of the contacts in the grooves and for the spacer and gasket between the plates. A polystyrene resin made by the General Cement Mfg. Company, Rockford, Illinois under the label Q-Dope was used at first, but was subsequently found to react with or absorb I_2 (or I_3^- ions). Paraffin and other waxes were found to adhere too weakly to the glass to offer adequate protection to the metal contacts. Similarly, evaporated SiO_2 , Tygon paint, rubber cement, Teflon paint, and epoxy resins (Hysol, Epoxi-Patch, Araldite) all appeared to be unsatisfactory, as judged by the observed discoloration of I_2 solutions in contact with plates protected by these insulators, suggesting either a reaction with or absorption of I_2 , or unsatisfactory adhesion to the groove surface.

Since the specifications for spacer and gasket material appeared less critical than those for the contact insulators, silicone rubber or Teflon gasket-spacers were found to be the least objectionable for experimental cells, whereas epoxy resin was used for "permanent" cell assemblies. In cases where these "permanent" cells had to be disassembled, it was found possible to dissolve the set resin with N, N-dimethyl formamide.

Finally, the electrolyte contained 3M Ag I plus 8 M NaI, and had pH values ranging from 3 to 9 (usually approximately 8).

F. Measured versus Expected Resistance of the Assembled Cells and the Basic Cause of the Observed Discrepancies

The over-all resistance of an assembled plating cell was measured by the Cahan-Ruetschi* square-wave pulse method.

The 100-kc square-wave calibrator output V_g (50 or 100 v) of a Tektronix 535 oscilloscope was connected to a series circuit comprising

* B. D. Cahan and P. Ruetschi, J. Electrochem Soc. 106, 543-7 (1959)

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a 10 μ fd condenser, a large current determining resistance $R_{c.d.}$ (10,000 ohms or 100,000 ohms), and the plating cell. The amplitude i_s of the square wave current pulse through the plating cell was then approximately

$$i_s \simeq V_s / R_{c.d.} \quad (40)$$

(i.e., 1 to 10 ma), and the plating cell resistance R_p was given by the instantaneous voltage changes ΔV_p , across the cell at the beginning or end of each pulse

$$R_p \simeq \Delta V_p / i_s \simeq R_{c.d.} \Delta V_p / V_s \quad (41)$$

The cells assembled as shown in Fig 5 could be evaluated even without actual plating experiments by simply comparing their resistance with the theoretical values

$$R_p \simeq \left[2a\rho_e + 0.5 \rho_g b^2 \right] / A \quad (7)$$

Setting $\rho_e \simeq 10$ ohm-cm, $a \simeq 0.05$ cm (a rather high value usually necessitated by the warping of the plates), $\rho_g \simeq 6$ ohms/square, $b \simeq 0.3$ cm, and $A \simeq 40$ cm², one would expect $R_p \simeq 0.032$ ohm. Actually, however, the large area (43 cm²) cells remaining to be delivered to the sponsor near the end of the project had resistances ranging from 0.09 to 0.22 ohm, i.e., at least 3 to 7 times the expected values. Furthermore, the cells filled with electrolyte showed increases in resistance of at least 20% after 3 to 5 days, suggesting a slow attack of the contacts by the electrolyte.

All observations point to spurious contact resistances as one of the main sources of experimental difficulty. These spurious resistances could be introduced at a number of points during the elaborate and complicated procedure involving numerous delicate operations. Furthermore, with the largest area cells, the probability of failure at every processing step was at least proportional to the plate area, which accounts for the low yield of satisfactory cells.

It is worth noting that the cells with a smaller area ($A \simeq 6$ to 16 cm²) discussed in the following section actually had resistances of only 0.14 to 0.4 ohm, in much better agreement with the theoretical values of approximately 0.1 to 0.2 ohm. These smaller cells also yielded the best results (highest measured plating speeds).

V. MEASUREMENT OF PLATING CURRENT AND OPTICAL DENSITY CHANGES

Several 525 μ fd 450 v electrolytic capacitors, connected in parallel, were charged up to the desired voltage and then discharged rapidly through the plating cell and a 0.1-ohm precision series resistor upon closing of a Type EM-1 Hg plunger type relay. The voltage across the 0.1-ohm resistor connected to one trace input of a Tektronix 502 oscilloscope gave the instantaneous current through the plating cell (cf. Fig 6). The second trace of the same oscilloscope showed the output of a photomultiplier tube circuit measuring the light transmitted through the shutter. Both simultaneous traces were photographed with a Polaroid camera.

The traces for the best experimental cells are shown in Fig 7, and the pertinent data are given and interpreted in Table II under the same test numbers (in Roman numerals). In each graph, the time coordinate is horizontal, beginning at the second line from the right and increasing from right to left. The vertical coordinate refers either to (1) the current or voltage increasing upward, in those traces which show an initial maximum followed by a typical downward capacitor discharge curve (V-trace) or (2) to the light transmission, decreasing upward, in the curves which show a steady upward climb towards an asymptotic value on the left-hand side.

In Test V, the (upper) light transmission curve shows an initial maximum followed by a slow decrease due either to partial spontaneous clearing of the shutter similar to that observed in Tests XXVIb and XXVIIb of Fig 8, or to a partial recovery of the photo-multiplier circuit output from an initial "overshoot". The upper bright spots (near the second vertical line from the right and between the second and fourth lines from the top) mark the steady state output of the photo-multiplier circuit when the light source was turned off. Hence, the asymptotes of the light transmission curves should all be located below the level of these upper bright spots. The actual upward displacement of the asymptotes was attributed at first to absorption of stray light upon closing the shutter, but was finally traced to transient overshooting by the photo-multiplier circuit. Because of this defect, and partly also because of the inaccuracy of the scale, light absorption values of more than 90% (or optical densities exceeding 1.0) are unfortunately uncertain in the tests of Fig 7. However, the times τ_1 , corresponding to an optical density change δ of at least 1.0, could still be estimated from these curves and are listed in the tenth column of Table II. Comparison of the time values in columns 8, 9, and 10 shows a close parallelism and near equality of τ_1 and the time constant of the capacitor discharge circuit. The higher values of column 8 are probably due to non-linear resistances in the circuit arising from a breakdown of spurious resistances under a high voltage. Because of the spurious and non-linear circuit resistances, the current and voltage traces are also subject to uncertainties. Hence, the actual charge Q_1 passed through the cell up to the time τ_1 was estimated by means of the relation

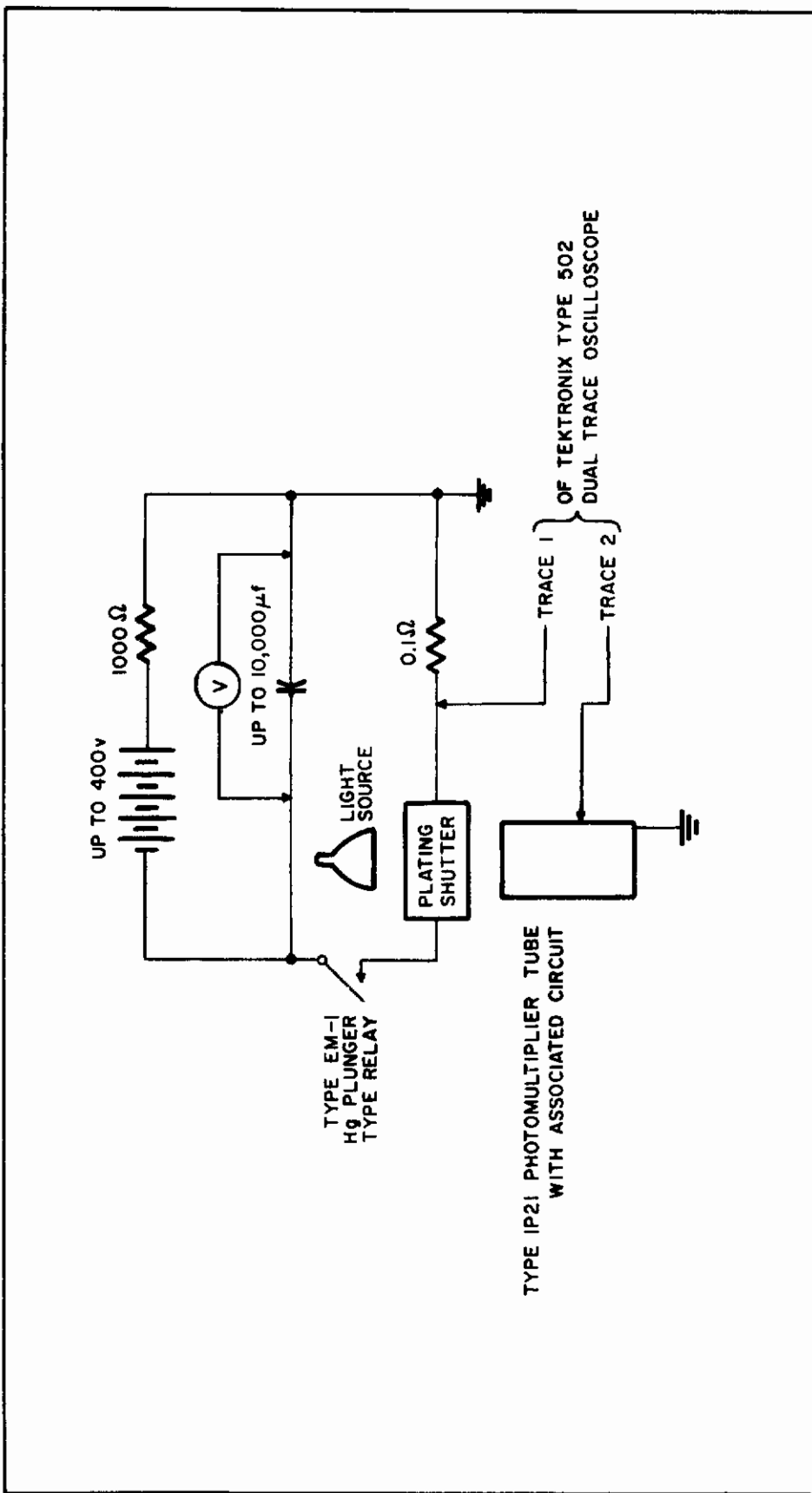


FIGURE 6 EXPERIMENTAL ARRANGEMENT FOR SIMULTANEOUS MEASUREMENTS OF PLATING CURRENT AND OPTICAL DENSITY

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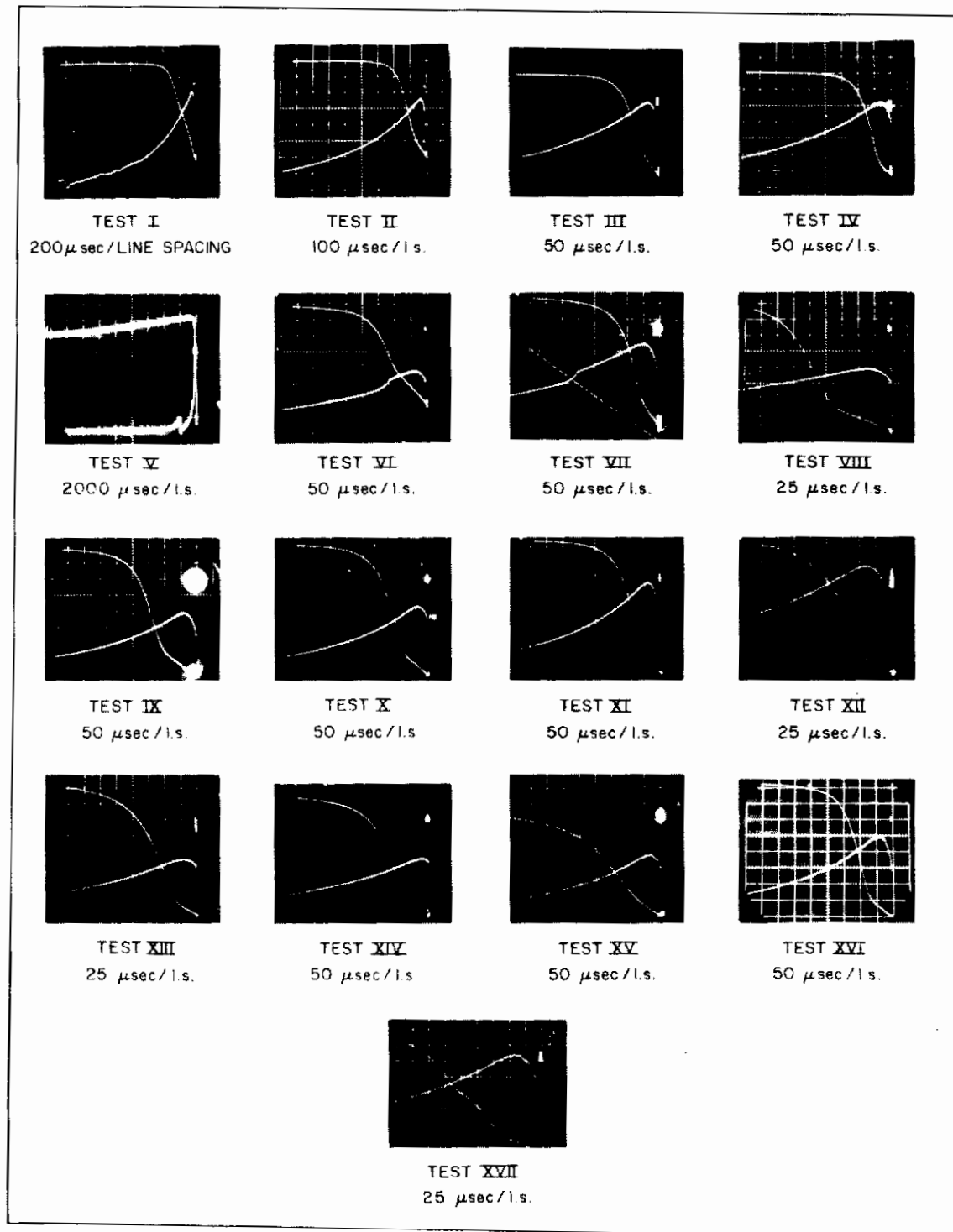


FIGURE 7 APPLIED CURRENT PULSES AND LIGHT ABSORPTION CHANGES IN SHUTTER CLOSING EXPERIMENTS OF LESS THAN 1000 μ secs DURATION

Table II. Pertinent Data and Interpretation of the Oscilloscope Traces of Figure 7

Test No.	Plate Spacing \bar{a} (cm)	Plated Area A (cm ²)	Cell Resistance (ohms)	Series Resistance (ohms)	Capacitance C (μ fd)	Voltage V (v)	Time Constant from RC Product V-Trace (μ sec)		τ_1 (μ sec)	Q (coul.)	q_d (coul/cm ²)	δ final (calcd)	Q_1/Q	q_{d1} (coul/cm ²)	δ_1 calcd	$(\tau_1)_{min}$ (μ sec)
							(μ sec)	(μ sec)								
I	0.09	6	0.40	0.2	1575	135	1000	600	600	0.21	0.035	1.3	0.65	0.023	0.8	260
II	0.038	"	0.25	"	"	"	700	"	400	"	"	"	0.55	0.019	0.7	180
III	0.043	"	"	"	"	"	"	400	300	"	"	"	0.5	0.018	0.65	160
IV	"	"	0.28	"	"	"	"	"	250	"	"	"	0.45	0.016	0.6	130
V	"	"	"	"	"	"	"	"	400	"	"	"	0.65	0.023	0.9	260
VI	0.06	15	0.15	0.14	2625	180	800	"	"	0.47	0.031	1.2	0.65	0.020	0.8	200
VII	"	"	"	0.12	"	300	700	500	"	0.79	0.053	2.0	0.5	0.027	1.0	370
VIII	0.045	16	0.16	"	"	"	"	"	300	"	0.049	1.9	0.5	0.025	1.0	310
IX	"	"	0.15	"	1575	135	500	300	400	0.21	0.013	0.5	0.7	0.009	0.4	40
X	"	"	0.14	"	"	200	"	"	"	0.31	0.016	0.6	0.7	0.010	0.4	50
XI	"	"	"	"	"	300	"	"	300	0.47	0.029	1.1	0.6	0.017	0.7	140
XII	"	"	"	"	"	400	"	"	250	0.63	0.039	1.5	0.5	0.020	0.8	200
XIII	"	"	"	"	1050	400	300	200	"	0.42	0.026	1.0	0.7	0.018	0.7	160
XIV	"	"	"	"	2100	135	600	400	500	0.28	0.018	0.7	0.7	0.012	0.5	70
XV	0.043	"	0.25	"	1575	"	"	350	"	0.21	0.013	0.5	0.75	0.010	0.4	50
XVI	"	"	0.20	"	"	182	"	"	400	0.29	0.018	0.7	0.7	0.013	0.5	80
XVII	"	"	0.19	"	"	250	"	300	300	0.39	0.024	0.9	0.6	0.014	0.5	100

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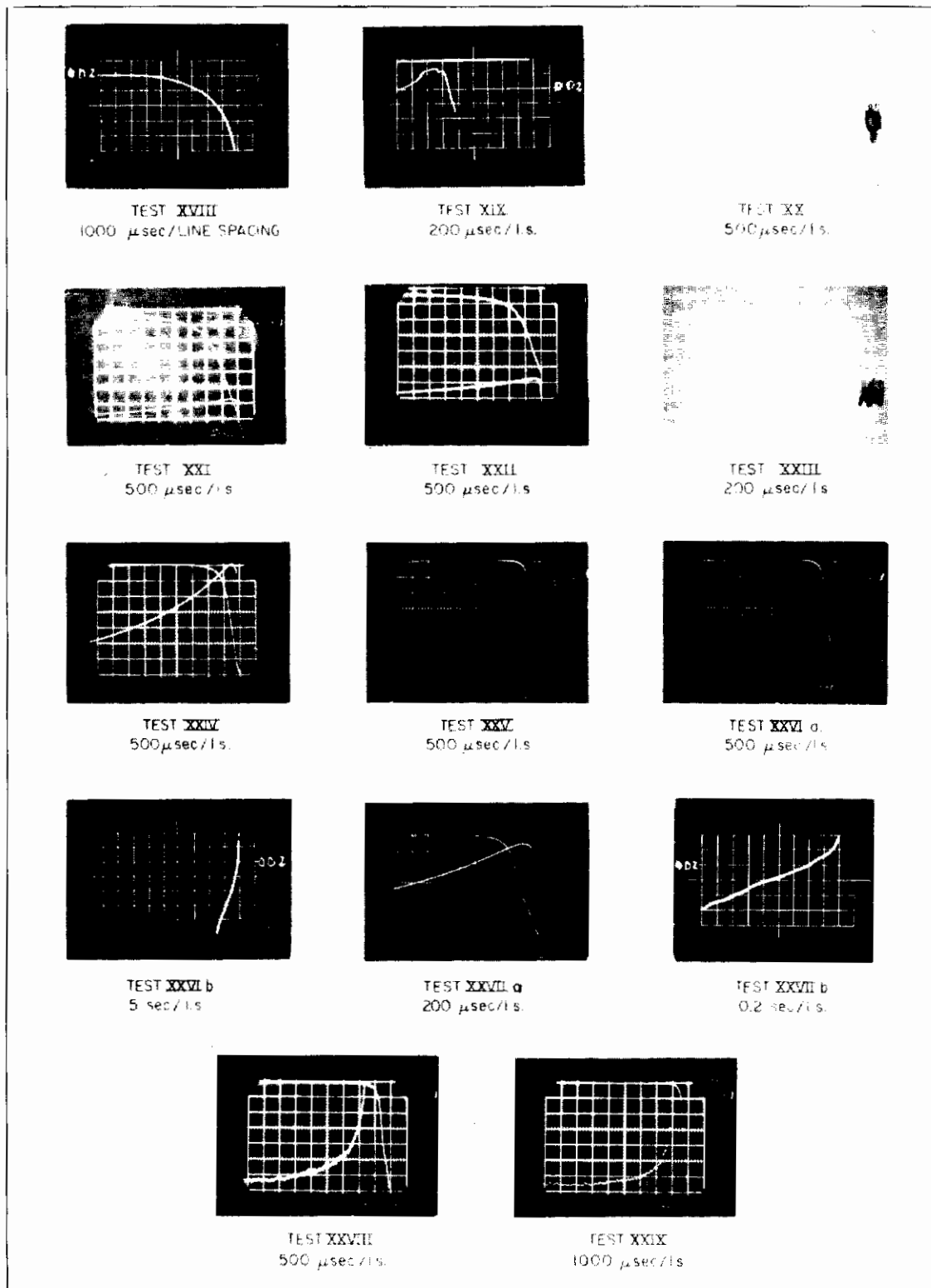


FIGURE 8 LIGHT ABSORPTION MEASUREMENTS OF IMPROVED ACCURACY AND SOME CURRENT PULSE SHAPES IN SHUTTER CLOSING EXPERIMENTS OF UP TO 10millisecs DURATION

$$Q_1/Q = 1 - e^{-\tau_1/\tau_c} \quad (42)$$

where Q is the total capacitor charge (column 11) deduced from the product CV of columns 6 and 7, and τ_c is the time constant of column 9. Division of Q by the area A of column 3 yielded the total charge density q_d of column 12, and multiplication of q_d by the Q_1/Q ratio (column 14) yielded the charge density q_{d1} passed up to the time τ_1 .

According to Fig 2 the actual optical density change δ_1 corresponding to a charge density q_{d1} should be

$$\delta_1 \simeq 38 q_{d1} \quad (43)$$

and similarly, for δ corresponding to 100% capacitor discharge

$$\delta \simeq 38 q_d \quad (44)$$

The calculated values of δ_1 (column 16) are usually less than the estimated actual value of at least 1.0. This may be due either to a higher actual absorption coefficient of the very thin films produced by the rapid plating process, or to marked local refractive index changes giving rise to increased reflections and increased turbidity.

The last column $(\tau_1)_{\min}$ gives the minimum values of τ_1 allowed according to the estimated diffusion rate limitation

$$(\tau_1)_{\min} \simeq 5 \times 10^{-6} q_{d1}^2 / c_p^2 \simeq 0.5 q_{d1}^2 \quad (10)$$

the concentration c_p of plateable ions being 0.003 mole/cc. Comparison of columns 10 and 17 shows that $(\tau_1)_{\min}$ was barely approached only in Tests VII, VIII, XII, and XIII, and was exceeded by a factor of 2 to 10 in all the other tests. Since the actual speed limitations in all these tests were due to circuit RC time constants rather than to electrochemical limiting factors, the results of Table II do not give any indication of the actual applicability of Eq 10, but they do at least suggest the absence of any more severe intrinsic speed limitation.

To check the accuracy of the τ_1 and q_{d1} values of Table II, measurements were made with a corrected photomultiplier circuit and more sensitive scales obtained with a Tektronix 535 oscilloscope and a type Z differential preamplifier. The traces are shown in Fig 8 and the pertinent data and interpretation in Table III. In Tests XVIII, XIX, XXV, XXVI, XXVIII, and XXIX, the V-Trace (current-or voltage-time curve) was not recorded.

Table III. Data and Calculations Pertaining to the Oscilloscope Traces of Figure 8

Test No	Plated Area A (cm ²)	Cell Resistance (ohms)	Series Resistance (ohms)	Capacitance C (μfd)	Voltage V (v)	Time Constant from RC Product (μsec)	V-Trace (μsec)	τ ₁ (μsec)	R (coul)	q _d (coul/cm ²)	δ _{final} calcd	δ _{final} measured	Q ₁ /Q	q _{dl} (coul/cm ²)	(δ ₁) calcd
XXVIII	6			4725	67				0.32	0.053	2.0	2.0			
XIX	3	0.44	0.12	2625	70	1,600			0.18	0.060	2.3	2.4			
XX	13.3	0.28	0.5	5250	180	4,100	3,500	5,000	0.94	0.071	2.7		0.7	0.05	1.9
XXI	"	0.20	0.4	"	"	3,100	3,500	1,500	"	"	"		0.4	0.03	1.1
XXII	"	0.18	0.3	"	"	2,500	3,000	1,300	"	"	"		0.3	0.02	0.8
XXIII	16.2	"	0.5	"	"	3,600	4,000	1,000	"	0.058	2.2		0.2	0.012	0.5
XXIV	"	0.16	0.4	"	200	2,900	3,000	600	1.05	"	"		0.2	0.012	0.5
XXV	"	"	0.3	"	"	2,400		400	"	"	"		0.15	0.009	0.3
XXVI	"	"	"	"	"	"		400	"	"	"	>2.0	"	"	"
XXVII	"	"	"	"	"	"		350	"	"	"	>2.0	"	"	"
XXVIII	"	"	"	"	"	"		400	"	"	"	3.0	"	"	"
XXIX	"	"	"	"	"	"		400	"	"	"	3.0	"	"	"

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Tests XXVIb and XXVIIb in Fig 8 are simultaneous recordings of the same photomultiplier outputs as in the respective Tests XXVIa and XXVIIa, but on more compressed time scales and a more sensitive (expanded) vertical (light transmission) scale. The downward slope in Tests XXVIb and XXVIIb shows the slow partial clearing in the absence of a continuous plating current following the initial charge pulse. Similarly, in Test XVIII, the slight decrease in light absorption after the first 1300 μ secs is probably also due to the same slow spontaneous clearing effect. In Tests XXVIII and XXIX, both curves show the photomultiplier output, but the noisy traces have an inverted and more sensitive light transmission scale (corresponding to optical densities of 3.0 and 2.0 for 0.4 and 4.0 line spacings from the bottom, respectively).

The time constants and τ_1 values of Table III are usually much longer than those in Table II due to breakage of the best experimental cells by the time the photomultiplier circuit was improved. However, the q_{d1} and $(\delta_1)_{calc.}$ values of Table III (columns 15 and 16) are usually comparable with, and thereby indirectly confirm those of Table II. The unusually high value of $(\delta_1)_{calc.}$ in Test XX is probably due to a non-uniformity of plating in the area directly in front of the photomultiplier tube. As mentioned above, the cells used in Tests XVIII through XXIX were generally poorer and less uniform than the earlier cells. Attempts to increase their plating speed by reducing the number of capacitors and charging to higher voltages invariably resulted in an incandescence of the grooves (cf. Fig 9) probably due to an excessive value of ρ_G and associated I^2R power dissipation in the conductive film in the groove walls. Furthermore, a non-uniform current distribution could result in permanently damaged spots in the conductive film adjacent to the electrolyte in areas where the current densities were at a maximum. Since any such damage would tend to enhance subsequent plating non-uniformities, a single passage of an excessive current pulse would usually be followed by incandescence and further deterioration even with lower (previously acceptable) current pulses.

In view of the extreme sensitivity of parallel circuits to imbalance under very high loads, it is almost surprising that the relatively high plating speeds of Table II could have been obtained. The average currents and current densities in Tests VII, VIII, XII, and XIII correspond to between 1000 and 1300 amps, and 70 to 80 amps/cm² for 250 to 400 μ secs over a relatively large area of 15 to 16 cm². It should be noted that Tests II through XIV were all performed with the same pair of matched plates, and that no damage due to the high current pulses was observed in these plates. It is also worth noting that these plates were obtained from an early batch of about 20 to 40 squares smaller to start with (2" x 2") than most of the other plates (2" x 5"), which may explain the relatively fair yield of 4 or 5 plates with satisfactorily low and uniform resistivity. However, even these best plates had the serious shortcomings of

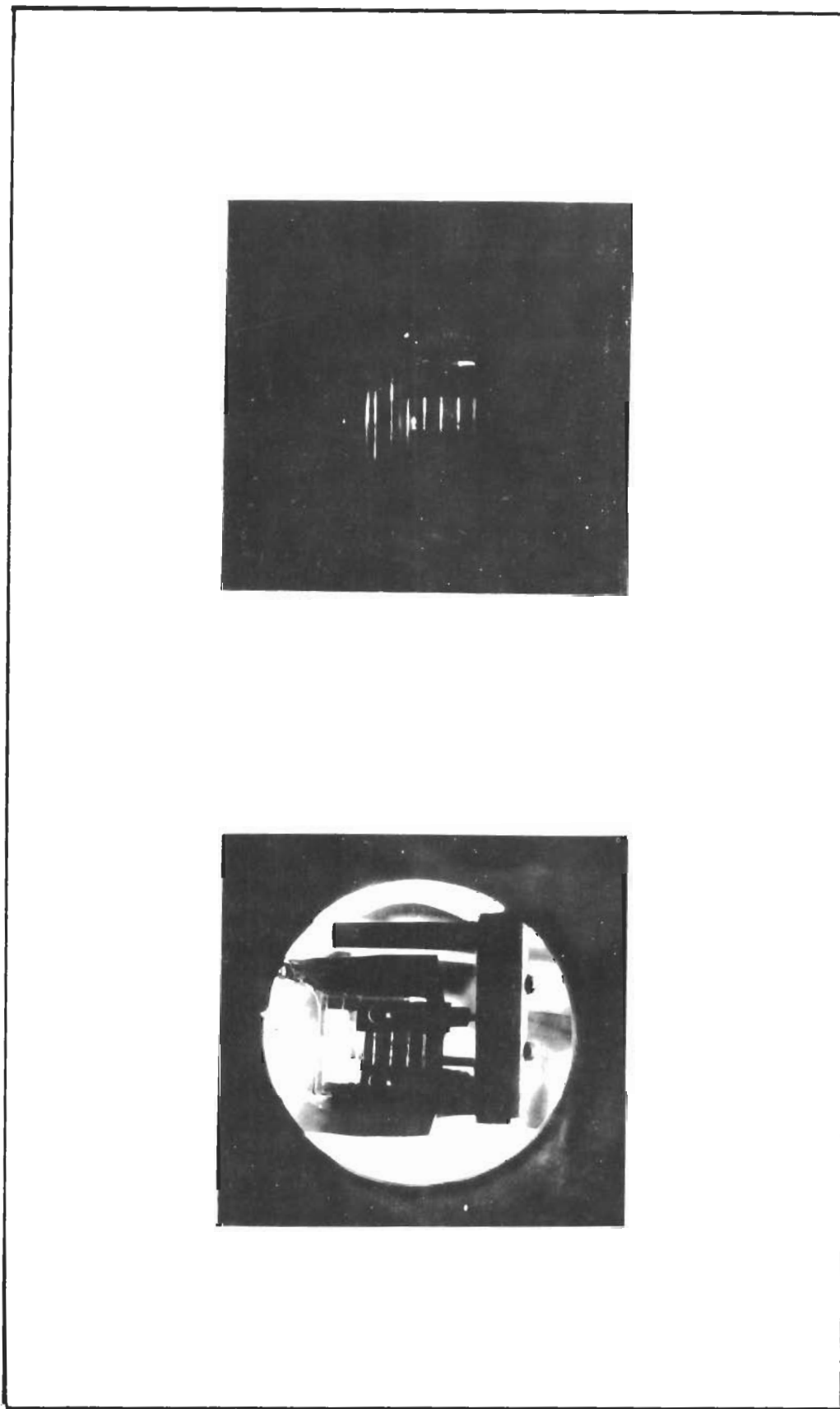


FIGURE 9 PHOTOGRAPHS OF IRREGULAR INCANDESCENT LINES RESULTING FROM A NON-UNIFORM DISTRIBUTION OF HIGH CURRENT PULSES THROUGH AN UNSATISFACTORY PLATING CELL

- a. Relatively poor light transmissivity (40 to 60%), resulting in an over-all light transmission of only 20% for the assembled cell; and
- b. excessive warping, necessitating cell spacings of 0.015" to 0.035", i. e., 4 to 9 times the design value of 0.004".

VI. RATE OF UNPLATING OF THE LIGHT SHUTTER

The time required for clearing of the light shutter was highly irreproducible and could vary from less than 10 secs to more than 5 min depending on cell structure. Since the gap widths a in most of the cells studied were 4 to 10 times larger than the design value of 0.01 cm (required to revert to 78% of the original transmission in 1 sec or 90% in 3 secs), and since the clearing time is proportional to a^2 , one would indeed expect the observed "clearing times" to range from 16 to 300 secs in cases where the proper reverse charge has been applied, and about four-fold longer "clearing times" without the reverse charge, in agreement with the actual observations. However, in addition to the effect of the spacing a , the following factors may further reduce the clearing rate:

- a. Any loss of the oxidizing component (I_3^- or IO_3^-) via a reaction with the insulating material or with the metal leads would result in incomplete clearing. Hence, faulty insulation may have been partly responsible for some observed irreproducibilities.
- b. In cases where reversed charge pulses were applied, current density non-uniformities different in the two pulse directions may produce an excess of Ag in some areas and of I_2 in others. Since the motion of I_3^- ions in directions parallel to the electrodes is extremely slow (considering the low a/L and a/w ratios) such areas of excess Ag and excess I_2 may remain dark for a very long time.

These last two factors may explain the type of discrepancy shown in Fig 10. The nominal gap width a being only 0.015 cm, one would expect a return to 78% of the original transmission in 2 secs rather than the 20 secs shown by the lowest curve. However, the actual gap width in the cell must have fluctuated by at least + 50%, each of the two plates having a surface unevenness of about 0.01 cm. Hence, a reverse charge pulse was likely to result in separate areas of excess Ag and excess I_2 . Shorting the cell terminals following the reverse charge pulse would then be expected to accelerate the rate of clearing of the Ag and I_2 spots via a type of battery discharge mechanism, as shown by the lower two curves of Fig 10, whereas no marked effect resulted from shorting when a reverse charge had not been applied, as shown by the upper two curves.

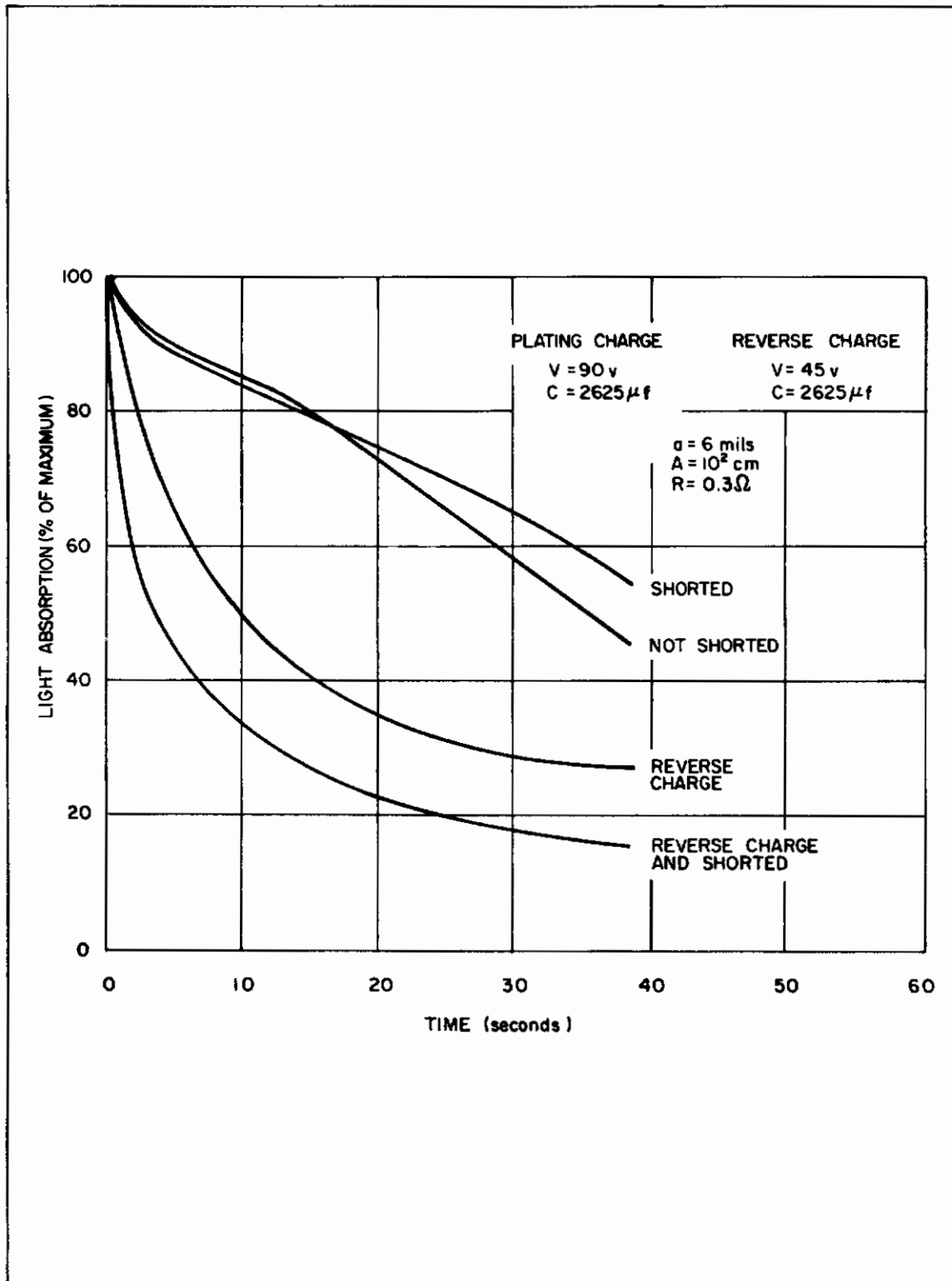


FIGURE 10 EFFECT OF A REVERSE CHARGE PULSE AND/OR SHORTING THE CELL TERMINALS ON THE RATE OF CLEARING OF A 6-mil GAP WIDTH LIGHT SHUTTER

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Summarizing, then, the observed rate of deplating usually agreed in first order of magnitude with theoretical expectations. Occasional cases of irreproducibility or of marked discrepancy appear attributable to faulty cell structures.

VII. CONCLUSIONS

1. Eq 9 leads to the unavoidable conclusion that in order to achieve an optical density of 4 within 50 μ secs, it will be necessary to place at least 5 shutters back-to-back. Since this result is based on the values of two intrinsic parameters, the boiling temperature and minimum resistivity of plating solutions, neither of which can be varied appreciably, there can be no possible way of by-passing this multi-layer requirement.
2. A further speed limitation associated with possibly insufficient mobility and concentration of plateable ions (Eq 10) would, at worst, have resulted in a further doubling of the required number of layers, if the charge requirement were determined by Eq 13. Fortunately, however, the lower charge requirements suggested by the experimental results (cf. Tables II and III) should render a five-layer shutter barely adequate even if Eq 10 were to prove strictly applicable.
3. Since the maximum plating speed allowable according to Eq 10 was actually reached or closely approached in four of the tests listed in Table II, the possibility of any further intrinsic speed limiting factors can probably be safely disregarded.
4. The unsatisfactory performance of the cells completed and remaining undamaged by the end of this contract can be clearly shown to be due in most respects to deviations from the original cell design. However, even if this design could have been achieved within perfect tolerances, it still could not have yielded an optical density of 4 within less than 500 μ secs, according to Eq 9.
5. The main difficulties in meeting the original design requirements were associated with the preparation of conductive glass plates having a sufficiently low and uniform surface conductivity, a good optical transmission, and a sufficiently flat surface. Other difficulties were associated with the introduction of spurious and unequal resistances in the contacts to the various parts of the conductive glass. These difficulties were aggravated by the requirement for large-area single lenses which resulted in a markedly increased probability of failure in the course of a number of highly delicate operations and by the sensitivity of heavily loaded, parallel circuits to even the slightest imbalance. Most of these difficulties would be eliminated in the design of Fig 11 based on series-connected subelements.

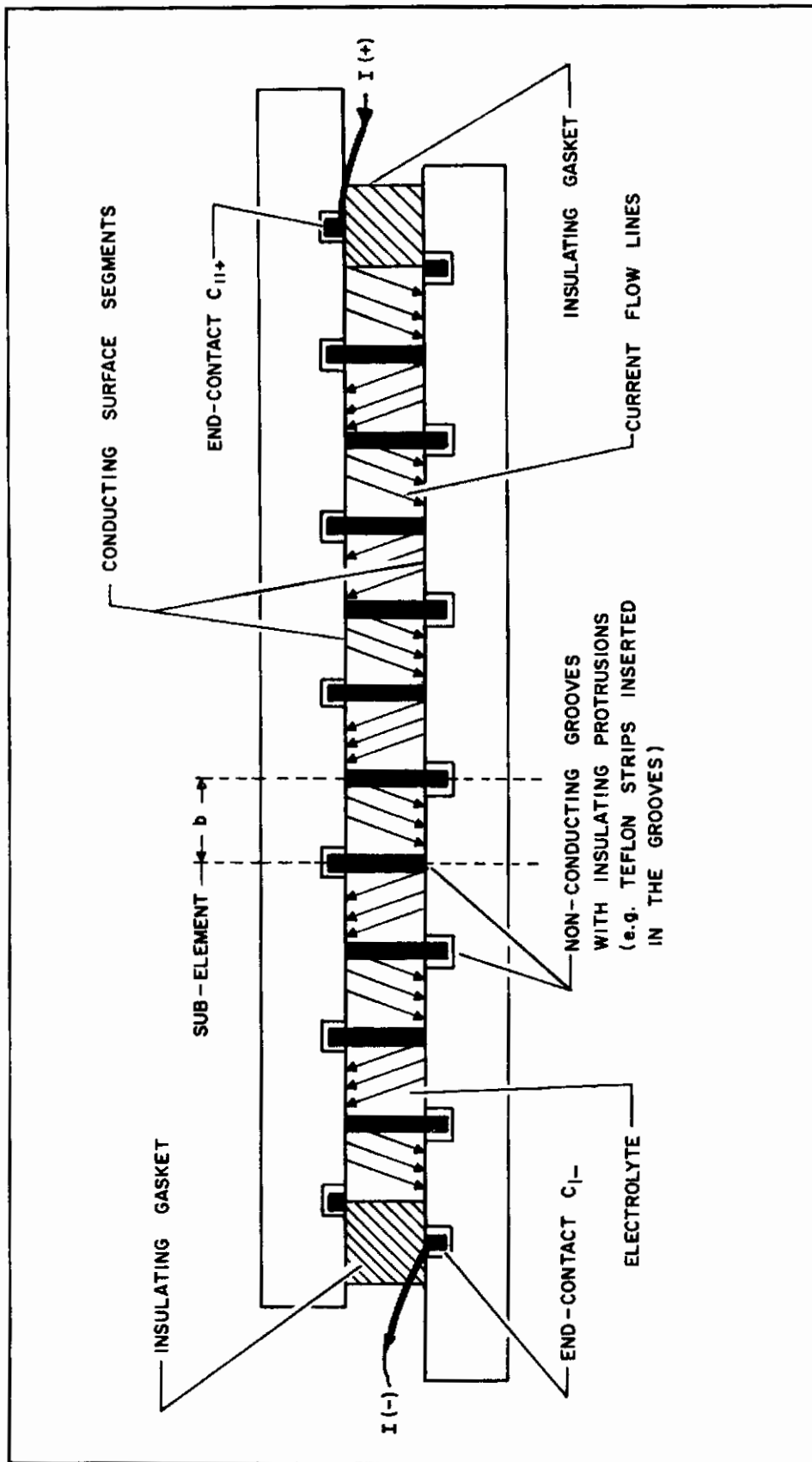


FIGURE 11 DETAILED DRAWING OF ARRANGEMENT 7 OF FIGURE 1

Conclusions

6. The experimental results are usually in fair agreement with theory. Discrepancies in rate of unplating are obviously related to the following main deviations from the design prescriptions:
 - (a) Uneven spacing between the electrodes; and
 - (b) non-uniform electrode surface resistivities and the presence of spurious resistances in the contacts to the individual subelements.
7. These deviations were also responsible for:
 - (a) The non-uniformities in plating density observed with unsatisfactory cells;
 - (b) circuit imbalances associated with these non-uniformities resulting in overloading of some of the parallel subelements; and
 - (c) irreparable damage of the overloaded subelements or of the contacts due to excessive local I^2R heat generation upon passage of excessive current pulses.
8. With satisfactory cells having negligible spurious contact resistances, the tin oxide coating was able to withstand average current densities as high as 80 amps/cm² for 250 to 400 μsecs over an area of up to 16 cm² even in solutions of neutral pH. No damage in the coating was observed even after more than 13 such high current pulses. The maximum plating speed expected on the basis of a first order estimate of diffusion rate limitations (Eq 10) was approached but not exceeded in four of the tests listed in Table II. Since the plating speed in all these tests was limited by the RC time constant of the circuit used, no conclusion can be drawn as to the actual importance of diffusion limited mechanisms.
9. Optical density changes of 1.0 or higher were obtained with an average charge density q_{dl} of 0.016 coul/cm² (in the tests of both Table II and Table III), i. e., 60 to 70% of the charge density calculated on the basis of the absorption constant of thick Ag layers. This better-than-expected darkening efficiency may be due either to variation of absorption constant with film thickness and method of formation (possibly related to defect and impurity concentration in the film), or to increased turbidity and/or multiple light reflections. A more thorough investigation of these results should have an important bearing both on the optimization of the performance of the light shutter and on the understanding of the properties of very thin films.

Contrails

ASSOCIATED ELECTRONIC CIRCUITRY

Mr. Ralph E. Husband

I. INTRODUCTION

This report describes the Engineering Department effort in designing and constructing the circuitry to be used with the plating cells.

The diagrams included with this report are not necessarily final. They are current with the present design, but may require revision by the time the deliverable breadboard models are complete. If changes are made, new schematics will be issued.

II. GENERAL DISCUSSION

An electronic package was developed and breadboarded that will detect a flash and produce an output current pulse suitable for plating a lens.

The electronic package is mounted in two chassis. One chassis contains the flash sensor and the signal-processing circuitry, and the other chassis contains the power supply, the energy storage capacitors, and the associated switching and triggering circuitry. All of the switches and the terminal for connecting the lens are located on the latter chassis. The two chassis are interconnected by a six-conductor cable, with a plug and receptacle at each end.

The studies carried out on the present program have shown that all the design specifications could not be met. Improvements could still be effected in the size and weight of the electronic package, and the time required for the lens plating.

The energy required to deposit a sufficient quantity of Ag requires a large bank of capacitors, causing the size and weight limitations to be exceeded. The size and weight could be reduced somewhat through the use of special subminiature components. However, the cost and delivery of such items would make their usage prohibitive at this time. In most places, high quality, standard, commercial components are used. Also, the circuits are packaged for convenience of use-not for maximum component density.

The voltage limitations of the lens restricts the plating time. The present lenses are limited to 100 to 150 volts before arcing occurs. At these

voltage levels, it is impossible to pass the required current through the lens in the desired time.

The contract originally specified that the AC line power be 400 cycle, three phase. For laboratory testing, however, the electronic package has been designed to operate from 60- to 400-cycle, single-phase line power.

III. CIRCUIT DESCRIPTION

The circuit for the electronic package is shown in the block diagram, Fig 1, and the complete schematics are shown in Figs 2 and 3. The operation of the various portions of the circuit is described in subsequent paragraphs.

A. Flash Sensor

The flash sensor is a Fairchild type FSP-5 phototransistor. It produces an electrical pulse with a waveshape approximating the intensity of the observed flash.

B. Pulse Differentiators and Amplifiers

Since the system is to discriminate against flashes requiring over 50 μ secs to reach maximum intensity, the signal from the sensor is differentiated. This results in a pulse having a width equal to the rise time of the flash intensity. This pulse is then amplified and differentiated again.

C. Timing Multivibrator

The timing multivibrator is a one-shot multivibrator whose function is to generate the 50- μ sec timing pulse to which the rise time of the flash intensity is to be compared. It is triggered by the pulse corresponding to the leading edge of the pulse generated by the first differentiator. The output pulse, of 50 μ secs duration, is then applied to the gate circuit.

D. Gate Circuit

The pulse from the second differentiator, corresponding to the trailing edge of the pulse from the first differentiator, is applied to the gate circuit. If the timing pulse from the timing multivibrator is also present, the pulse passes through the gate circuit to the trigger circuit. If the timing pulse is not present, the pulse is absorbed in the gate circuit. Thus, the gate circuit compares the rise time of the flash intensity to a timing pulse, and provides an output pulse only when the rise time is less than 50 μ secs.

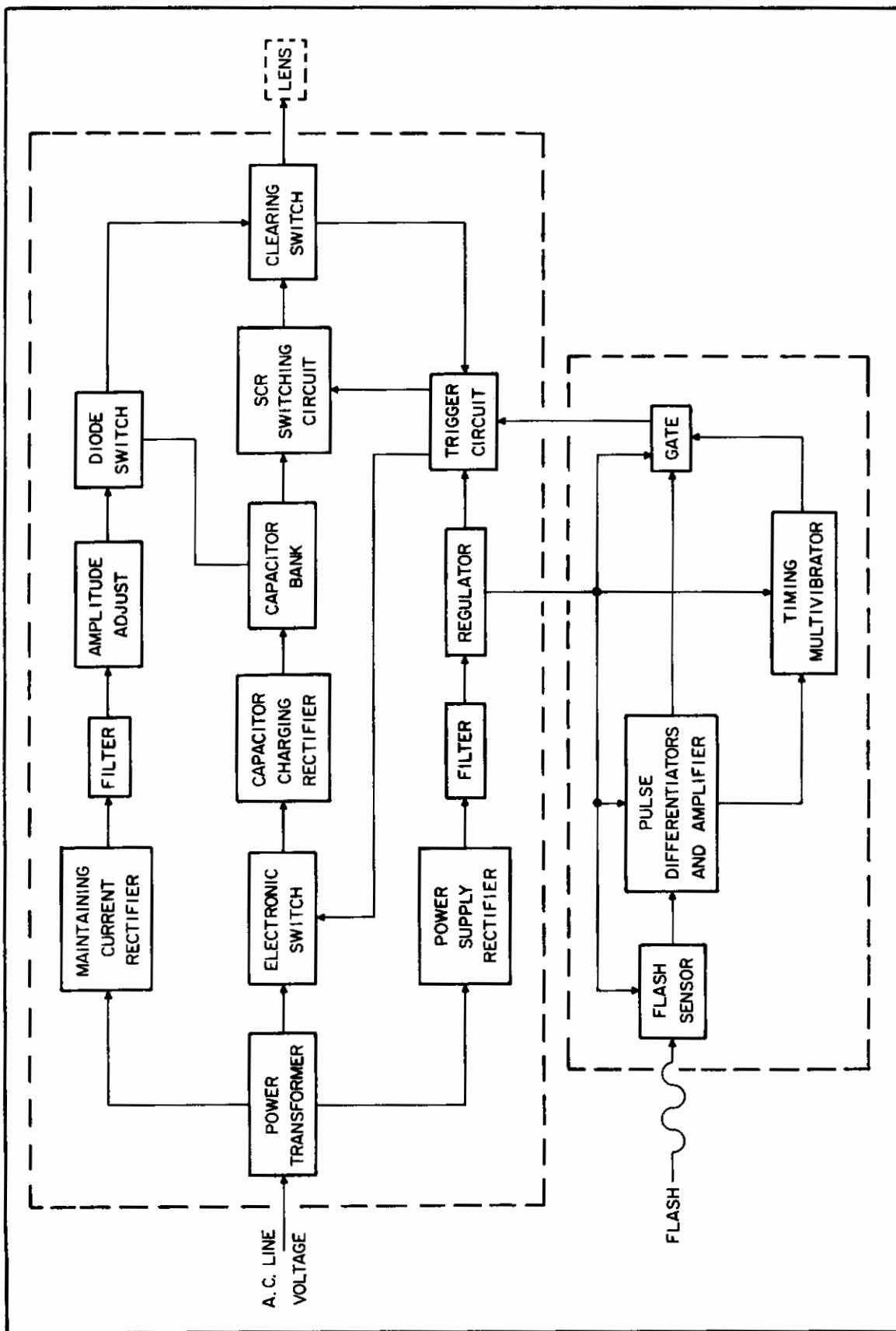


FIGURE 1 BLOCK DIAGRAM - ELECTRONIC PACKAGE

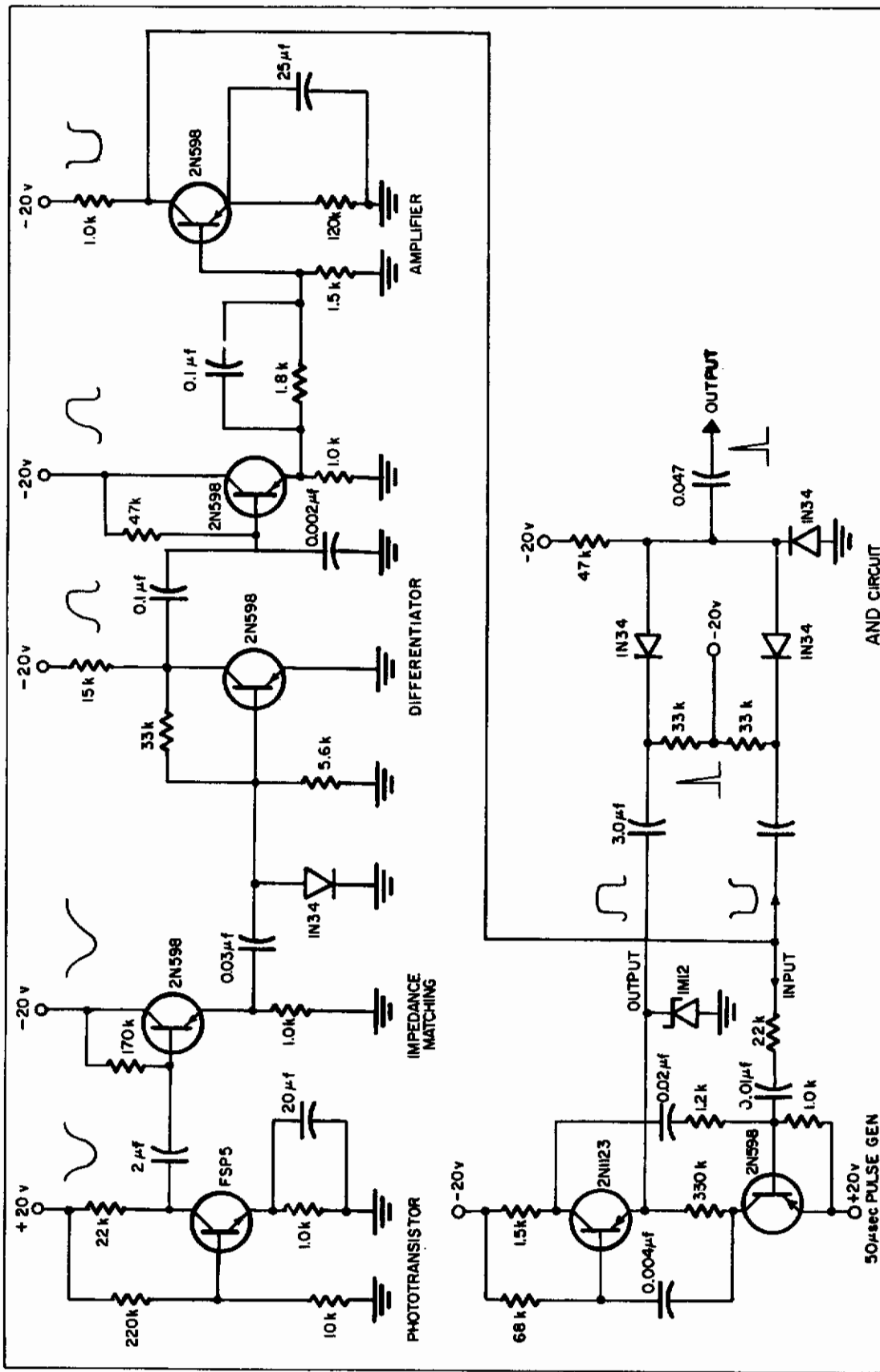


FIGURE 2 FLASH DETECTOR AND CIRCUIT

E. Triggering Circuit

The triggering circuit consists of a Shockley diode and a capacitor-resistor network. The pulse from the gate circuit triggers the Shockley diode, which, in turn provides a discharge path for the capacitor. The capacitor discharge provides a current pulse of sufficient amplitude to trigger the silicon controlled rectifiers. The Shockley diode is also triggered, when the clearing switch is operated, to provide the trigger for the clearing current pulse.

The charge path of the capacitor includes a relay. One set of contacts connects a resistor in series with the Shockley diode, to ensure turn-off of the Shockley diode. The other set of contacts controls the electronic switch in the capacitor bank charging circuit (see I. 1). The relay sensitivity and the capacitor charging current are such that the normally closed contacts of the relay will be open for 40 to 50 μ secs each time the triggering circuit is operated.

F. Silicon Controlled Rectifiers (SCR's)

The SCR's in the lens plating circuit act as a switch to control the plating current flow through the lens. When they are triggered, they allow the energy storage capacitor bank to discharge through the lens. When the discharge current has fallen to the turn-off level, the SCR's are turned off automatically, allowing the capacitor bank to recharge.

Four SCR's are included in the circuit. Due to the lens limitations, only one would actually be required, but if a better lens becomes available, the four will be required to allow plating of the lens in the desired time. The connections to the capacitor bank are such that each group of capacitors must discharge through its respective SCR. This eliminates the need for matched SCR's for parallel operation.

G. Capacitor Bank

The capacitor bank consists of 16 aluminum electrolytic capacitors. These capacitors total 8400 μ fd, and are charged to 400 volts to supply > three coulombs of charge to plate the lens.

The capacitor discharge circuit also contains a tapped inductor. The inductor shapes the discharge pulse, rounding off the leading edge of the current pulse, and sharpening the trailing edge. The tap on the inductor provides a pulse to trigger the Shockley diode in the maintaining current power supply (see III. I. 2).

H. Clearing Switch

This switch reverses the polarity of the current pulse applied to the lens. When it is desired to clear the lens, it is necessary to apply a reverse current to the lens to speed the clearing time. The switch also provides a manual trigger to the triggering circuit, so that the lens will be cleared when the switch is operated. The fourth pole of the switch opens the maintaining current circuit, to prevent additional plating from this circuit (see III. I. 2).

I. Power Supply

The power supply converts the power from the AC line to the various DC voltages and currents required by the electronic package. The AC input requirement is 115 volts, single phase, 60 to 400 cps. There are three secondaries on the power supply to supply the following DC requirements:

1. Capacitor Charging Circuit

This circuit supplies the 400 volts DC to charge the capacitor bank. It consists of an electronic switch and a full-wave bridge rectifier. The electronic switch is controlled by the relay in the triggering circuit (see III. E), and removes the AC input voltage during the capacitor bank discharge. If the charging current were not interrupted at this time, it would flow through the SCR's keeping them in the "on" condition.

2. Maintaining Current Circuit

When the lens has been plated, it is necessary to apply a small maintaining current to maintain the plated condition. This circuit provides the current. The circuit consists of a full-wave rectifier, a capacitor input filter, a current amplitude adjustment resistor, a Shockley diode, and one pole of the clearing switch, as well as the lens. The Shockley diode is triggered by a pulse from the inductor in the capacitor discharge circuit (see III. G). Thus, the maintaining current is applied when the capacitor bank is discharged, and continues to flow until the clearing switch is operated.

3. Regulated Power Supply

This circuit provides the positive and negative regulated DC voltages for the operation of the transistors in the electronic package. It consists of a full-wave rectifier, capacitor input filter, and a single stage zener diode regulator.

IV. PROBLEMS ENCOUNTERED

A. Lens

The main difficulty encountered in the Engineering Department tests has been in the lens. The lenses obtained thus far have not been able to withstand the voltage required to allow rapid plating. A decrease in the lens resistance would also allow a higher current with the same applied voltage.

Another trouble observed in the lens has been unevenness of plating. As Ag begins to accumulate in a local area, the surface resistivity is reduced, causing higher current density, and a more rapid Ag plating. As a result, the Ag from the solution is all deposited in small areas, leaving other areas transparent.

When the clearing switch is operated, the Ag does not return to solution, but instead, appears to be electroplated to the opposite glass surface. Therefore, the reversal of the plating charge may not be a satisfactory method of clearing. When the maintaining current is removed, the Ag will gradually go back into solution. However, this process is very slow for complete clearing. After the initial action has taken place, there is an excess of Ag in some places, and an excess of I in other places, as evidenced by clear solution adjacent to the opaque Ag spots, and yellow solution in areas where the glass is clear. Thus, considerable time may be required to complete the reaction between the Ag and the I.

B. Flash Characteristics

The exact characteristics of a nuclear flash are not known, and it has not been determined that the rise time of the flash intensity is the preferred characteristic to base detection upon. The discrimination for the present circuit is based upon the 50- μ sec maximum rise time of the flash intensity as specified in the original contract. A circuit was developed to discriminate for flashes that reached maximum intensity in at least 150 μ secs but less than 1000 μ secs after initiation, but this circuitry is not included in the models to be shipped.

In the laboratory experiments, a gas-discharge tube (General Radio type 631-B Strobotac) was used as a flash source.

V. CONCLUSIONS

A workable model of nuclear flash protection goggles has been built, but is not completely satisfactory. Improvements to the present design, especially in the lens, may result in an item suitable for use by the armed forces.*

VI. FUTURE DEVELOPMENT

A. Flash Detection and Discrimination

A study program should be undertaken to determine the characteristic of a nuclear flash most suitable for discriminating and triggering. This may be undertaken independently of the development of a protective device. Until the nature of the flash is known, the best protective device cannot be developed.

B. Capacitor Bank

If the lens plating time can be reduced, it will be possible to modify the capacitor bank to provide a more ideal current pulse. A pulse forming network, similar to a lumped constant delay line, may be useful as an energy device. Many techniques used in transmitter pulse work may also be useful in this circuit.

C. Circuit Simplification

Once a workable circuit is obtained, many circuit simplifications are obvious. This is also the case with the present electronics package. One of the most obvious is the elimination of the electronic switch in the capacitor charging circuit. If the capacitors can be completely discharged within the time of one-half cycle of the AC power source, the switch can be eliminated. The capacitors could be charged from a half-wave rectifier circuit, using the same diodes that are used for isolating the SCR's. During the half cycle the rectifiers are blocking, the capacitor bank could discharge and the SCR's could turn off. Thus the switch would be unnecessary.

Another item that should have further investigation is the difference in voltage between aircraft ground and the power supply common (see III. I. 3). At present, there may be up to 400 volts' difference in potential between these points. It would be advantageous to have them at the same potential.

* Editor's note: Required improvements in the lens design have been discussed in the "Conclusions" part of "Section I - Cell Research and Development."