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RADIOGRAPHIC AMPLIFIER SCREENS - FABRICATION PROCESS AND CHARACTERISTICS

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Prepared by
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16. Abstract

This report describes the fabrication process and transfer characteristics for solid state radiographic image transducers (radiographic amplifier screens). These screens were developed for use in real-time nondestructive evaluation procedures that require large format radiographic images with contrast and resolution capabilities unavailable with conventional fluoroscopic screens. This work was directed toward screens usable for in-motion, on-line radiographic inspection by means of closed circuit television.

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SUMMARY

This report describes the fabrication process developed for solid state radiographic image transducers called radiographic amplifier screen (RAS) panels. The screens consisted of a photoconductive and electroluminescent (PC-EL) layer sandwiched between two electrodes. Three of these experimental RAS panels were made by using glass substrates and one was made by using a beryllium substrate. The dimensions of the glass panels ranged from 10 by 10 inches (25.4 by 25.4 cm) to 8 by 10 inches (20.3 by 25.4 cm). The beryllium panel was 3 by 3 inches (7.6 by 7.6 cm).

The RAS panels were developed for use in nondestructive evaluation (NDE) operations requiring large format (over 500 sq cm) radiographic images with contrast and resolution capabilities unavailable with conventional fluoroscopic screens. The work reported herein was directed toward RAS panels usable for in-motion, on-line radiographic inspection by means of closed-circuit television.

The transfer characteristics for the experimental RAS panels produced in this contractual effort are given in this report. The objectives and consequently the method of fabrication were somewhat different from those reported under a previous NASA Marshall Space Flight Center contract. It was required that faster response, higher resolution screens be explored. In addition, it was required that the possibility of using a beryllium substrate be explored to improve

response to longer X-ray wavelengths.

The requirements set forth by the contract were met by the delivered glass substrate panels except that the resolution was lower: 300 instead of the targeted 500 lines per inch. The beryllium substrate presented some problems. These problems were principally due to serious nonuniformities in the thin film of beryllium oxide covering the surface.

1. INTRODUCTION

This work was undertaken in order to provide radiographic image transducers suitable for nondestructive evaluation purposes. These transducers are usually interfaced with closed circuit television systems to provide a safe, convenient in-motion, on-line inspection method. Current methods used in industry and medicine utilize various types of fluoroscopic screens. The image transducers developed in this effort are different from conventional fluoroscopic devices in that they provide higher contrast, higher brightness, and/or higher resolution.

In this report the fabrication processes and characteristics of radiographic amplifier screens (RAS) will be described, which were made on contract NAS3-19902 from November 13, 1975 to May 12, 1976.

The development work of such radiographic amplifier screens was made previously under the support of the Marshall Space Flight Center - NASA.[1-3] In the present work program the goal was to fabricate four 8" x 10" size amplifier screens with somewhat different characteristics than those made for the MSFC.

The work on this program was performed at the Westinghouse Research Laboratories, Pittsburgh, Pa. by D. Leksell and Z. Szepesi as principal investigator. Managerial supervision was provided by F. T. Thompson, T. P. Brody and D. H. Davies.

2. OBJECTIVES AND RESULTS

The characteristics aimed to be approached by those of the delivered four amplifier screens are listed in Table I.

ITEM NO.	CHARACTERISTICS	OBJECTIVES	UNITS
1	X-ray range	10 - 150	kVolts
2	Output spectrum	500 - 600	nm
3	Output brightness	10^{-3}-1	fL
4	Driving voltage	100 - 200	Volts
5	Driving frequency	50 - 1000	Hz
6	Max. current	5	mA/in^2 at 60 Hz
7	Resolution	500	ℓ/in
8	Min. detectable radiation	20	mR/min or higher at 70 kV
9	Contrast (gamma)	6	
10	Rise time constant	0.1	sec
11	Decay time constant	0.1	sec

TABLE I. GOAL CHARACTERISTICS OF RAS-s

The delivered screens met the objectives under item Nos. 2 to 6.

The resolution (item No. 7) of the panels was not much higher than 300 ℓ/in.

The minimum detectable radiation (8) with one screen (RAS-1648) was about 20 mR/min, with the others was somewhat higher, up to 200 mR/min.

The specification for maximum contrast (9) was met by two screens (RAS-1542 and 1626) with reasonably low driving voltage and higher than 100 Hz driving frequency.

The rise and decay time constants (10 and 11) of the screens depend on the x-ray intensity. With high enough intensity the response time was less than 0.1 sec so that the amplifier screens can be used with a few msec pulsed excitation, requiring about the same dose as with a longer excitation. However, the decay time constants were somewhat higher than 0.1 sec. The fastest panels were: RAS-1542, RAS-1626 and RAS-1666.

Since the glass substrate absorbs appreciably the low energy x-ray photons below 20 keV, to satisfy the first item, one radiographic amplifier screen had to be fabricated on beryllium substrate. A number of experimental panels were made on Be, but the limited effort was not enough to solve the problems presented in this construction. The main problem here was the non-uniformity of the Be surface. Since the Be oxidizes easily, a thin film of BeO covers the surface. This would not present any difficulty, if it would be thick enough and uniform. But probably it is very thin and has a large number of weak spots. It was suspected that the $CdCl_2$ doping, contained in the PC powder, attacks the Be through the weak spots of the oxide coating. Therefore in one experiment LiCl was substituted for the $CdCl_2$, however it gave much stronger reaction with the Be than the $CdCl_2$ doped layer. Heavier metal chlorides probably could have weaker reaction.

Three methods were tried first to improve the surface structure of the Be plate:

1. Acid etching

2. Passivation of the surface, proposed by the manufacturer of the Be plates: Kawecki-Berylco Industries.

3. Sputtering an Al_2O_3 film to the Be plate.

The last method gave the best results. The delivered RAS-1656 was made by this method. However, this screen still shows some spottiness, probably due to the thinness of the Al_2O_3 film. It is hoped that thicker Al_2O_3 coating would eliminate the disturbing structure.

Beside the Be substrate panel, four RAS-s on glass substrates were delivered. Table II gives the list of the delivered RAS-s with their maximum voltage ratings. Figures 3 to 6 show the transfer characteristics of these panels measured with the optimum driving voltage and frequency for good gain. With higher frequency, the gain does not change much, however higher brightness is obtained with higher input intensity and the contrast increases. With lower voltage the gain decreases, but the contrast increases.

RAS No.	Vmax VRMS
1542	300
1626	250
1648	120
1666	170

TABLE II. DELIVERED RAS-s AND THEIR MAXIMUM VOLTAGE RATINGS

The maximum voltage on the Be-substrate panel (RAS-1656) is about 120 VRMS.

3. CONSTRUCTION OF RADIOGRAPHIC AMPLIFIER SCREENS

The solid state radiographic converter is a thin flat screen, constructed by sandwiching a photoconductive (PC) and an electroluminescent (EL) layer between two electrodes as shown in Figure 1. The semiconductive film and the black layer between the PC and EL layers are of secondary importance: the first for providing ohmic contact to the PC layer, the second for eliminating optical feedback.

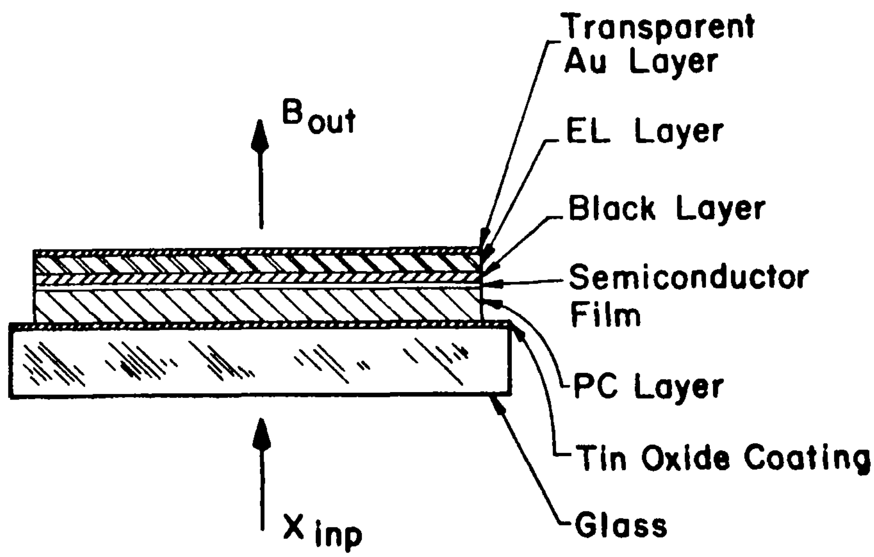

FIGURE 1. CONSTRUCTION OF A PC-EL SANDWICH TYPE IMAGE CONVERTER

The electrodes of the sandwich are transparent to x-rays on the PC side and to visible light on the EL side. The PC layer is sensitive to the incident x-rays, i.e. its resistance decreases with increasing x-ray intensity. Projecting an x-ray pattern on the PC layer causes a visible image of the same size to be displayed on the EL layer. An AC voltage connected to the two electrodes is required for the proper functioning of the converter screen.

Considering one element of the radiographic converter, one sees that, electrically, the PC element is connected in series with the EL element. (The semiconductive and black elements are very thin, consequently they have very low impedances and do not appreciably influence the electric circuitry). When the PC element is not irradiated and its impedance is many times higher than that of the EL element, most of the voltage will be across the PC side. Consequently, the voltage across the EL element will be low, resulting in a very low brightness. When the PC element is exposed to x-rays its resistance decreases, resulting in a higher voltage and higher brightness on the EL element.

Figure 2 shows transfer characteristics (output brightness vs. input irradiation) of a light sensitive PC-EL image intensifier for different constructions of the amplifier screen, where the capacitance ratio of the EL element (C_{EL}) to the PC element (C_{PC}) is different. Notice the large slope of these transfer characteristics, corresponding to high contrast sensitivity. If the capacitance ratio C_{EL}/C_{PC} of the screen is made larger, the contrast will be greater and the background brightness lower.

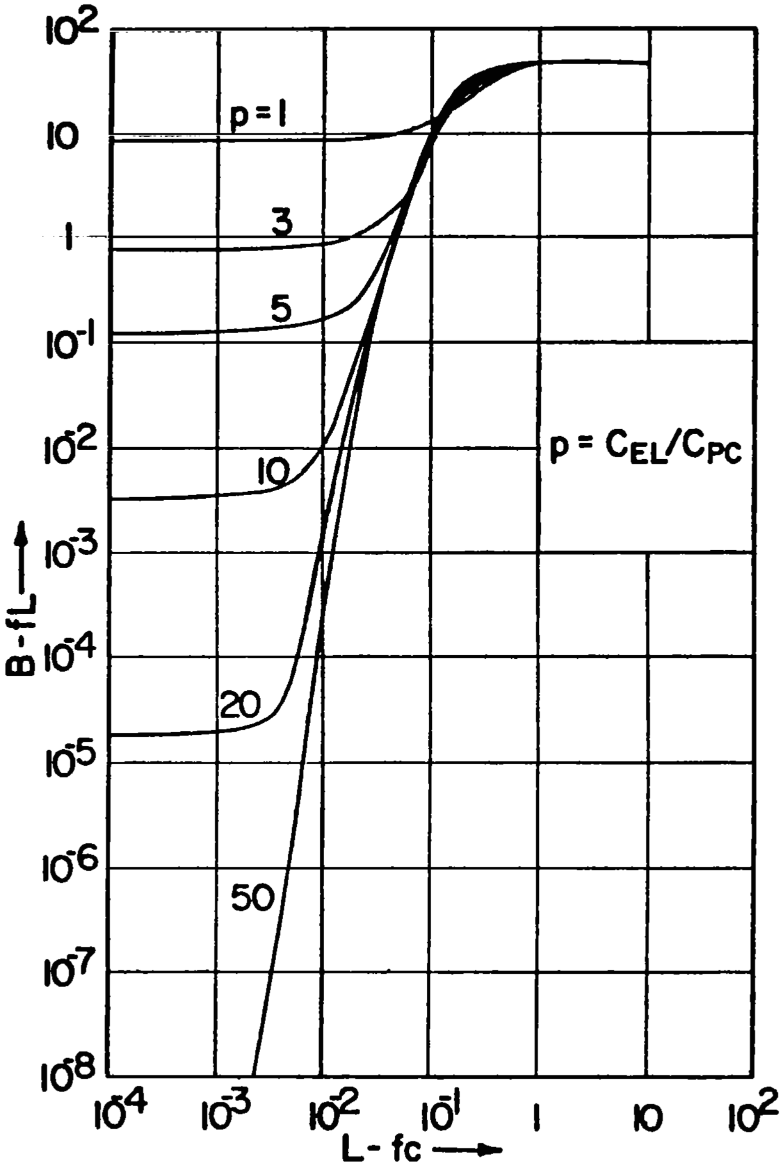

FIGURE 2. CALCULATED TRANSFER CHARACTERISTICS OF PC-EL IMAGE INTENSIFIERS WITH DIFFERENT CAPACITANCE RATIOS.

If the characteristics of the PC and EL elements are known separately, one can calculate the approximate transfer characteristics of the PC-EL sandwich.

The following equation describes the current (I) dependence of the PC element in its useful range from the illumination (L) and the applied voltage (V_1):

$$I = c_o \, (c_d + L^n) \, V_1^{\,m} \tag{1}$$

where m, n, c_o, c_d are constants for a given PC cell and characterize its opto-electronic behaviour. From equation (1), the conductance (g_1) of the PC element is:

$$g_1 = c_o \, (c_d + L^n) \, V_1^{\,m-1} \tag{2}$$

The brightness (B) vs. voltage (V_2) dependence at a frequency (f) of the EL element is given by the equation:

$$B = B_o f^{\alpha} \, e^{-\sqrt{A/V_2}} \tag{3}$$

where α, B_o, A are constants for a given EL panel. Other data needed for the calculation of the transfer characteristics of the PC-EL amplifier screen are:

C_2 the capacitance and g_2 the conductance of the EL element and $p = \frac{C_2}{C_1}$, the capacitance ratio of the EL to the PC element. If the susceptances of the PC and EL elements are $S_1 = \omega C_1$ and $S_2 = \omega C_2$ respectively, and the driving voltage on the sandwich is V_o, the voltages V_1 and V_2 are given by equations (4) and (5):

$$V_1 = V_o \; \frac{g_2^{\,2} + S_2^{\,2}}{(g_1+g_2)^2 + (S_1+S_2)^2} \tag{4}$$

$$V_2 = V_o \frac{g_1^{\,2} + S_1^{\,2}}{(g_1+g_2)^2 + (S_1+S_2)^2} \qquad (5)$$

and the brightness of the amplifier screen can be calculated from equation (3). The slope of the transfer characteristic curve

$$\gamma = \frac{d\ (\log B)}{d\ (\log L)} \qquad (6)$$

can be calculated also through a quite complicated formula. In the case of $m = 1$, $c_d = 0$ and $g_2 = 0$, the maximum slope of the transfer characteristic curve also can be calculated by a not extremely complicated formula.

Based on the above equations a computer program was written in FORTRAN language and a parameter study of the PC-EL sandwich was made in a previous program supported by the Naval Training Device Center.[4-5] The transfer characteristics shown in Figure 2 were constructed from the parametric and empirical data.

4. FABRICATION PROCEDURE FOR RADIOGRAPHIC AMPLIFIER SCREENS

A. Panel Fabrication

1. Substrate Preparation:
   a. Etch off about 1/8" wide band of the tin-oxide coating on two opposite side of the substrate glass (Schott Tempax or Corning Pyrex with tin-oxide coating).
   b. Clean the glass substrate as described in Part B below.
2. Preparation of CdSe-CdS powder. See Part C below.
3. Settling of the PC powder. See Part D below.
4. Sintering. See Part E below.
5. Clean up on two apposite sides, where the tin-oxide coating was not etched off, about 1/8" wide band of the PC layer.
6. Evaporate 1.4g CdSe at 18 inch distance in high vacuum on top of the sintered CdSe layer.
7. Spray 2 layers of 5% Ucilon White* Type 400-9.
8. Bake in forced air oven at 100^{o}C (212^{o}F) for 30 minutes.
9. Brush 2 layers of 25% Ucilon White on 2 edges above the etched tin-oxide.
10. Repeat step 8.
11. Spray 5 or 6 layers of green EL phosphor, Westinghouse type VB-242P, and 3 layers of clear coat (steps 1 to 6 of Part F) using mixtures 1 then 2.
12. Brush 3 layers of Ucilon on 2 edges above the etched tin oxide.
13. Bake at 100^{o}C (212^{o}F) for 30 minutes in forced air oven.

* Made by M&T Chemicals, Inc., Rahway, New Jersey

14. Apply Emerson-Cuming V-91 silver epoxy with rubber pad applicator to the two opposing Ucilon coated edges. Attach lead wires to one of these edges and one to the open tin-oxide edge with the silver epoxy.

15. Bake at $135^{o}C$ ($275^{o}F$) for 15 minutes.

16. Evaporate top transparent gold electrode PbO + Au (step 7 of Part F).

17. Pretest.

    a. Sensitivity
    b. Time response
    c. Imperfections, spots, bright edges

18. Spray several coats of Krylon crystal clear spray coating, Type 1302, on top of gold layer.

19. Bake panel for 30 minutes at $80^{o}C$ ($176^{o}F$).

20. Apply about 50g (for 8" x 10" panels) of Emerson-Cuming No. 1266 epoxy to the center of the coated substrate.

21. Place a precisely cut cover glass against the epoxy on top of substrate and carefully align.

22. Wipe excess epoxy from edges as it squeezes out and apply a flat steel plate on top of cover glass as a weight, heavy enough to hold cover glass parallel and near the panel during cure.

23. Allow to cure at room temperature for 16 hours and remove excess epoxy with razor blade, taking care not to damage electrodes.

B. <u>Glass Substrate Cleaning</u>

1. Mechanically clean glass substrate with very fine $CaCO_3$ - water paste.

2. Wipe off $CaCO_3$ powder under copious water flow.

3. Place glass in a beaker of deionized water dependent upon the size of the piece and rinse thoroughly by overflow.

4. Drain off the rinse water to allow introduction of approximately 5-10% water solution of each of formic acid and hydrogen peroxide. The following solution was generally used:

   1250 cm^3 water
   100 cm^3 formic acid
   250 cm^3 hydrogen peroxide

5. Heat this solution to the 70-80°C (160-175°F) range, being careful not to allow the temperature to exceed 80°C (175°F). When over 75°C (168°F) has been reached, remove the beaker from the hot plate and allow to react at least for 30 minutes. The temperature will maintain itself for this period in a useful range. At the end of this time overflow deionized water rinse for 30 minutes.

6. Ultrasonically clean in deionized water for 5 minutes.

7. Ultrasonically clean in electronic grade isopropanol for 5 minutes.

8. Place glass piece above boiling isopropanol, where it will heat up. When taken out it dries immediately.

C. <u>Preparation of CdSe-CdS Powder</u>

1. Weigh 90 grams of CdSe and 10 grams CdS powder (G.E. electronic grade) and mix it in a Pyrex beaker.

2. Place the well mixed powder in a quartz boat and heat it slowly in nitrogen atmosphere until the temperature reaches 1075°C (1966°F). Bake it for 30 minutes at this temperature and cool down still in nitrogen atmosphere.

3. Grind the material in diamonite mortar.

4. Place this material in a beaker and mix to it 400 mg of high purity selenium powder.

5. Weigh 4 gram of dry $CdCl_2$ and 500 mg NH_4Cl, dissolve them in about 20 ml deionized water and add to the powder mixture.

6. Mix a 1% water solution (by weight) of $CuCl_2 + 2\ H_2O$ (Fisher Certified), and add 2.5 ml slowly to the CdSe-CdS mixture under constant stirring.

7. Dry this mixture in an 80°C oven.

8. Prebake the powder mixture at 540°C (1004°F) for 90 minutes in a quartz dish with a cover in air atmosphere.

9. After cooling, grind the material in a diamonite mortar.

D. <u>Settling of PC Powder</u>

1. Weigh about 68 grams of the prepared CdSe-CdS powder, transfer it to a ceramic ball milling jar, mix about 100 ml Xylene with it and ball mill for nineteen hours.

2. Place the substrate glass plates in a perfectly horizontal plane at the bottom of a 12" x 12" glass jar.

3. Fill the jar with a 1.0% ethyl cellulose Xylene solution (filtered through a 8 μm size Millipore filter) to about 4" height above the substrate glasses.

4. Pour the ball milled PC mixture in the settling jar and let it settle until the Xylene clears up (about 2 hours).

5. Siphon off cushion and let panel dry in tank 10 to 16 hours.

6. Remove panel from tank and transfer to forced air oven and bake at 80°C (176°F) for half an hour. Increase the temperature to 135°C (275°F) and bake for an additional half hour.

E. Sintering of PC Layer

1. Place panel on a Vycor plate and cover with a pyrex dish.

2. Bake in a furnace of 535°C (995°F) for 70 minutes (air atmosphere).

3. Turn the Vycor plate with the panel 180° and bake an additional 20 minutes.

4. Remove panel from furnace and allow to cool under a strong airflow on the pyrex dish.

5. Place the panel in a 190°C (374°F) furnace (air atmosphere) and age for 16 hours.

6. Cool the panel under room light.

F. EL Layer Preparation

The EL layers were deposited by spray coating. A "deVilbiss" type EX spray gun with suction feed and a pressure of 18 psi nitrogen was normally used.

The schedule of the preparation of the EL layer was the following:

1. Spray a layer of spray mixture No. 1 (see below) onto the substrate. The layer should be good and wet but not running.

2. Let the layer air dry for a minute or two and bake it in a forced air furnace at 135°C (275°F) for 10 minutes.

3. Repeat steps 1 and 2 three to four times so that altogether four to five EL layers were sprayed, giving about 8 mg/cm^2 coating.

4. Bake for 30 minutes instead of 10 per 2 above, after the spraying of the last layer.

5. Spray a thin layer (3 to 4 layers) of clear coat (mixture No. 2) (weight about 0.6 to 1 mg/cm^2) on top of the phosphor layer for increased electric strength and smoother surface.

6. Give a final heat cure of 30 minutes at 135°C (375°F).

7. Evaporate a semi-transparent conductive lead-oxide and gold film in high vacuum on top of the sprayed layers. With a substrate to boat distance of 18 inches, 64 mg of PbO is evaporated first, followed by the evaporation of the Au. Latter evaporation is monitored by measuring the resistance of the deposited layer on a microscope slide or by using a quartz crystal thickness monitor. The evaporation is stopped when this resistance on the microscope slide is about 50 ohms/square or the frequency change on the thickness monitor is about 700 Hz.

Composition of spray mixtures:

1. Phosphor-plastic spray mixture:

   36g Westinghouse VB-242P EL phosphor
   90 ml 5% solution of cyanoethyl starch (CS)*+
   90 ml 5% solution of cyanoethyl sucrose (CES)*

Plastic solutions (5%)

   40g plastic (CS or CES)
   220 ml dimethyl formamide (DMF)
   580 ml acetonitrile

2. Clear coat:

   1:1 mixture of 5% CS and 5% CES solutions (see formula above).

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* Sold by Eastman Kodak Co, Rochester, N.Y.

\+ Sold by Techwest Enterprises Ltd, Vancouver BC, Canada.

5. DISCUSSION AND RECOMMENDATIONS

As it was discussed in Section 2 of this report, the delivered panels more or less approached the required characteristics, excepting the resolution. Furthermore, the image quality of the RAS on the Be substrate was not satisfactory.

Concerning the resolution, one could meet or surpass the required 500 ℓ/in resolution with a similar PC-EL type amplifier screen as the sintered powder construction, but with evaporated thin film PC and EL components. Some experimental work has been carried out in this field by Westinghouse several years ago. Evaporated PC films have been fabricated and evaporated EL films have been developed.[4-7] Continuing this work should result in amplifier screens with highly improved characteristics. However a major effort would be needed for successful completion of this program.

Concerning the Be substrate amplifier screens it is thought that the problems could be solved successfully by a moderately small effort. A series of experiments with different dielectric coating of the Be plate and/or changing the PC doping materials should result in acceptable characteristics.

Another way for decreasing the loss of the low energy x-ray photons, would be to build the PC-EL sandwich in an inverse order: deposit first the EL layer on a glass substrate and above it the PC layer.

In this construction a very thin (less than 100 μm thick) glass cover above the PC layer could be enough for protection against humidity, giving rise to a very small loss for even less than 5 keV x-ray photons. Some problems and limitations exist in this approach, but a medium size effort could result in acceptable characteristics.

6. CONCLUDING REMARKS

A fabrication procedure was described for radiographic amplifier screens (i.e., radiographic image transducers) having transfer characteristics suitable for use in a closed-circuit television X-ray inspection system. The devices described herein consist of photoconductive and electroluminescent (PC-EL) layers formed on appropriate substrates. In this work the substrates investigated were glass and beryllium. The glass substrate devices were successful in meeting the general requirements of the contract specifications. More work will be required to overcome the low quality of the images produced with beryllium substrates. Methods for achieving or surpassing the target resolution of 500 lines per inch were indicated.

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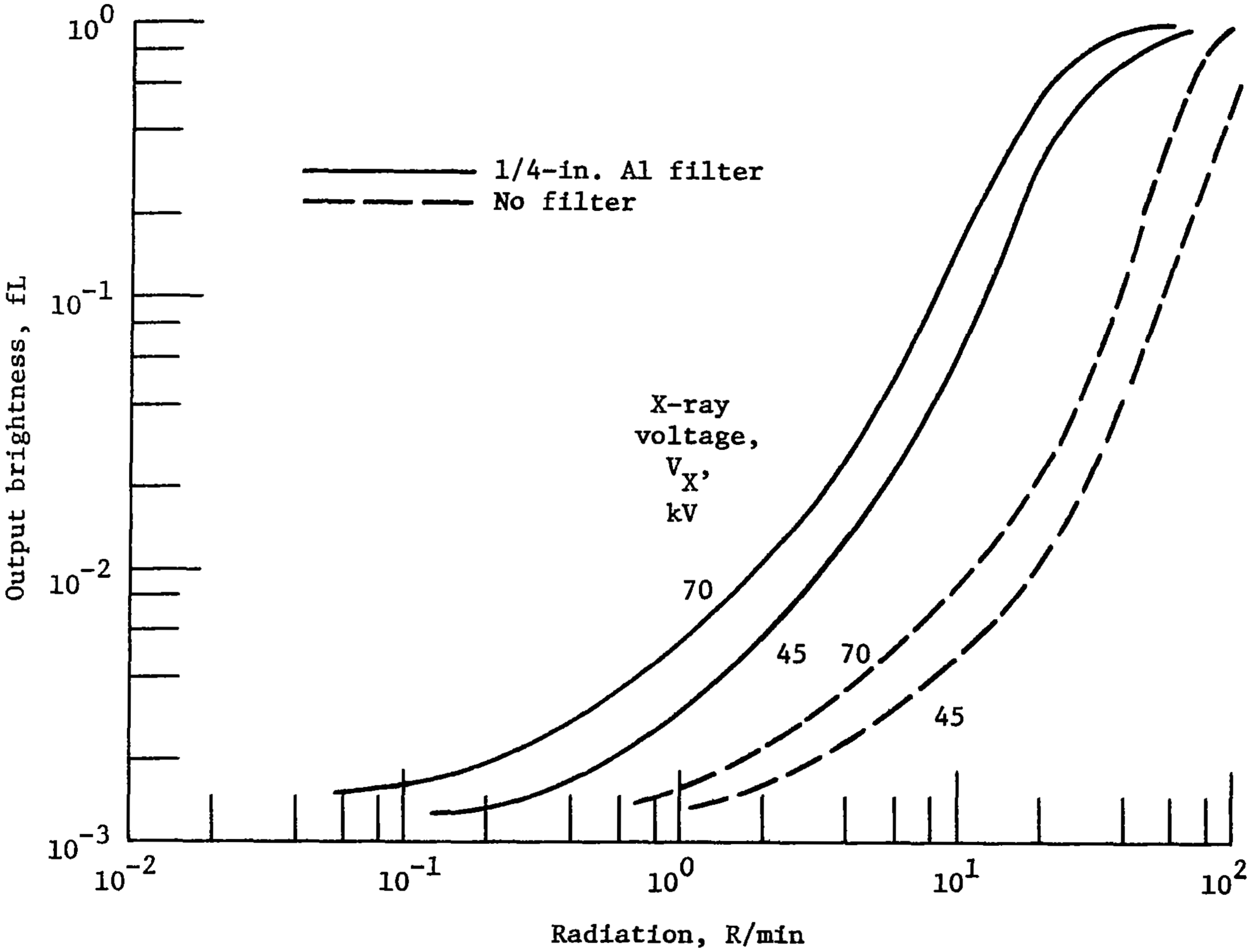

Figure 3. - Transfer characteristics of RAS-1542. Driving voltage, 300 volts; frequency, 60 hertz.

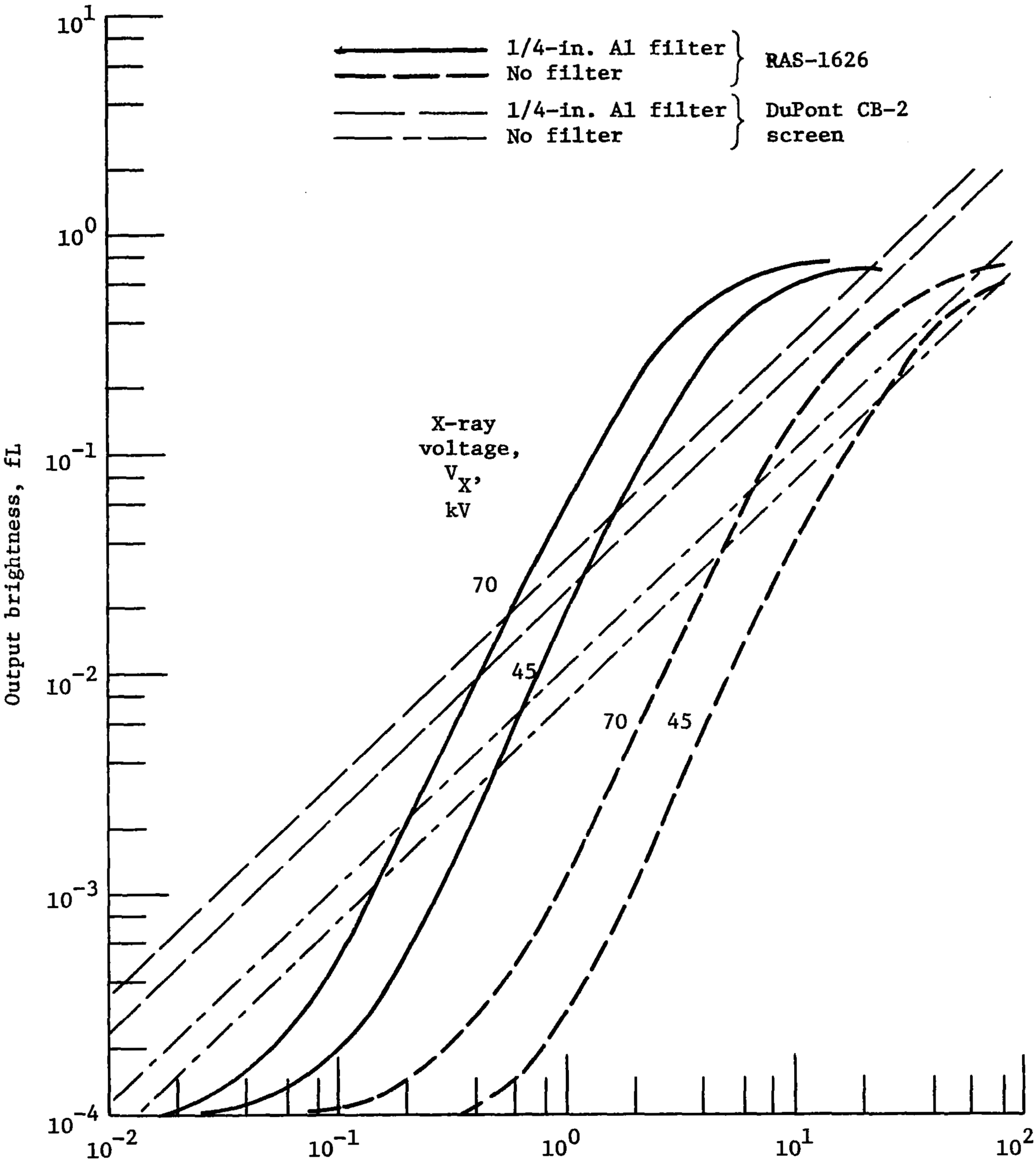

Figure 4. - Transfer characteristics of RAS-1626. Driving voltage, 250 volts; frequency, 60 hertz.

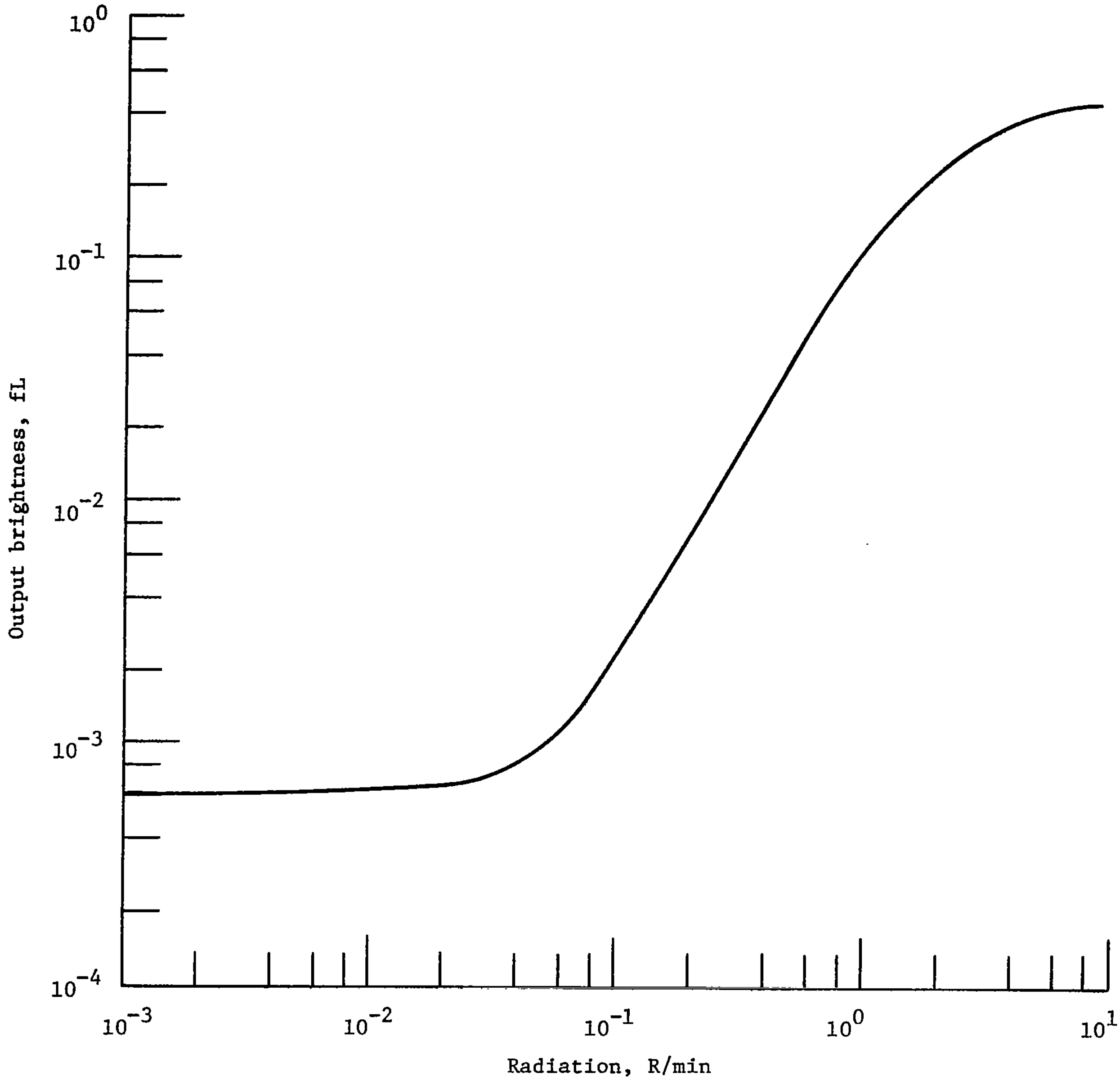

Figure 5. - Transfer characteristics of RAS-1648. Driving voltage, 120 volts; frequency, 60 hertz; 1/4-inch aluminum filter; X-ray voltage, 70 kilovolts.

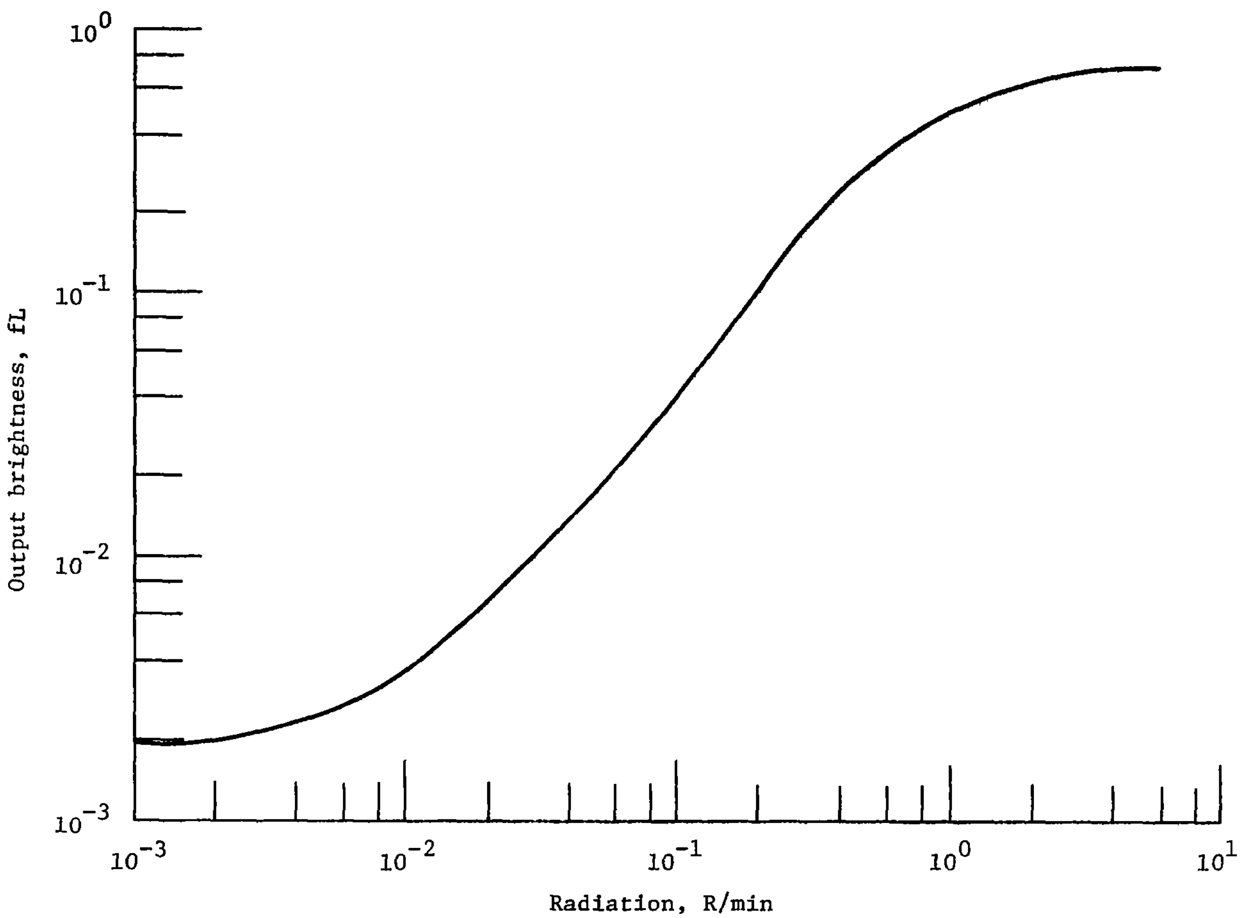

Figure 6. - Transfer characteristics of RAS-1666. Driving voltage, 150 volts; frequency, 60 hertz; 1/4-inch aluminum filter; X-ray voltage, 70 kilovolts.

NASA-Langley, 1977