CHEMICAL ARRAY STUDIES

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### Chemical Array Studies

The feasibility of developing continuous photoconductive layer arrays for mapping applications was studied. The procedures for preparing both the zinc oxide binder resin, and the undoped sintered cadmium sulfide, continuous photoconductive layers are presented. Special configuration area arrays with large multi-electrodes for beam centering purposes and for diffraction pattern detectors were devised. The mapping applications of the chemical arrays such as position detection, area, and center of mass continued.
measurements of uniformly dense-image patterns are described. Both zinc oxide and cadmium sulfide photoconductive layers were used to fabricate one- and two-dimensional arrays. Successful results were obtained for a one-dimensional 10-wire electrode, linear array. The fabrication of area chemical arrays were not successful. To fabricate a workable special configuration area array, more sophisticated methods such as sputtering and vacuum deposition techniques are necessary. A negligible error was obtained for the analysis of chemical arrays as position detection and area measurement. A larger error resulted for the center of mass measurement.
PREFACE

This was a subtask of the work authorized by the U.S. Army Engineer Topographic Laboratories, Fort Belvoir, Virginia under DA Project — Task Area Work Unit NO: 4A161102B52C/1752CS20002 entitled: "Application of Sensing Arrays to Mapping."

The authors would like to thank Mr. H. A. Hodes, U.S. Army Electronics Command, Fort Monmouth, N.J. for supplying the doped sintered cadmium sulfide layers on NESA glass used for this work.
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CHEMICAL ARRAY STUDIES

INTRODUCTION

SCOPE. This report covers the results of the research effort on the development of chemical arrays and their military applications. Although work began in 1974 and continued until 1977, the in-house effort amounted to 2 months or less each year.

BACKGROUND. The discrete element arrays presently available have a loss of spatial signal that is the result of the presence of metalized electrodes and of other dead spaces fabricated in the body of the arrays. Using such arrays to sample photographic imagery produces a loss in data that is related to the extent of such dead spaces. The loss of data is exhibited by reduced edge sharpness and detail in the sampled images. One solution to the loss of a spatial signal in array-type image processing is the method of using continuous photoconductive layers. This permits the entire image source to be used, which therefore permits operation with virtually no loss of spatial signal. The quality of the image processing, as far as such arrays are concerned, is then dependent upon the number of sampling elements per unit area in the array, the scattering of light within the layer, and the photometric response of the photoconductive layer. The concept of a continuous photoconductive layer may be applied in the design and fabrication of photosensitive devices for specific applications that do not require high resolution, but are not so simple as the single element photodetectors. Specific applications include object position detection, photographic pattern area measurement, and center of mass measurement for object-images.

CHEMICAL ARRAY CONFIGURATIONS AND THEIR MAPPING AND MENSURATION APPLICATIONS

A chemical array consists of a continuous photosensitive layer deposited on NESA* glass, a material that has a transparent conducting surface. An assembly of equally spaced wire electrodes is brought in contact to this surface to constitute an array configuration. The conducting side of the NESA glass serves as the common return for all electrodes. By arranging the configuration of the wire electrodes, various types of chemical arrays, such as single line (or linear) and square (or area) arrays, can be fabricated. Normally, a d.c. voltage (magnitude varies with the types of chem-

*NESA is a trademark of PPG Industries, Inc.
ical layer used) is applied between all electrodes and the common return. A load resistor is inserted between the array and the d.c. voltage supply to produce the output signal. The electric current going through each wire electrode is determined by the degree of conduction of the chemical layer where the wire contacts it and is proportional to the magnitude of image light intensity falling on the layer through the NESA glass.

Chemical arrays can be used in a wide range of sensing applications that do not require high resolution. One advantageous use for chemical arrays is sensing large areas without loss of spatial signal energy input. This is because a chemical array consists of a continuous layer of sensing medium that can be made relatively larger than the available size of solid state discrete array chips. Some chemical array applications are summarized next.

**CHEMICAL ARRAYS AS OBJECT POSITION DETECTORS.** The Object Position Detector scheme uses a one-dimensional chemical array as shown in figure 1. The side-view of the array is shown with an arbitrary width and with a defined position reference axis. A rectangular light image is projected as shown, and its center line with respect to the position reference axis is to be determined. With the weights, adder, and lowpass filter as shown, the output of the position detector \( X_0 \) with respect to the input image center position \( X \) is shown in figure 2 (Stair-Shaped) for image size \( nM \), where \( n \) is a positive integer and \( M \) is the center to center distance between wire electrodes. If a perturbation (image physical motion) signal of \( Bf(t) \) is introduced between the image and the array with the constraint that \( \frac{1}{T} \int_0^T Bf(t) dt = 0 \) and that \( T \) is a period of \( f(t) \), then the perturbation amplitude may be \( B \gg M/2 \), and \( f(t) \) may be a family of triangular waves. Then the instantaneous input position \( X_i(t) = X + Bf(t) \), and the system output \( X_0 \) after the lowpass filter is \( X_0 = C X \), where \( C \) is a constant.

A perfect linear relationship between the true image center position \( X \) and the position detector output \( X_0 \) is obtained (see figure 2), and a zero error position is measured.

**CHEMICAL ARRAYS FOR AREA MEASUREMENT.** The proposed area measurement system uses a two-dimensional chemical array, a signal processor, and an output indicator (figure 3). The system measures the relative size of uniformly dense area patterns. The threshold gates in the signal processor quantize the signal appearing in each wire electrode into either “on” or “off”, depending on the signal level in relation to the threshold value. An area measurement error was produced from the quantization around the edges of the image under measurement. To reduce the area

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Figure 1. One-Dimensional Position Detecting System.
Figure 2. Input-Output Relationship for Position Detecting System.
Figure 3. Area Measurement System.
measurement error, two-dimensional sinusoidal and triangular image perturbations were introduced to the system. Some typical image shapes of various size were used as test patterns, and the measurement error was evaluated for three types of system operation. The results are shown in Table 1. The area measurement error, $E$, was defined to be

$$E = \frac{|A_a \cdot A_m|}{A_a}$$

where $A_a$ is the actual area of the image pattern and $A_m$ is the measured area of the image pattern. A considerable reduction in measurement error was obtained for all image shapes with the introduction of the sinusoidal perturbation, and a zero error measurement was obtained with triangular perturbation (table 1).

**CENTER OF MASS MEASUREMENT USING A CHEMICAL ARRAY.** The area measurement system just discussed was extended to measure the center of the mass for two-dimensional, uniformly dense image patterns of arbitrary shapes. A pair of reference axes are defined (see figures 4 and 5). The measuring process takes two steps. First, the weight from each electrode is set to equal 1 (figure 4), and the area of the image pattern is measured. Second, the weights from electrodes are set according to figure 5 automatically. Now, the moment of the same image about the X-axis is measured. The center of mass of the image is obtained by dividing the measured moment by the measured area. The center of mass about the Y-axis can be obtained in a similar manner by arranging the weight of the threshold gates. As was the case in area measurement, both sinusoidal and triangular image perturbations were used to reduce the center of mass measurement error. Selected image shapes were used as test patterns. It was concluded that both image perturbations resulted in a better measurement accuracy; however, zero error, perfect measurement was not achieved.

**PREPARATION OF CONTINUOUS PHOTOCONDUCTIVE LAYERS**

The preparation method for the zinc oxide binder photosensitive layer and the sintered cadmium sulfide photosensitive layer are different. The zinc oxide binder material is prepared as a coating slurry in a volatile solvent and flow-coated on suitable conducting substrates. The zinc oxide layer is then air-dried in the dark. The cadmium sulfide material is prepared as a coating slurry in warm glycerin with cadmium chloride that serves as a flux in the sintering step. The slurry is coated on suitable conducting substrate using the doctor-blade method, is heated to drive off the glycerin, and is sintered at elevated temperatures in a furnace with a gas tight retort and under a nitrogen atmosphere. Although it is possible to produce a photosensitive layer made up on cadmium sulfide-binder material, the sintered layers have the greater photosensitivity.

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Table 1. Area Measurement Error for Various Image Shapes.

<table>
<thead>
<tr>
<th>IMAGE SHAPE</th>
<th>AREA MEASUREMENT ERROR E (%)</th>
<th>STATIC IMAGE</th>
<th>SINUSOIDAL PERTURBATION</th>
<th>TRIANGULAR PERTURBATION</th>
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<tr>
<td>Square</td>
<td>21.0</td>
<td>0.531</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Rectangle</td>
<td>32.0</td>
<td>0.531</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Circle</td>
<td>3.135</td>
<td>0.101</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ellipse</td>
<td>9.502</td>
<td>1.045</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Triangle</td>
<td>13.164</td>
<td>1.360</td>
<td>0</td>
<td></td>
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NOTE: \( w = \triangle/100 \) was used for computation.
Figure 4. Weight Arrangement for Area Measurement.

Figure 5. Weight Arrangement for Moment Measurement.
However, it is not possible to produce sintered zinc oxide layers because the high temperatures used would produce nonstoichiometric zinc oxide with decreased resistivities that destroy their utility.

ZINC OXIDE-BINDER LAYER PREPARATION. A zinc oxide-binder resin slurry is made with the aid of a high-speed blender (1 liter capacity, 10,000 rpm). The materials used are as follows:

2. 60 percent Silicone Resin in Xylene: SR-82: General Electric Co.
8. NESA Glass, 0.3 by 10 by 15 centimeters, 80 ohms/square: Pittsburg Plate Glass Industries Inc.

The slurry is prepared by weighing out 200.0 grams of the zinc oxide into the blender’s removable container. To this is added a solution of 50.0 grams of the silicone resin (SR-82) dissolved in 120.0 grams of additional xylene. After stirring the mixture with a spatula it is blended in the high-speed blender for 5 minutes. The dye sensitizers, dissolved in methanol (i.e. 26.4 mg fluorescein, 8.2 mg rose bengal, 15.2 mg bromophenol blue dissolved in 22 ml methanol) are then stirred into the slurry, after which the mixture is blended for an additional one-half minute. The slurry is transferred to a 250-milliliter aspirator bottle equipped with tubulature, a red rubber condenser hose, and a hose clamp. After cooling for 1 hour, the coating slurry is flowed on NESA glass with the aid of the aspirator bottle. To do this, a suitable piece of plywood is arranged so that the front surface of the board makes a 15° angle with the vertical. The NESA glass rests against the board, and the zinc oxide binder slurry is applied through the hose across the top of the plate, making certain that the slurry flows completely down the substrate. After 1 minute, the layer is placed in a horizontal position and allowed to dry overnight in the dark. The layers are stored in the dark.

SINTER CADMIUM SULFIDE LAYER PREPARATION. A cadmium sulfide, cadmium chloride slurry is made with the aid of a hotplate heated to 100 to 125° C. The materials used are as follows:

4. NESA Glass: 0.3 by 5 by 6.25 centimeters: 200 ohms/square: Pittsburg Plate Glass Industries Inc.
The slurry is prepared by weighing out 11.0 grams of cadmium sulfide and 1.10 grams of dehydrated cadmium chloride (CdCl₂·2½H₂O, the Analar Grade, that was heated at 194°C overnight) in a 100-milliliter beaker. The thoroughly mixed compounds are then stirred into a second 100-milliliter beaker containing 11.0 grams glycerin. The mixture is stirred for 30 minutes while being warmed on a hotplate at 120°C. Approximately 30 milliliters of a somewhat flowing, bright yellow slurry is obtained, a sufficient quantity to coat two 5- by 6-centimeter NESA Glass plates. Paper tape (0.635 centimeter wide) is used to prepare a mold on the clean plates (the NESA plates are boiled in a Sparkleen solution for about 30 minutes, rinsed in distilled water, and air dried) by applying two to four layers of the adhesive paper tape along the outer edges. The NESA plates are then warmed on the hotplate for 15 minutes, and the hot slurry is poured into the mold on both plates. The plates are removed from the hotplate and placed on top of aluminum foil on a side bench. A microscope glass slide is used to draw down the slurry level with the top of the paper tape. The excess slurry is collected on top of the foil. The coated NESA glass is returned to the hotplate at 120°C for 2 hours. During this time, the cadmium sulfide, cadmium chloride mixture settles and releases entrapped air bubbles, producing a more nearly homogeneous layer. The temperature of the hotplate is increased to 200 to 250°C until the glycerin is evaporated, in about 30 minutes. The paper tape mold is removed, and the bright yellow layers on the NESA glass are installed on top of steel plates in a gas-tight retort in a Lindberg furnace, which has been preheated to 250°C. The laboratory arrangements for the sintering step are shown in figure 6. After 15 minutes, the ultrahigh purity nitrogen is turned on at a flow rate of 1.15 liters per minute as determined on the bubble-meter installed in the fume hood. This was found to correspond to 10 units on the Lab-Crest (Fisher Scientific Co.) flowmeter that is used to monitor continuously the nitrogen flow rate. The effluent from the gas-tight retort is scrubbed in the gas-washing bottle to remove any toxic cadmium compounds (e.g. cadmium chloride) evaporated in the sintering step. The water trap would prevent any back pressure from forcing the water from the gas-washing bottle toward the furnace. After 45 minutes the furnace temperature is increased to 675°C for the sintering step. After a second 45-minute period, the furnace is turned off, but the nitrogen flow is continued for an additional 5 hours at a reduced flow rate (5 units on the flowmeter, 0.50 liter per minute on the bubble-meter). When the temperature in the furnace drops to 240°C, the sintered cadmium sulfide layers on NESA glass are removed and placed in a dessicator to cool to room temperature. The sintered layers are treated with brush applications of a 5 percent (by dry weight) solution of silicone resin in xylene. Thus, 5 grams of a 60 percent solution of silicone resin in xylene is diluted to 60 grams total weight with xylene. The materials used are as follows:

1. 60 percent Silicone Resin in Xylene: SR-82: General Electric Co.
3. Silicone Grease: Silicone Lubricant: Dow Corning
The 5-percent solution of silicone resin is applied to the cadmium sulfide layer four times, with drying between applications. Then, silicone grease is applied and rubbed down with Kimwipes tissues after warming the plates in an oven at 80°C for 10 minutes. The back of the NESA glass is washed first with 6N-sulfuric acid to remove a brown stain and then, with a Sparkleen solution. Both sides of the sintered cadmium sulfide NESA glass plates are rinsed with warm tap water and dried. The completed layers are finished off with plastic electrical tape over the exposed NESA glass surface and sides of the glass plate.

OBSERVATIONS AND DISCUSSION. The zinc oxide-binder resin layers on NESA glass produced a working photoconductive medium that has a good spectral response below 400 nanometers and between 450 and 650 nanometers. No real problems were encountered in their preparation. Still, the zinc oxide-binder photoconductive layers were found to not exhibit the photosensitivity of certain sintered layers of copper, chlorine-doped, cadmium sulfide photoconductive layers prepared by Hodes. It was the low response rise time of the doped cadmium sulfide layers that suggested preparing undoped to moderately doped sintered cadmium sulfide layers. The sintered cadmium sulfide layer preparation described above is a modified procedure to that described by Hodes, primarily from the point of view of the materials employed. Problems did arise that were not resolved, and thus undoped sintered cadmium sulfide layers that were photoconductive could not be prepared. The details will be described next.

The cadmium sulfide selected was 99.999 percent (5-9's) pure, the grade believed needed to produce the improved response rise time being sought. The cadmium sulfide used in the layers prepared by Hodes was 99.97 percent (3-9's) pure, based on doping at 300 ppm with cupric chloride. The 5-9's pure cadmium sulfide required a minimum of twice the weight of glycerin to produce a free-flowing slurry described by Hodes. One may conclude that the 5-9's pure cadmium sulfide has a range of smaller particle size in addition to being undoped. The sintering step itself produced NESA glass that was no longer conducting. In addition, the sintering step also produced a yellowish-green cadmium sulfide layer, which previously had been a bright yellow layer, with regions of gray-green color near the outer perimeter of the layer. Superficial scraping of the surface exposed a bright yellow color in the interior of the cadmium sulfide layer. The reason for the disappearance of the doped tin oxide layer that constitutes the conducting layer of the NESA glass is not clear. Efforts to determine those factors that lead to the loss of the tin oxide layer disclosed that NESA glass exposed to cadmium chloride in the furnace produced a loss of conductivity beneath that compound, and glass exposed to both cadmium chloride and cadmium sulfide produced a total loss of the conducting tin oxide layer. No further insight was obtained as to the processes leading to the loss of the tin oxide layer nor was there in-
sight as to the nature of the superficial yellowish-green color and darker gray-green color seen on the surface of the sintered cadmium sulfide. The results obtained are strikingly different to those obtained by Hodes with doped cadmium sulfide.

EXPERIMENTAL ARRAY FABRICATION AND TEST RESULTS

LINEAR ARRAY. A 10-wire electrode linear array assembly was fabricated in-house. This assembly was brought in contact with a small NESA glass chip coated with zinc oxide (ZnO) or cadmium sulfide (CdS) to constitute a linear chemical array as shown in figure 7. The ZnO layers were prepared in-house. The CdS layers used were prepared by Hodes. The array was tested for signal-to-noise ratio, uniformity of response, response versus bias voltage, response rise time, and cross-coupling between electrodes with both ZnO and CdS sensing layers. Fairly successful test results were obtained. It was further concluded that the sintered CdS layer produced an array with increased photosensitivity compared to the ZnO layer. Further insight into the relationship of elemental impurity concentrations in CdS-layer-response rise time, photosensitivity, and frequency response was found to be necessary. This linear array may be used for the position detection system described earlier.

SPECIAL CONFIGURATION AREA ARRAYS. Attempts were made to fabricate two-dimensional arrays with relatively large electrodes for beam-centering (or pointing) purposes and for a diffraction pattern detector used in optical data processing.Unsuccessful results were obtained on the uniformity of response, which was traced to poor contact between the CdS layer and electrodes. To obtain better contact between the layer and electrodes, the CdS layer on NESA glass was placed in a vacuum frame with the electrode pattern etched on a flexible copper-clad Mylar film. The electrodes and the CdS layer on NESA glass were then forced to contact each other in the vacuum frame, which operated with reduced pressure. Although there was improvement, a nonuniform response was still obtained from each electrode and even within an electrode. This demonstrated that continuous and uniform contact between the electrodes and the photoconductive layer was not achieved. Determination of the center of the beam was not possible. The experimental setup and the electronic portion of the beam centering system are shown in figures 8 and 9, respectively. At this point, to fabricate a workable area chemical array a more sophisticated method such as sputtering and vacuum deposition may be necessary. The cost to acquire the new technique, talent, and equipment was beyond the scope of this effort.

Figure 7: Ten-Wire Electrode Chemical Array.

Diagram showing components such as spring, screw, connector, wire, terminal board, layer, clamp, holder, and NESA glass.
Figure 9. Electronic portion of beam centering system.

Note: D11, D12, D13, ARE MC1428G DIFFERENTIAL AMPLIFIERS.

ARRAY ELECTRODES
CONCLUSIONS

On the basis of this study the following conclusions were reached:

1. Continuous photoconductive layers can be fabricated.

2. Both zinc oxide and cadmium sulfide layers can be used to fabricate arrays.

3. Successful results were obtained with a linear array.

4. The fabrication of two-dimensional arrays requires more sophisticated fabrication methods, such as sputtering or vacuum deposition.

5. Measurement errors for position and area measurements are negligible.

6. Larger measurement errors were observed for center of mass measurement.
Chen, Pi-Fuay


20 p.; 25½ cm. (U.S. Army Engineer Topographic Labs.; ETL 0130)

Prepared for Office, Chief of Engineers, U.S. Army.

1. Photoconductive layers
I. Gladden, James W. II. Title
III. (Series)