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THERMOCHROMIC DISPLAY MATERIALS FOR USE UNDER WIDE VARIATIONS IN AMBIENT ILLUMINATION LEVELS

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SINGER
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THERMOCHROMIC DISPLAY MATERIALS FOR USE UNDER WIDE VARIATIONS IN AMBIENT ILLUMINATION LEVELS

Contract NAS 12-89

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ABSTRACT

This report documents the results of a three-year program to synthesize inorganic thermo-chromic materials and to utilize them in display devices insensitive to the effects of high ambient illumination levels. The research was conducted at Singer-General Precision, Inc. and sponsored in part by the NASA Electronics Research Center under Contract NAS 12-89. For completeness, this report summarizes the results of the first two years of effort, and also provides   details as to the accomplishments of the third year. Similar details for the earlier efforts may be found in NASA-CR-80016 and NASA-CR-86031.

Four general categories of materials have been synthesized, all of which can provide rapid and reversible color changes as a result of either an order-disorder reaction or a change of lattice spacing: (1) the ternary halides, having the general formula $M_2M'H_4$, where M is copper, silver or gold, M' is mercury, cadmium or zinc and H is a halide; partial sub-stitutions within this class of materials have also been studied extensively as a means for changing the transition temperature, (2) the ternary chalcogenides, having the general formula $M_2M'X_4$ where M is indium, gallium, or aluminum , M' is mercury, cadmium, or zinc and X is sulfur, selenium or tellurium; partial substitution within these compounds is also possible, (3) the $Al_2O_3-Cr_2O_3$ system, and (4) the PbI_2-AgI system .

Applications which have been studied have included: (1) the use of localized electrical heating to provide a numeric indicator, (2) the use of thermochromics in a cathode ray tube, wherein "writing" is accomplished by the thermal energy in an electron beam (3) laser "writing" on thermochromics, (4) the use of combinations of thermochromics with electro-luminescent phosphors to produce a display readable under all conditions of ambient illumination, and (5) the use of thermochromic materials as a computer input device; this ap-plication is based upon the differential electrical conductivity of the high and low tempera-ture forms of the material.

Additionally, this research has made possible the development of a display of the output of a fluidic system; research in this area has been conducted by the Martin-Marietta Corporation under Contract NAS 12-532 and reported as NASA-CR-86105.

The most promising materials developed by Singer-General Precision, Inc. is the PbI_2-AgI system. All fired compositions were found to be thermochromic with a sharp reversible color change from yellow to orange at about $130°C$ (DTA). Weight loss studies showed no loss in weight under a vacuum of 10^{-7} Torr at room temperature for 80 days. In addition, these compositions were stable at least to $375°C$ (comparable to CRT bakeouts). However, the system proved to have complicated phase diagram relationships.

Several sealed cathode ray tubes have been fabricated with faceplates containing a coating of $PbI_2 \cdot 2AgI$ thermochromic followed by a coating of P-14 phosphor. Some tubes also contained an aluminum coating over the phosphor for enhancement of the color change. These tubes were designed to produce phosphor fluorescence when the electron beam strikes the phosphor. Fluorescence and phosphorescence should be seen through the thermochromic. In addition, at higher beam energies, the energy of the beam absorbed by the phosphor should generate enough heat to induce a thermochromic transition in the $PbI_2 \cdot 2AgI$.

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ADMINISTRATIVE INFORMATION

1.   INTRODUCTION

This is the Final Report under Contract NAS 12-89 which summarizes the three year investigation of thermochromic materials for display applications. Details of earlier work (through November 1967) can be found in technical summary reports covering work performed in the first (NASA CR-80016) and second (NASA CR-86031) year of the contract. Results from this earlier work are briefly summarized in Section 2 of this report; details may be found in the indicated references. A comprehensive account of work performed during this past year is given in Sections 3 and 4.

This study has been directed towards the design and evaluation of displays suitable for use under wide variations in ambient illumination levels. These displays should be useful in aircraft, space vehicles, and other situations in which high ambient illumination conditions occur, due either to sunlight or artificial light. Most conventional displays become visible by emission of light (luminescence) rather than by reflection of ambient illumination. For this reason these devices tend to saturate at emission brightness levels that are too low to be seen clearly in conditions of high ambient background light. An additional drawback of some displays is that they contain moving parts and hence have the potential for mechanical failure.

The objective of this program was to evaluate the device potential of materials that undergo changes in reflectivity or color as a function of temperature (thermochromic). Changes should be more easily seen under conditions of high ambient illumination. Combinations of such materials with systems of the light-emissive type might also lead to displays readable at all ambient illumination levels with approximately constant contrast. Possible embodiments of thermochromic materials included cathode ray tubes (CRT), alpha-numeric displays, and computer input devices.

The color change in thermochromic materials can be of varying sorts, depending upon the particular underlying mechanism responsible. Slow transitions will take place, for

example, when the mechanism involves the breaking and reformation of chemical bonds. On the other hand, rapid color transitions may be observed in materials where the underlying mechanism is an order–disorder solid–state phase transition. The change in color in these materials is the result of a small movement and rearrangement of certain small cations in an otherwise rigid lattice of closely packed anions.

This program was divided roughly into two parts, one involving the search for thermochromic materials suitable for certain display applications; the other the investigation of the application of these materials in various display devices. After a review of the early results, each part is presented separately.

2. SUMMARY OF EARLY RESULTS

2.1 MATERIALS

Prior to the start of this program a number of thermochromic iodides were known and had been described which had the general formula $M_2M'I_4$ where M was either Ag^{+1}, Cu^{+1}, or Tl^{+1} and M' was either Hg^{+2} or Cd^{+2} [1]. The two best examples were silver mercuric iodide and copper mercuric iodide. These materials exhibit vivid color transitions at convenient temperatures, i.e. yellow to orange at $50.5^{\circ}C$ for Ag_2HgI_4 and red to black at $69.5^{\circ}C$ for Cu_2HgI_4, as well as sharp increases in electrical conductivities upon changing forms. The mechanism for their thermochromic change is via an order–disorder transition. However, in this program it was found that both materials are unstable under heat and high vacuum environments, and emit vapors of HgI_2 under these conditions. This made them unusable for CRT applications where high heat and vacuum stabilities are absolute requirements.

In an attempt to obtain a wider selection of thermochromics with a wider range of transition colors and temperatures, stabilities, and relevant thermodynamic properties, it was decided to then synthesize a wider range of ternary iodides, chalcogenides and partially substituted derivatives thereof. Compositions of interest included $Ag_2Hg_{1-x}Cd_xI_4$ (X=O – 0.40), $Ag_2HgI_{4-x}Br_x$ (X=0.17 – 1.40) and $AgI \cdot PbI_2$ mixes. Substitutions included Au for Ag and Cu; Sn, Pb, Zn, and Cd for Hg; and Cl and Br for I.

2.1.1 SUBSTITUTED TERNARY IODIDES

An analysis of the mechanism for thermochromism in silver and copper mercuric iodide – the disordering of the cations in an unchanged iodide anion lattice, gave rise to the idea that substitution of small amounts of another element in the lattice could cause sufficient change in the crystal field to bring about a change in color. In addition, it was thought that depending upon the size and type of the ion being substituted a change in the transition temperature might be observed.

Some of the substitution compounds prepared in which cadmium was substituted for mercury and bromine and chlorine were substituted for iodine are shown in Tables 1 and 2, taken from references 2 and 3, respectively.

TABLE 1

Transition Temperature of $Ag_2Hg_{1-x}Cd_xI_4$ As A Function of X

X	Transition Temperature Range (^oC)
0	$47^o - 51^o$
0.05	$48^o - 55^o$
0.10	$48^o - 58^o$
0.15	$52^o - 63^o$
0.20	$51^o - 65^o$
0.25	$56^o - 67^o$
0.30	$62^o - 77^o$
0.35	$64^o - 82^o$
0.40	$68^o - 88^o$

TABLE 2

Transition Temperatures of Bromine-Substituted and Chlorine-Substituted Ternary Iodides

Thermochromic	T_{trans} ^oC
Ag_2HgI_4	50.5
$Ag_2HgI_{15/4}Br_{1/4}$	43 ± 1
$Ag_2HgI_{15/4}Cl_{1/4}$	43 ± 1
Cu_2HgI_4	69.5
$Cu_2HgI_{15/4}Br_{1/4}$	50 ± 1
$Cu_2HgI_{15/4}Cl_{1/4}$	50 ± 1

It was evident that by partial substitution, one can successfully shift transition temperatures without significantly affecting transition colors. Cadmium substitution in silver mercuric iodide raised the transition temperature; bromine and chlorine lowered it.

Stability tests of Ag_2HgI_4 and Cu_2HgI_4 [4] have shown that both are unstable with respect to vacuum and heat by evolving HgI_2. Thus, it was reasoned that by substituting a different element completely for Hg, stability might be induced in the thermochromic. We substituted Pb for Hg and conducted stability tests. The results were encouraging in that lead-substituted compounds showed no sign of decomposition over a period of 80 days at 10^{-6} Torr (Figure 1).

2.1.2   TERNARY CHALCOGENIDES

The selection of chalcogenides as candidates for investigation is based on the similarity between their crystal structure and that of the ternary mercuric iodides. [5] It seemed very likely that some of these ternary chalcogenides would exhibit an order-disorder reaction involving the mobility of the cations at some particular transition temperature and that such a reaction would be accompanied by a change in color of the compound. In addition, chalcogenides are usually more thermally stable than the corresponding iodides.

The general formula for chalcogenides can be given as MM'_2X_4 where here M=Zn, Cd, or Hg; M'=Ga, In, Al and X=S, Se or Te as seen in Table 3. Most of the possible 27 combinations of these nine elements have been successfully synthesized, as well as some where selenium was partially substituted for sulfur. In addition, the compound $CaIn_2S_4$ was prepared.

The only composition noteworthy of mention is $CdIn_2S_4$. It was found to be very stable at $100^\circ C$ and tends to change color from dull-orange to orange-red at $95-100^\circ C$ [6]. The shift in the reflection spectrum was about $500\overset{\circ}{A}$. The color change, however, was too gradual and the visual contrast too weak for this material to be of practical use.

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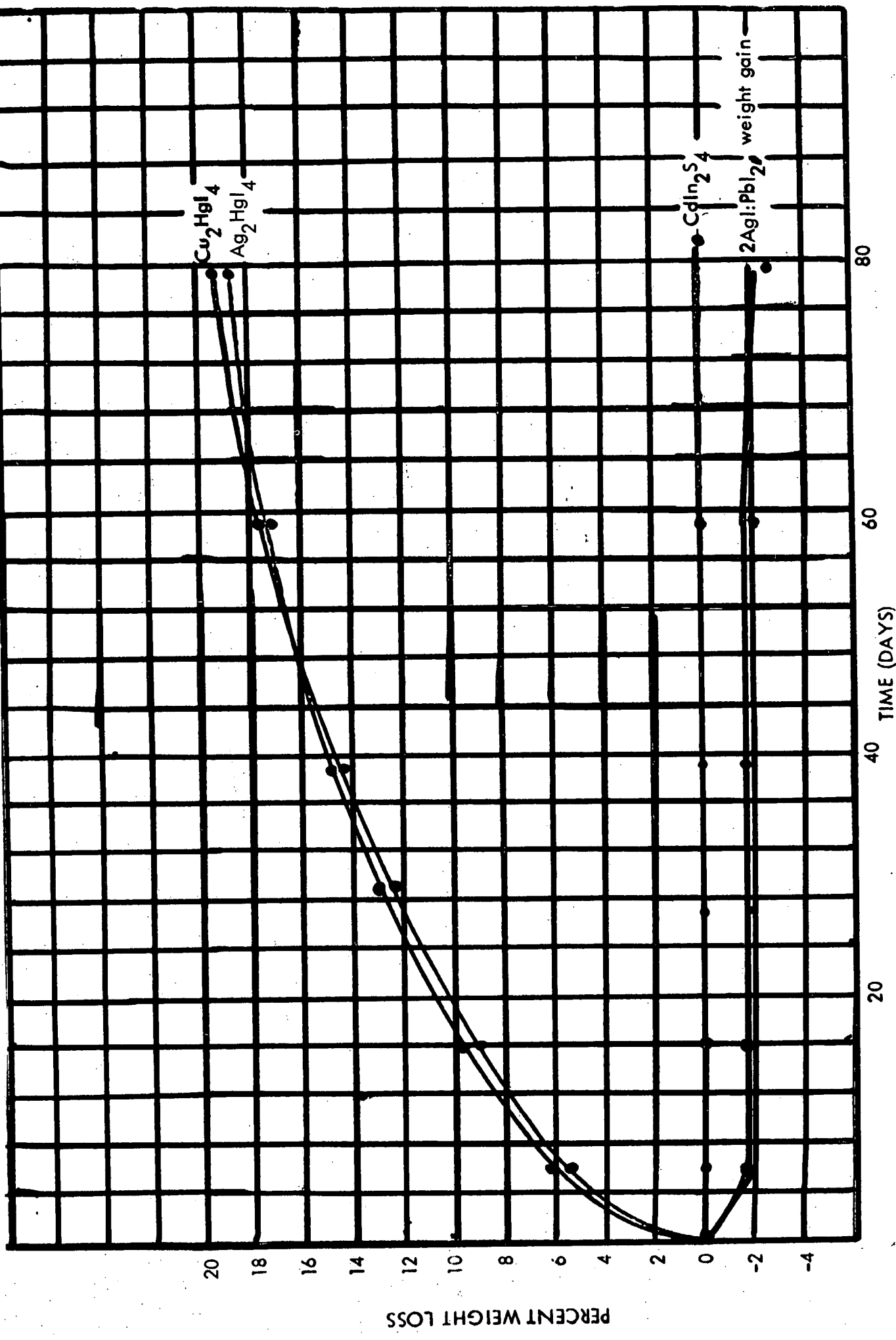
WEIGHT LOSS OF THERMOCHROMICS AT ROOM TEMPERATURE AND 10^{-7} TORR (CONTINUOUSLY PUMPED)

FIGURE 1

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TABLE 3

DESCRIPTION OF TERNARY CHALCOGENIDES

Compound	Color	X-ray	Reflectivity Shift($\overset{\circ}{A}$)
$ZnGa_2S_4$	pale green	Tetragonal	100
$ZnGa_2Se_4$	olive green	Tetragonal	100
$ZnGa_2Te_4$	black	Cubic	None
$CdGa_2S_4$	tan	Tetragonal	40
$CdGa_2Se_4$	rust brown	Tetragonal	80
$CdGa_2Te_4$	black	Tetragonal	250
$HgGa_2S_4$	yellow	Tetragonal	n.d.
$HgGa_2Se_4$	purple black	tetragonal	200
$HgGa_2Te_4$	black	Cubic	150
$ZnIn_2S_4$	yellow	unknown structure	120
$ZnIn_2Se_4$	black	Tetragonal	n.d.
$ZnIn_2Te_4$	black [a]	--------	----
$CdIn_2S_4$	dullish orange	Cubic Spinel	500
$CdIn_2Se_4$	black	Cubic	n.d.
$CdIn_2Te_4$	black	Tetragonal	n.d.
$HgIn_2S_4$	black	Cubic Spinel	n.d.
$HgIn_2Se_4$	black	Tetragonal	n.d.
$HgIn_2Te_4$	black	Tetragonal	n.d.
$ZnAl_2S_4$	light grey	Spinel	None
$ZnAl_2Se_4$	purple black [a]	--------	----
$ZnAl_2Te_4$	brown	Tetragonal	None
$CdAl_2S_4$	brown	Tetragonal	n.d.
$CdAl_2Se_4$	black [a]	--------	----
$CdAl_2Te_4$	black	Cubic	n.d.
$HgAl_2S_4$	black	Tetragonal	n.d.
$HgAl_2Se_4$	black [a]	--------	----
$HgAl_2Te_4$	black [a]	--------	----
$ZnGa_2S_3Se$	yellow-green	Tetragonal	75

n.d. = not determined

(a) = color obtained from literature

--- Attempts to prepare these compounds were unsuccessful

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2.2 CRT EXPERIMENTS

It was calculated that it was possible to achieve a thermochromic change in materials such as Ag_2HgI_4 with the power available from the electron beam of a cathode ray tube. Therefore a magnetic focus, magnetic deflection, automatic scan, demountable cathode ray tube apparatus was assembled. The apparatus was connected to a large capacity vacuum reservoir and the system was continuously evacuated to remove out-gassing products and to maintain cathode operations. Using this apparatus, a proof of principle, demonstrating the heating effect of the electron beam to induce thermochromic changes in various materials, was obtained.

Reversible thermochromic changes were induced in Ag_2HgI_4 utilizing various substrate materials to intercept the electron beam. Among the substrates examined were 0.003-0.005" thick conducting glass and nickel foils. A sandwich configuration consisting of magnesium oxide, Ag_2HgI_4, and thin conducting glass in which the electron beam was allowed to strike the magnesium oxide layer showed some promise. However, it was difficult to induce reversible thermochromic transitions if Ag_2HgI_4 was exposed directly to the electron beam. It tended to decompose. It was concluded that in order to use Ag_2HgI_4, it would be necessary to find an encapsulation method to stabilize this thermochromic.

2.3 NUMERIC DISPLAY DEVICE

For the purpose of demonstrating the practical applications potential of thermochromic materials, a numeric display device was built. The thermochromic was encapsulated in a transparent plastic matrix behind a glass panel. Nine segments of nichrone wire connected to a power supply were embedded in back of the thermochromic material. By selective heating of the wires, and in turn the adjacent thermochromic, it was possible to display all of the ten numerals independently. Numeric display devices of this kind were successfully constructed with the incorporation of silver and copper mercuric iodide. A photograph of the prototype display unit is shown in Figure 2. A detailed account of this device is given in the First Annual Report[7].

FIGURE 2

3. RECENT PROGRESS

Efforts during the past year were concentrated on preparing thermochromic materials suitable for the cathode ray tube application. In particular, it was important that the thermochromic materials possess sharp color transitions and have the transition temperatures and corresponding thermodynamic properties at a convenient range of energies in order to utilize conventional CRT beam energies. Inherent in the fabrication of a CRT is the bakeout procedure which always takes place at elevated temperatures and high vacuum. The thermochromic material must be stable under such fabrication conditions and also under the subsequent long term exposure to high vacuum. Success was obtained in this area with the further development of the lead iodide – silver iodide system. Late in this program, this material was successfully incorporated and operated in a sealed CRT.

A second application of thermochromic materials that was briefly considered was in a computer input tablet. For this application, in addition to the properties mentioned in the previous paragraph, the thermochromic transition in the material has to be accompanied by a discontinuous change in electrical conductivity.

3.1 MATERIALS

Up to this year, silver mercuric iodide was still the most suitable thermochromic for the applications under consideration. It reversibly changes sharply from yellow to orange at precisely $50.5^{\circ}C$. In addition, the color change is accompanied by a sharp increase in the electrical conductivity.[1] The principle drawback of Ag_2HgI_4, however, was its demonstrated instability toward the evolution of HgI_2 under heat and high vacuum. One obvious approach to using Ag_2HgI_4 was encapsulation in a vapor impervious container which would inhibit decomposition and evolution of HgI_2. Thus, as is detailed in Section 3.2.2, studies were conducted on employing this thermochromic in various protective media.

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Parallel to encapsulation experiments, the research effort during the past year has been directed toward finding a thermochromic material that could successfully be used in an unprotected form in a CRT. Two approaches were taken in the search for suitable materials. One involved the continued study of substitution compounds, where various elements were substituted into previously prepared thermochromics. The other approach involved a search for new thermochromics, completely unrelated to the ones prepared thus far. The best thermochromics to evolve from the search are the fired $PbI_2 \cdot AgI$ compositions. These will be discussed independently.

3.1.1 SUBSTITUTION COMPOUNDS

Numerous substitution compounds were prepared. Substituted iodides were synthesized by firing at 400-500°C for 1-2 days; substituted chalcogenides were fired in evacuated quartz tubes at 900°C for two days. Substitutions included Au for Ag; Zn, Cd, and Pb for Hg: and Br for I in the ternary iodides. Se was also substituted for S in $HgGa_2S_4$. In all, 34 substitution compounds have been synthesized in this series. Some of the general observations with regard to these compounds include:

- Thermochromism in the cation substituted ternary halides was generally weak with only slight color changes.

- Cadmium and zinc-containing compounds were often found to be light-sensitive. Discoloration took place on exposure to ambient light levels.

- Except for $AuCuCdI_4$ which was stable up to 350°C, gold-containing compounds all demonstrated instability upon heating.

- None of the substituted chalcogenides showed thermochromic properties.

- None of the compounds were superior to Ag_2HgI_4 in their

thermochromic properties or with respect to the practical
properties under consideration, and therefore were not
investigated in greater detail.

A summary of all the substitution compounds prepared during the past year, and their
important properties are shown in Table 4.

3.1.2 $PbI_2 \cdot AgI$ THERMOCHROMIC COMPOSITIONS

This system had first been investigated earlier in the program[8]. A range of compositions
had been synthesized which had demonstrated high vacuum stability as well as fairly con-
venient transition temperatures (100 - 140°C) from yellow to orange, depending on composi-
tion. However, discoloration had been found to take place under vacuum and this caused
a low priority to be assigned to this system. It was decided to reinvestigate this system
and attempt to eliminate the undesirable discoloration process.

Mixtures ranging from 5 to 33 mole percent PbI_2 in AgI were prepared. Firing schedules
for the $AgI \cdot PbI_2$ compositions ranged from 15 hours to 4 days over temperatures of
400 - 600°C. Firings were conducted in evacuated (10^{-1} Torr) pyrex ampoules in an open-
ended Sensitronic tube furnace. Cooling of these samples necessarily proceeded somewhat
rapidly. Optimal firing conditions were generally found to be at 450°C for a two day
duration. The thermochromic properties of the products were tested both visually and
instrumentally. Differential thermal analysis (DTA), x-ray and chemical studies were
made of the $AgI \cdot PbI_2$ fired compositions in an attempt to determine their structural natures.
DTA methods were used also to study some of the system's thermodynamic properties.

Upon visual inspection, all of the lead iodide-silver iodide compositions were found to be
thermochromic at approximately 130°C, color changes being more pronounced with
increasing PbI_2 content. Based on visual data, the best composition of lead iodide with
silver iodide appeared to be $PbI_2 \cdot 2AgI$ (33 mole percent PbI_2).

TABLE 4

DESCRIPTION OF SUBSTITUTION
COMPOUNDS

Nominal Compositions *	Color Change	Temperature	Remarks
1. $ZnI_2 \cdot 2AgI$	Green-yellow → orange-yellow	150-180°C	Poor color contrast
2. $ZnI_2 \cdot 2CuI$	No change	--------	Light sensitive
3. $ZnI_2 \cdot AgI \cdot AgBr$	No change	--------	--------
4. $ZnI_2 \cdot CuI \cdot CuBr$	Grey → green	~150°C	Poor color contrast
5. $ZnI_2 \cdot AuI \cdot AgI$	Greenish-yellow → dark green	Continuous	Irreversible change, accompanied by evolution of iodine.
6. $ZnI_2 \cdot CuI \cdot AuI$	No change	--------	--------
7. $CdI_2 \cdot 2AgI$	Yellow → yellow-orange	~250°C	Poor color contrast. Light sensitive
8. $0.05AgBr \cdot 1.95AgI \cdot CdI_2$	Yellow → orange	Continuous	Poor color contrast. Light sensitive.
9. $0.10AgBr \cdot 1.90AgI \cdot CdI_2$	Yellow → orange	Continuous	Poor color contrast. Light sensitive.
10. $CdBr_2 \cdot 2AgBr$	Yellow → orange	Continuous	Poor color contrast.
11. $0.05AgI \cdot 1.95AgBr \cdot CdBr_2$	Yellow → orange	Continuous	Poor color contrast. Light sensitive.
12. $AgBr \cdot AgI \cdot CdI_2$	Pale yellow → yellow	~150°C	Poor color contrast.
13. $CdI_2 \cdot 2CuI$	Green-yellow → orange	180 - 220°C	Poor color contrast. Light sensitive.
14. $0.05CuBr \cdot 1.95CuI \cdot CdI_2$	Green-yellow → orange	181 - 210°C	Poor color contrast. Light sensitive.
15. $0.10CuI \cdot 1.90CuI \cdot CdI_2$	Green-yellow → orange	168 - 208°C	Poor color contrast. Light sensitive.
16. $CdBr_2 \cdot 2CuBr$	No change	--------	-------------------
17. $0.05CuI \cdot 1.95CuBr \cdot CdBr_2$	No change	--------	Light sensitive.

No.	Composition*	Color change	Temperature	Remarks
18.	$0.10CuI \cdot 1.90CuBr \cdot CdBr_2$	No change	----------	Light sensitive.
19.	$CdI_2 \cdot CuI \cdot CuBr$	Tan → green	~150°C	Color change irreversible.
20.	$AgI \cdot CdI_2$	Tan → yellow	60 - 90°C	Poor color contrast. Light sensitive.
21.	$AgI \cdot 2CdI_2$	Pale yellow → bright yellow	130 - 170°C	Poor color contrast. Light sensitive.
22.	$CuI \cdot CdI_2$	Yellow-green → orange	190 - 200°C	Poor color contrast. Light sensitive.
23.	$CuI \cdot 2CdI_2$	Yellow-green → orange	180 - 200°C	Poor color contrast. Light sensitive.
24.	$0.16AgBr \cdot 1.84AgI \cdot PbI_2$	Yellow → orange	~120°C	------------
25.	$PbBr_2 \cdot 2AgBr$	No change	------------	------------
26.	$PbI_2 \cdot 2AgBr$	Pale yellow → dark yellow	160 - 190°C	------------
27.	$PbI_2 \cdot CuI \cdot CuBr$	No change	------------	------------
28.	$PbI_2 \cdot 2AuI$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
29.	$AuI \cdot AgI \cdot PbI_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
30.	$1.5AuI \cdot PbI_2 \cdot 0.5AgI$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
31.	$CuI \cdot AuI \cdot PbI_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
32.	$AgI \cdot AuI \cdot CdI_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
33.	$AuI \cdot CuI \cdot CdI_2$	Grey → green	~140°C	Gradual transition. Poor color contrast.
34.	$AuI \cdot AgI \cdot PbBr_2$	No change	--------	Decomposes with the evolution of iodine. Light sensitive.

*Based on materials charged.

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All mixtures fired at 600°C could be viewed for thermochromism only after a slight deposit of iodine contained in them had been removed by vaporization. Initially, on first preparation all products tended to discolor under fluorescent lighting. However, the tendency to discoloration decreased after repeated thermal cycling through the thermochromic transition. After grinding of the fired compositions, each was tested for thermochromicity, both visually on a temperature-controlled hot plate, and instrumentally using DTA methods.

3.1.2.1 DTA ANALYSES

DTA methods are most useful with a phase transition. The transition appears as a symmetric exothermic or endothermic peak in the thermogram depending on the nature of the transition and the experimental conditions. In addition the method can yield valuable information on the purity of prepared compounds, and to what extent a reaction between the separate components has taken place. Thus, optimal preparation techniques can be determined. Also, DTA methods can supply valuable information on the heat stabilities of materials, which is an important factor in CRT applications.

It should be noted that a quirk or impurity in our apparatus reproducibly gives a small inflection in the DTA curve at about 151°C. This is unfortunate since it also corresponds to a transition in pure AgI. However, the appropriate correction is easy to make because of the vast difference in areas under a true transition and the inflection error.

Figures 3 and 4 show DTA thermograms of two initially fired $PbI_2 \cdot 2AgI$ compositions in the horizontal furnace. DTA thermograms of an unfired mechanical mixture of identical composition (Figure 5) and of the two components PbI_2 (Figure 6) and AgI (Figure 7) are also shown. In every figure the upper curve represents the transition observed during heating while the lower curve traces the corresponding reverse process during cooling. Differences in the temperature of transition are probably due to a supercooling phenomenon in the cooling cycle. The following conclusions may be drawn from the results obtained on these first specimens.
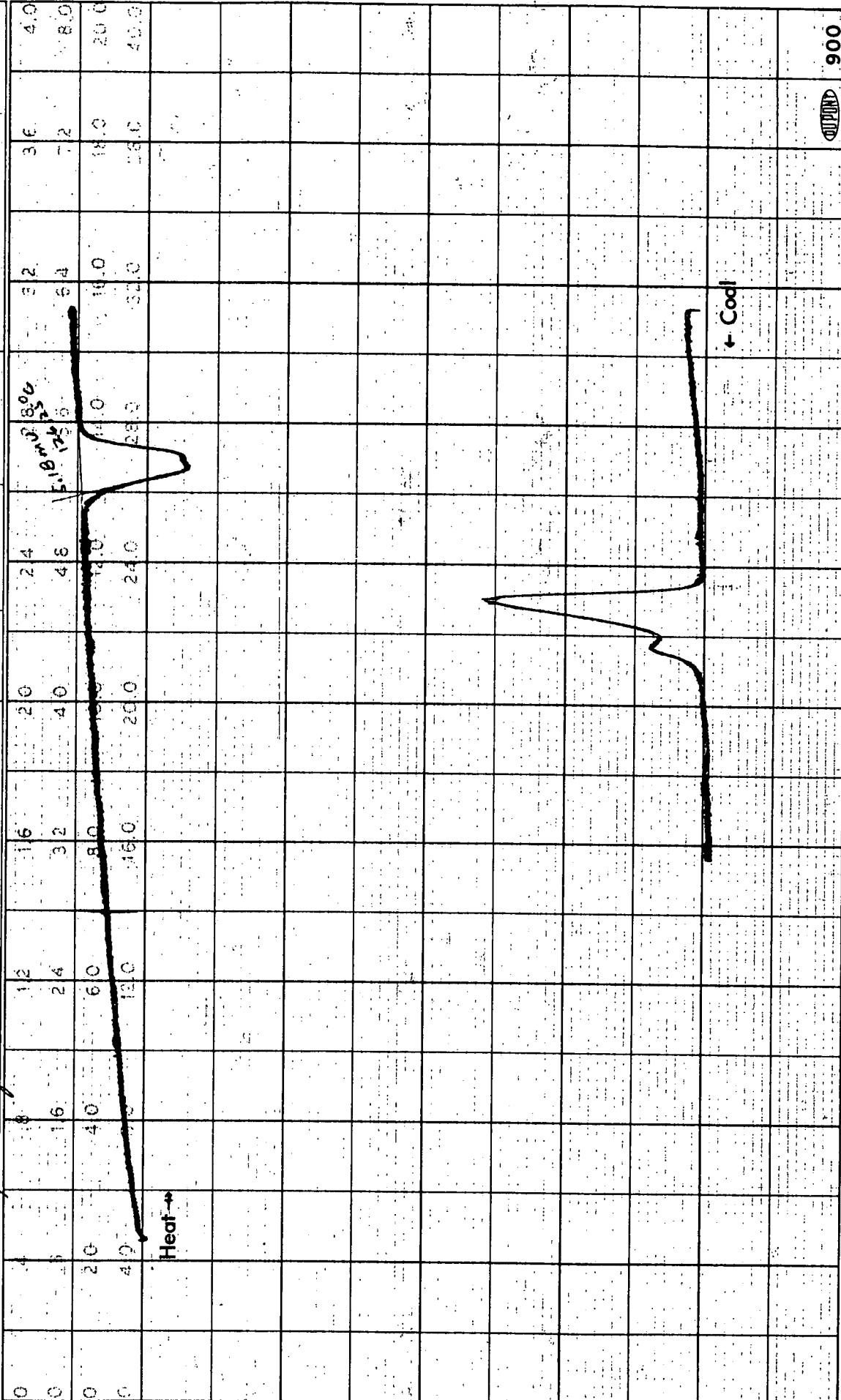
SAMPLE:_____ RUN NO.:_____

FIGURE 3

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SAMPLE: *Sample 14*

PbI$_2$:2AgI components fired at 450°C for 15 hours.

ORIGIN: *Flint and Monk*

SIZE: *5.633*

REF.

PROG. MODE: *Heat*

RATE: *2°* °C/MIN. START *25*°C.
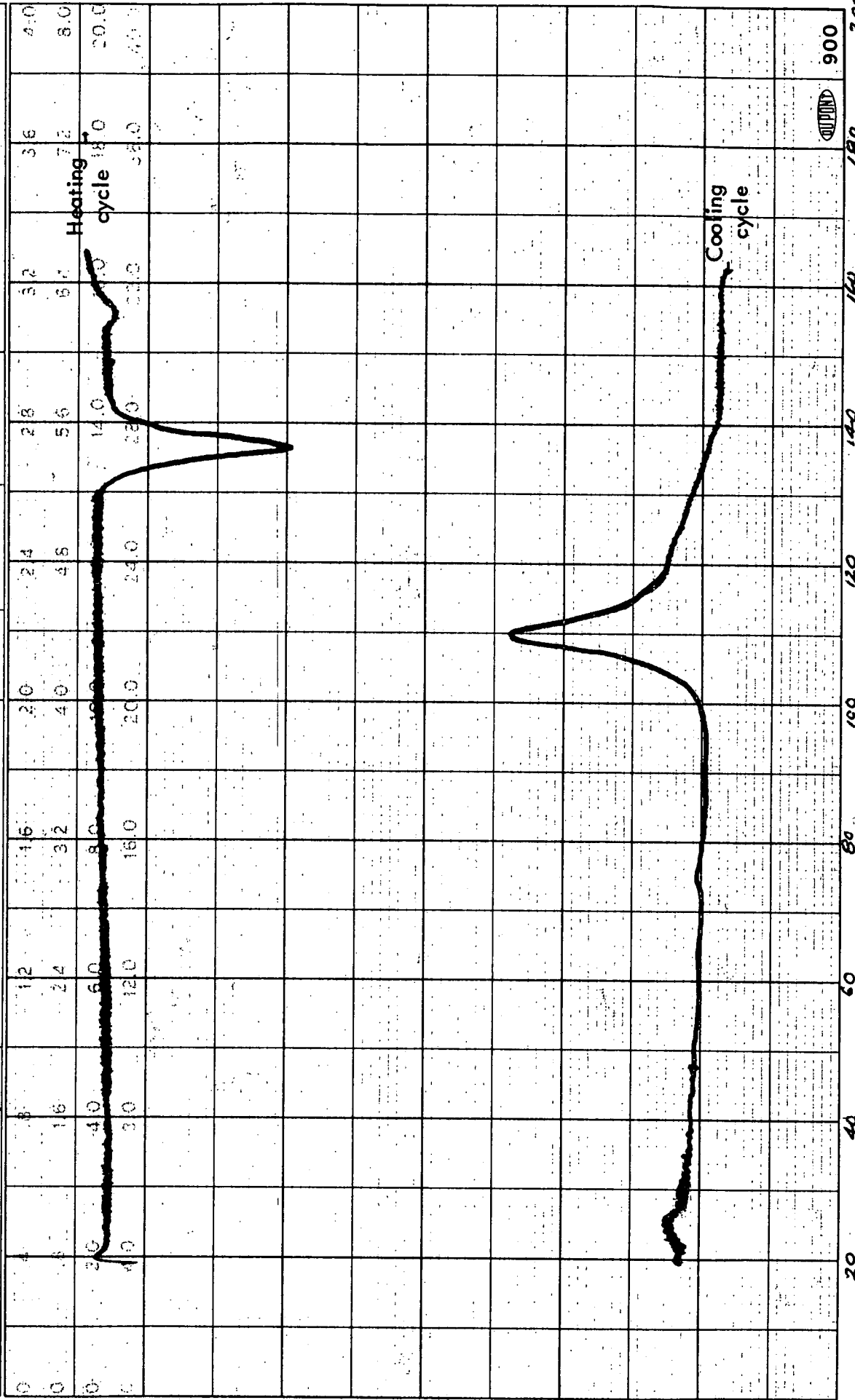
ATM. *N$_2$, 76°* MM RUN NO. *68-69*

DATE

OPERATOR

BASE LINE SLOPE

SCALE: *0.8* MV/IN.   T   △T   *0.002* MV/IN.

SHIFT: *0* IN. *as req'd* IN.

Heating cycle

Cooling cycle

EXO ← △T → ENDO

THERMOCOUPLE, REF. JUNCT. _____ °C) FIGURE 4

T (MILLIVOLTS):

(DUPONT)

200 °C   900   180   160   140   120   100   80   60   40   20

(17)

SAMPLE: *Same as sample #9*
Mechanically mixed PbI$_2$·2AgI

ORIGIN: *Fluxo Mengle*

SIZE— *6.219 mg*

REF. *Empty Pan*

PROG. MODE *Heat*

RATE ＿*2*＿ $\frac{°C}{MIN}$ START *23* °C.

ATM. *N$_2$, 760*

SCALE ＿＿＿＿＿＿

SHIFT ＿＿＿＿＿＿

RUN NO. *61266*

DATE ＿＿＿＿＿＿

OPERATOR ＿＿＿＿＿＿

BASE LINE SLOPE ＿＿＿＿＿＿

	T $\frac{mV}{IN}$	ΔT $\frac{mV}{IN}$
	IN.	IN.

Heating cycle

Cooling cycle

EXO ← ∇ T → ENDO

THERMOCOUPLE, REF. JUNCT ＿＿＿＿＿ °C) FIGURE 5

T (MILLIVOLTS:

DUPONT

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SAMPLE: _LEAD IODIDE_

ORIGIN: _NEWZEL_

				ATM.	_H₂_ , _760_	MM	RUN NO.	_68_
SIZE							DATE	_8/22/69_
REF.								
PROG. MODE _Heat_				SCALE	T	△T	OPERATOR	
RATE _2_ /_20°C_ _MIN_, START _23°C._					_0.8/2.0_ $\frac{MV}{IN}$	_0.04_ $\frac{MV}{IN}$	BASE LINE SLOPE	
				SHIFT	_0_ IN.	_61/84_ IN.		

heat →

←—Cool

| EXO | | | | | | | | | | ← ▽T → | | | | | | | | | ENDO |

0		4.0					8.0				12		16		20		24		26		28		30		32		35		4.0
0		8.0					40				24		32		40		48		56		64		72		8.0
0		20.0					10.0				5.0		8.0		10.0		12.0		14.0		16.0		18.0		20.0
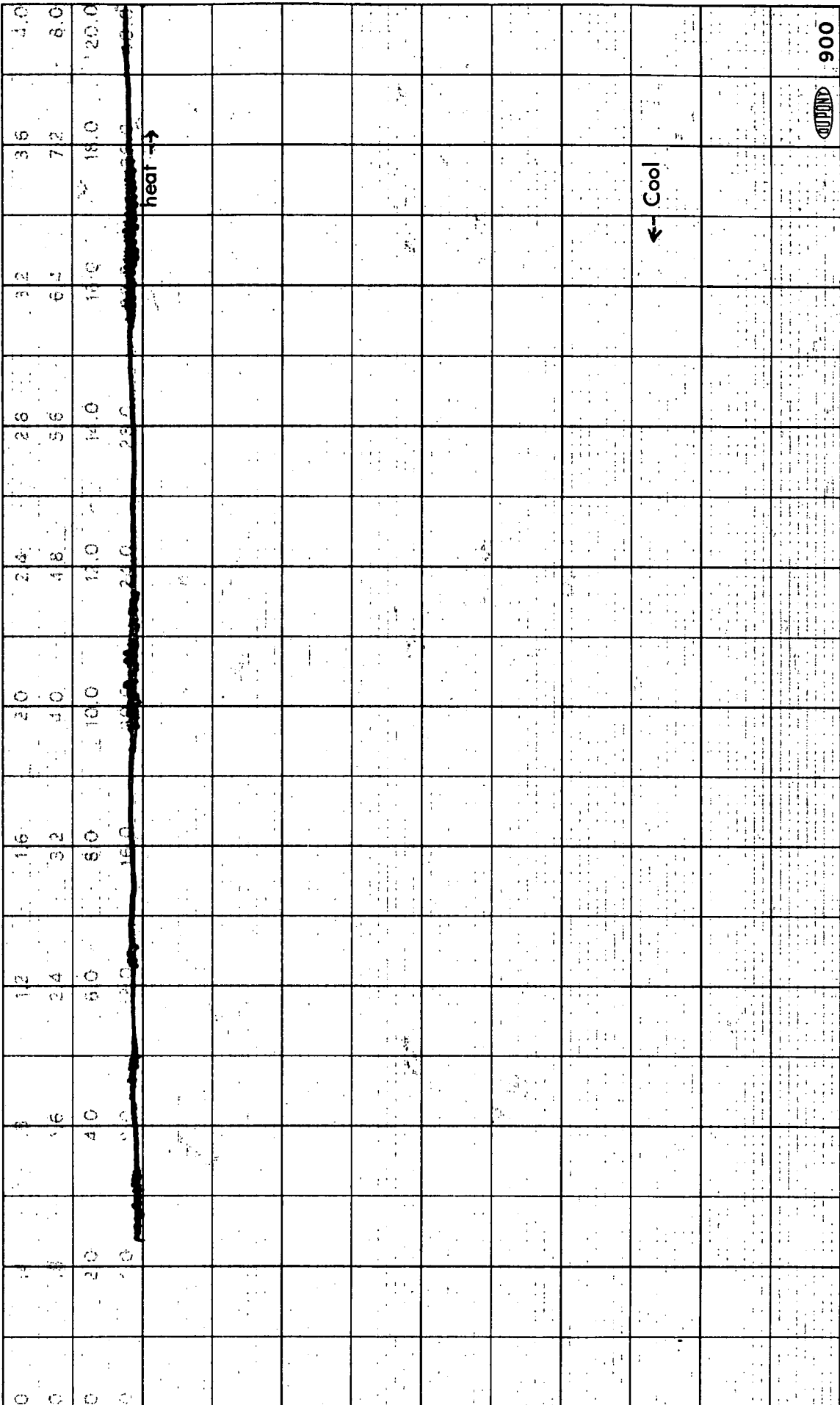
T (MILLIVOLTS);   THERMOCOUPLE, REF. JUNCT. _____ °C)

20   40   60   80   100   120   140   160   180   900   200°C

DUPONT

FIGURE (6)

19

FIGURE 7

FIGURE 8

SAMPLE: #9
PbI₂ : 2As₃ I
COMPONENTS FIRED AT 450°C
FOR 2 DAYS

ORIGIN: Y2 niczel

SIZE 16.8×8 mg
REF. .4T kin
PROGRAM MODE Heat
RATE 5 °C/MIN, START 23°C

ATM. N₂ 76₀

	T	ΔT
SCALE SETTING	50 °C/IN	0.1 °C/IN

RUN NO. 63
DATE 9/5/88
OPERATOR _____

T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

EXO ← ∇T → ENDO

Heating cycle →

poor hermetic seal

ΔT zero shift

21

SAMPLE: # 14

2 Ag I · Pb I₂
COMPONENTS FIRED AT 450L
FOR 15 HOURS

ORIGIN: FLINT/MENZEL

SIZE 15.898 mg

REF. MT Pan

PROGRAM MODE Heat

RATE 15 °C/MIN .START 25 °C

ATM. N₂ 760

	T	ΔT
SCALE SETTING	50 °C/IN	0.2 °C/IN

RUN NO. 68-78

DATE 8/30/68

OPERATOR D. Yee

Heating cycle →

EXO ← ∇T → ENDO

T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)   FIGURE 9

0   50   100   150   200   250   300   350   400   450   50

31

22
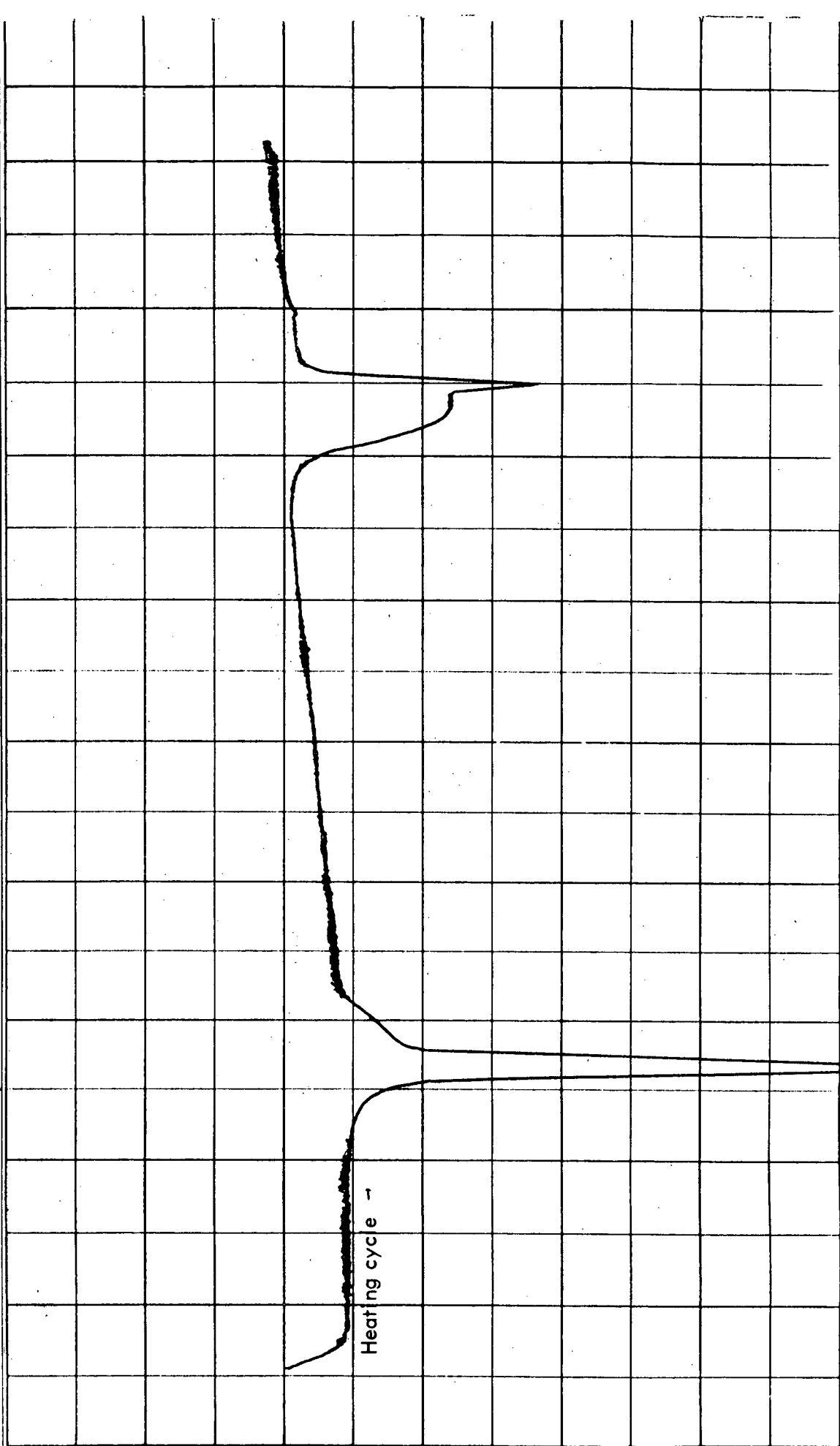
o   A relatively sharp phase change undoubtedly corresponding to a AgI
    type order-disorder transition is observable in the fired compounds
    beginning at 126°C (Figures 3 and 4). This corresponds to the transi-
    tion temperature observed visually.

o   The fired compositions are chemically different from the starting
    ingredients, since a thermogram (Figure 5) of the mechanical (unfired)
    mixture of ingredients did not show the thermochromic transition near
    126°C but did show an endothermic peak at 152°C corresponding to a
    phase transition obtained for AgI alone (Figure 7).

o   Figures 8 and 9 show subsequent heating of the fired $PbI_2 \cdot 2AgI$ com-
    position to over 400°C in order to check their stabilities at higher
    temperatures. The lack of any peaks up to 370°C (where melting
    occurs) indicates the high stability of the $PbI_2 \cdot 2AgI$ composition to
    that temperature, which is comparable to the bakeout temperature of
    the CRT. These results are very encouraging since they satisfy an
    important thermal requirement for successful thermochromic CRT
    displays.

A literature search for information in the $AgI \cdot PbI_2$ mixed composition was undertaken.
According to Weiss, et al [9], PbI_2 is miscible in AgI only to the extent of five mole per-
cent; at this composition they reported a phase transition to occur at 100°C. Aside from
immiscibility above 5 percent PbI_2, and increased conductivity, no other properties were
reported. Tubrandt and Eggert [10] reported in 1920 the phase diagram for the system
$PbI_2 \cdot AgI$. A simple diagram was indicated with a eutectic composition at $PbI_2 \cdot 4AgI$. The
eutectic had a reported melting point at 395°C. No comment was made about thermo-
chromism in these references, but a $\beta \to \alpha$ transition were reported for all transitions,
around 110°C - 115°C.

Thus, our results did not agree with those found in the literature. The reported transition at 110°C for the 5 mole percent system[9] was not confirmed by any DTA peaks at 100°C, only peaks at 130°C and 150°C were observed. We found, in general, that the magnitude of the DTA peaks at 130°C increased with increasing PbI_2 content in the 5 - 33 percent range while the AgI peak at 150°C showed a corresponding decrease. At 25 - 30 mole percent PbI_2 content, the AgI peak completely disappeared and only the one at 130°C was observed. DTA thermograms of AgI composition with 5, 10, 20, and 30 percent PbI_2 content are shown in Figures 10 through 13 respectively.

3.1.2.2 THERMODYNAMIC PROPERTIES OF $PbI_2 \cdot 2AgI$

Using the DTA curves, the heat of the thermochromic phase transition (at 130°C) of the $PbI_2 \cdot 2AgI$ fired composition was evaluated. The relationship is given by:

$$\Delta H_{(mcals/mg)} = \frac{EA\Delta T_s T_s}{Ma} \qquad \text{where}$$

E = calibration coefficient, mcals/$^\circ$C-min.

A = peak area, sq in.

ΔT_s = Y-axis sensitivity setting, $^\circ$C/in

T_s = X-axis sensitivity setting, $^\circ$C/in

M = sample mass, mg.

a = heating rate, $^\circ$C/min.

Three independent determinations of the heat of transition were made. It was found to be

$$\Delta H_{tr} = 3.6 \pm .4 \text{ mcals/mg}$$

In comparison, the heat of transition for Ag_2HgI_4 was found to be 1.55 mcals/mg [11].

SAMPLE: _5/5 ⁴⁄₈ 2 mₐβ₄ I_

ORIGIN: _Menzel_

SIZE _Read_

REF. _MT Pan_

PROGRAM MODE _line_

RATE _10_ $\frac{°C}{MIN}$, START _23°C_

ATM. _v_ _76c_

	T.	_76c_	$\triangle$ T.
SCALE SETTING	20	$\frac{°C}{IN}$	_0.1_	$\frac{°C}{IN}$

RUN NO. _123_

DATE _10-123_

OPERATOR _Dfr_

→ Heat

EXO ← $\triangle$ T → ENDO

0   20   40   60   80   100   120   140   160   180   200

900

T °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

FIGURE 10

25

SAMPLE: 10% PbI_2 in AgI

ORIGIN: Merryl

SIZE 12.959 mg

REF. beach 15T/in

PROGRAM MODE heat

RATE 15 °C/MIN, START 27°C

ATM. Air 760

	T	ΔT
SCALE SETTING	20 °C/IN	0.5 °C/IN

RUN NO. 115

DATE 10/8/68

OPERATOR

→ Heat

EXO ← ∇T → ENDO

T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

FIGURE 11

26

SAMPLE: 2c% PbI in AgI

ORIGIN: Menoge

SIZE 16.987mg

REF. 4T Perni

PROGRAM MODE heat

RATE 10 °C/MIN, START RT °C

ATM. Air Tbe

T 20 °C/IN.

ΔT 6.2 °C/IN.

SCALE SETTING

RUN NO. 118

DATE 10/9/68

OPERATOR Duf

→ Heat

EXO ← ▽T → ENDO

T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES) FIGURE 12

900

27

SAMPLE: 30% PbI₂ in AgI (600°, 1 day)

ORIGIN: Minergie

ATM. Air Dun

REF. My Pan

PROGRAM MODE Heat

RATE 10 °C/MIN, START 27 °C

SIZE 7.196 mg

T ___ ΔT ___

SCALE SETTING 20 °C/IN · 0.1 °C/IN

RUN NO. 116

DATE 10/9/68

OPERATOR Dolan

EXO ← ▽T → ENDO

Heat

T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES) FIGURE 13

28

Attempts were also made to determine heat capacities of $PbI_2 \cdot 2AgI$ at various temperatures by DTA methods. A typical thermogram is shown in Figure 14. The top part of the closed loop represents a blank run; the lower part of the loop is a differential thermal analysis of a $PbI_2 \cdot 2AgI$ sample. Heat capacities at a given temperature are proportional to the distance between the upper and lower parts of the loop. Seven such thermograms were made. Results were too scattered to obtain any conclusive values for the heat capacities.

3.1.2.3 X-RAY DIFFRACTION ANALYSIS ON $PbI_2 \cdot 2AgI$ SYSTEM

X-ray diffraction analyses were performed to determine the nature of the fired compositions of AgI and PbI_2. Mechanical mixtures of the two components were also analyzed. The results could not be interpreted in support of either a new compound (e.g. Ag_2PbI_4) or a solid solution.

A sample of the fired yellow powder (nominal composition $PbI_2 \cdot 2AgI$) was subjected to x-ray diffraction analysis. The material was ground to fine powder in a boron carbide mortar, packed in a 0.3 mm quartz capillary and mounted in a powder camera. A 10 hour exposure of CuKα radiation ($\lambda = 1.54$ Å) was made at 35 kv, 15 ma. Figure 15-A is a reproduction of the photograph. The diffraction lines are tabulated in Table 5, Column 2. (A cylindrical camera plastic chart was used for the interpretation, sufficiently accurate for the resultant data). All observed lines can be accounted for by reference to published data on AgI and PbI_2.

A further attempt to verify this was undertaken by fine powdering a mechanical mixture of PbI_2 and AgI_2 using the same proportion as that of the original sample. Figure 15-B is the resulting x-ray diffraction pattern. The same experimental conditions apply, except that the exposure was of 4 hour duration. Table 5 Column 1 lists the observed d spacings. The diffraction lines appear at similar d spacings to those of the fired material. Intensity relationships are roughly comparable (differences here could be attributable to inhomogenities

SAMPLE:
PbI₂·2Ag⁺
Sample in beaker

SIZE 11.003 mg

REF. MT Pan

PROGRAM MODE Heat

RATE 10 °C/MIN ,START 29 °C

ATM. Air 760 mm

T	ΔT
20 °C/IN.	0.2 °C/IN.

SCALE SETTING

RUN NO. 160

DATE 12/2/68

OPERATOR DYla

ORIGIN: J. Menczel

BLANK

SAMPLE

EXO ← ∇T → ENDO

30
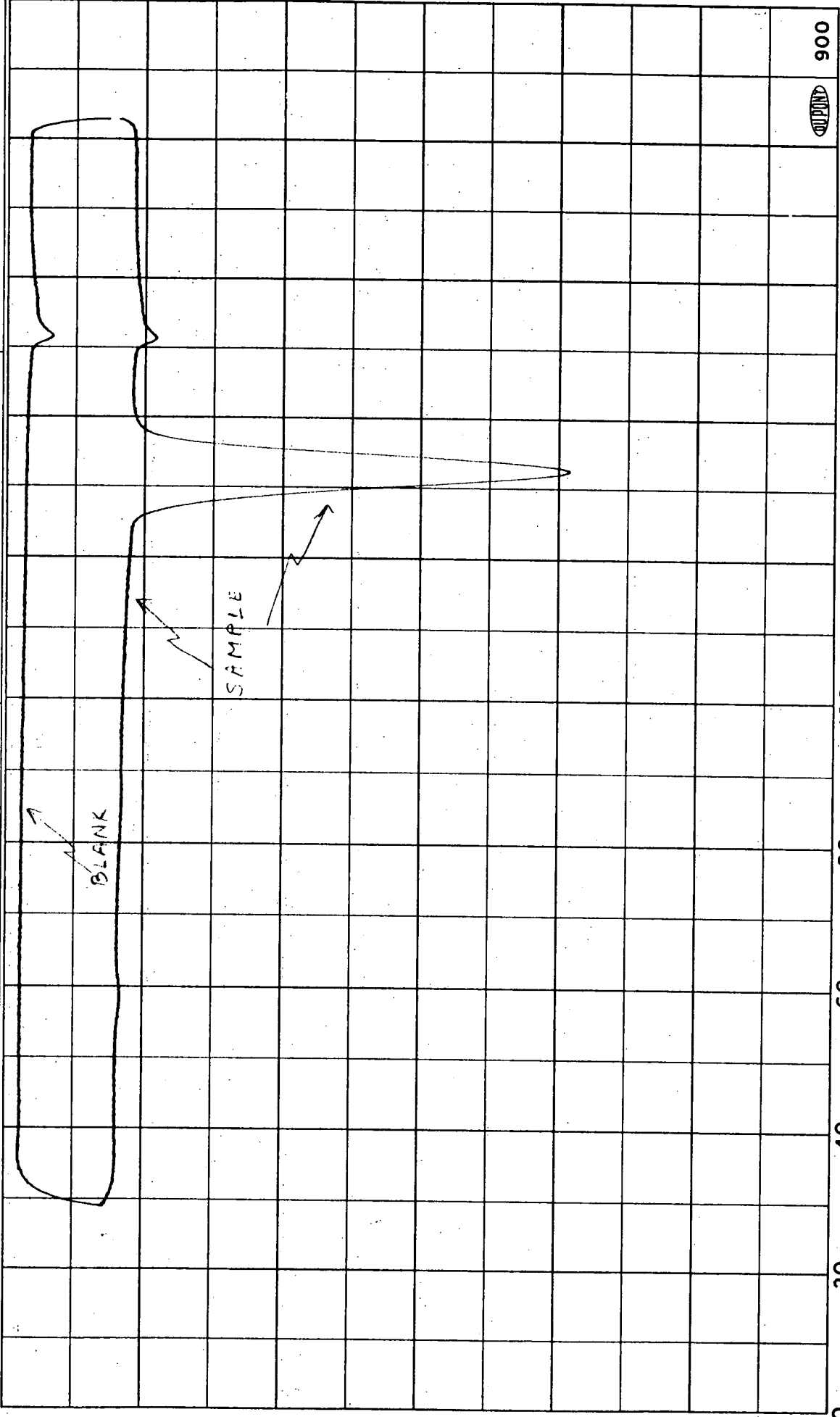
T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

FIGURE 14

0   20   40   60   80   100   120   140   160   180   200

900
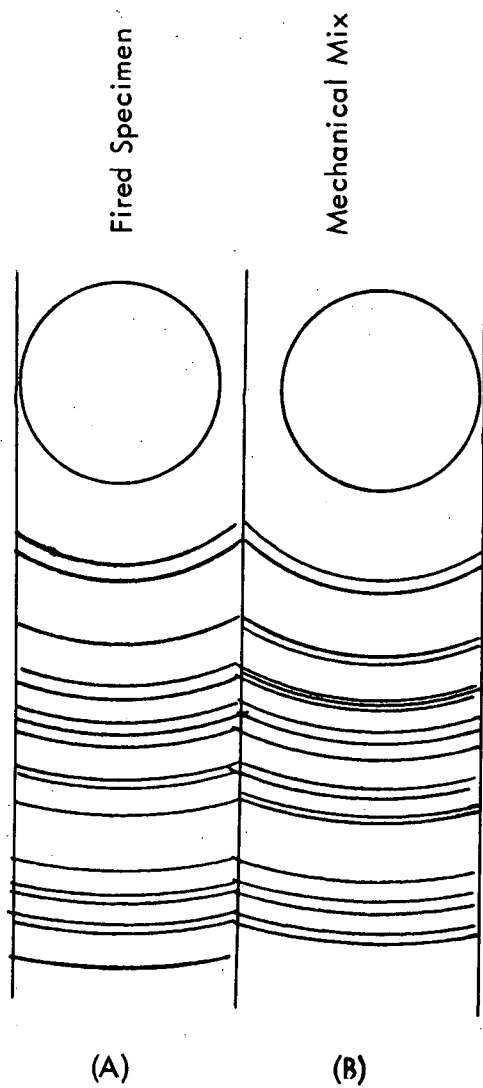
FIGURE 15

TABLE 5

X-RAY DIFFRACTION SPECTRUM FOR $PbI_2 \cdot 2AgI$ SYSTEMS

1) d(hkl)	2) d (hkl)	γ-AgI	3) (hkl)	4) PbI_2 (hex.)	(hkl)
6.9	6.8			6.98	001
3.7	3.71	3.75	111		
3.42	3.40			3.44	101
2.6	2.6			2.61	102
2.31		2.30	220	2.33	003
2.26	2.27			2.28	110
2.17				2.17	111
2.00	2.00			2.00	103
1.96	1.95	1.96	311		
1.89	1.88			1.90	210
1.74	1.74			1.75	004
1.72	1.71			1.72	202
1.62	1.62	1.62	400	1.63	113
1.50		1.49	331	1.50	203
1.46				1.46	211
1.39	1.41			1.39	114
1.38	1.38			1.37	212
	1.37				
1.32	1.32	1.33	422	1.32	105, 300
	1.31			1.29	301
	1.26	1.25	511	1.25	213

1) The d spacings observed from a mechanical mix of AgI (Matheson, Coleman and Bell – CB627 SX 195) and PbI_2 (City Chemical Corp.– WC372).

2) The d spacings observed from fired mixture of AgI and PbI_2 – same proportions as in 1) above.

3) d spacings, NBS Circular 539, IX , pg. 49, a–6.495Å, Space Group F43 m.

4) d spacings as reported by N.B.S. (circular 539, V, p.35) Lattice constanta a=4.557Å, C=6.979Å   Space Group P3m1.

32

in the powder samples or to a slight loss of AgI in the fired material). It would seem reasonable to assume that Ag_2PbI_4 would be a larger "molecule" than either AgI or PbI_2. This would create a larger unit cell, thus, larger lattice constants and new lines would be generated. If the result were a mixture of x percent PbI_2, y percent AgI, and (100-x-y) percent of Ag_2PbI_4 the same conclusions hold except the Ag_2PbI_4 lines would appear with intensities proportional to concentration.

A possible explanation for the apparent discrepancy between the x-ray and DTA data could be the decomposition of the fired composition as a result of x-ray bombardments, since a severe discoloring of the materials was observed upon the completion of the x-ray analyses. Another possible explanation for the varying results obtained by the two methods may be that the solubility of PbI_2 in AgI was exceeded, thus overshadowing the evidence of new compound or solid solution formation that may have been present.

3.1.2.4 $PbI_2 \cdot 2AgI$ SOLUBILITY STUDIES

Efforts were made to identify the chemical nature of the $PbI_2 \cdot AgI$ fired compositions by solubility studies. The solubility of PbI_2 in water at $100^\circ C$ is 0.41 g/100 ml [12], that of AgI is negligible. Solubility studies might indicate whether a profound chemical change had occurred on firing the $PbI_2 \cdot AgI$ compositions or whether the system was a complex solid solution phase. Fired and unfired compositions of silver and lead iodide in the mole ratios of $PbI_2 \cdot 2AgI$ (about equal weights) were accurately weighed into round-bottom flasks, containing 50 ml of water and refluxed at $100^\circ C$. Three determinations were made with the following results.

First Determination

Reflux Time: 7 hours	Initial Weight	Undissolved Residue
Unfired Mixture	0.4148 g	0.1884 g
Fired Mixture	0.4183 g	0.3064 g

Only the residues were weighed in this determination.

Second Determination

Reflux Time: 18 hours	Initial Weight	Undissolved Residue	Solute Residue
Unfired Mixture	0.4153 g	0.1988 g	0.1081 g
Fired Mixture	0.4212 g	0.2294 g	0.0383 g

Third Determination

Reflux Time: 20 hours	Initial Weight	Undissolved Residue	Solute Residue
Unfired Mixture	0.4143 g	0.2158 g	0.1129 g
Fired Mixture	0.4153 g	0.2787 g	0.0184 g

The weights of the dissolved and undissolved residues in both the fired and unfired mixtures were independently determined. The amounts of undissolved residues were found to be approximately equal in the two mixes, with slightly less of the unfired material remaining undissolved. However, judging from the amounts of dissolved residues obtained from both mixes, it is quite clear that the solubility rate of the fired mixture is the lower of the two.

It should be noted that the total weight of undissolved residue plus solute residue does not add up to the initial weights of the materials. This may be attributed to experimental losses. However, hydrolysis of lead iodide during refluxing and subsequent drying of residues with the evolution of hydrogen iodide, should not be ruled out.

DTA analyses were performed on solutes and residues obtained in determinations two and three. Both solutes had peaks only at $400^{o}C$ (PbI_2). The residue of the unfired mixture revealed only one peak at $150^{o}C$ (AgI), whereas three peaks appeared in the thermogram for the fired mixture. These peaks showed up at $130^{o}C$, $150^{o}C$, and $375^{o}C$.

The following conclusions may be drawn from the results obtained:

1. The structures of the fired and unfired mixtures are not identical as shown by the lower solubility rate of the fired mixture.

2. The solute is probably PbI_2, with subsequent hydrolysis. This is also supported by the DTA analysis of the residue where the peaks at $130^{o}C$ and $150^{o}C$ correspond to fired mixture and excess silver iodide, respectively.

It is clear from these results that the properties of the fired products are distinctly different from a physical mixture and that we are probably dealing with a solid solution.

3.1.3 Al_2O_3-Cr_2O_3 COMPOSITIONS

The investigation of alumina-chromia compositions was undertaken due to reports in the literature[13] which indicated thermochromic properties. Ruby changes color reversibly from red to green upon heating. The temperature at which the color change occurs was reported to be inversely proportional to the chromium content in the Al_2O_3. Since these materials are expected to be stable at very high temperatures due to the melting points of the components (Al_2O_3 melts at $2054^{\circ}C$, Cr_2O_3 at $2435^{\circ}C$), they might be interesting candidates for CRT applications.

Compositions of Al_2O_3 with 5-40 percent Cr_2O_3 content were mixed and fired for varying lengths of time between $1350 - 1500^{\circ}C$. Color transition temperatures of the fired materials were determined on a hot plate with a surface thermometer. Color changes were found to be reversible and went from red to grey to green upon heating. However, the transformations took place gradually over a wide temperature range which depended in part on the prior history of the sample. The mode of preparation of ingredients charged and properties of fired powders are summarized in Table 6. The thermochromic properties of these specimens appear to be dependent on the temperature of firing.

Additional work on the ruby-type compounds included differential thermal analysis (DTA) thermograms to determine the nature of the color change. No peaks were observed on the thermograms for any of the Al_2O_3-Cr_2O_3 materials at their color-transition temperatures. This verifies that color changes are due merely to continuous lattice expansions, rather than order-disorder phase changes. Due to the high temperature of the thermochromic transitions and the relatively poor contrast phase changes, further work on the ruby-type materials was abandoned.

TABLE 6

PROPERTIES OF Al_2O_3-Cr_2O_3 COMPOSITIONS

Specimen Number	Mole % Cr_2O_3	Mode of Preparation	R.T. Color After Firing	Approx. Temp. Change to Grey, $^\circ$C	Pronounced Temp. Change to Green, $^\circ$C
R-1	5	1500°C, 12 hrs.	Light ruby red	> 400	---
R-2	10	1500°C, 12 hrs.	Light ruby red	200	350
R-6	10	1300°C, 38 hrs.	Very light ruby red	150	290
R-7	15	1350°C, 24 hrs.	Reddish grey	---	150
R-3	20	1500°C, 12 hrs.	Ruby red	140	375
R-4	30	1500°C, 12 hrs.	Very dark	Color change too slight to determine	
R-5	40	1500°C, 12 hrs.	Very dark	Pronounced temperature changes	

3.2 APPLICATIONS

Several applications have been considered and evaluated during this contract period in con-
junction with the unusual properties of thermochromic materials. Primarily, the effort was
concentrated in the use of thermochromics in a CRT, but brief studies were also conducted in
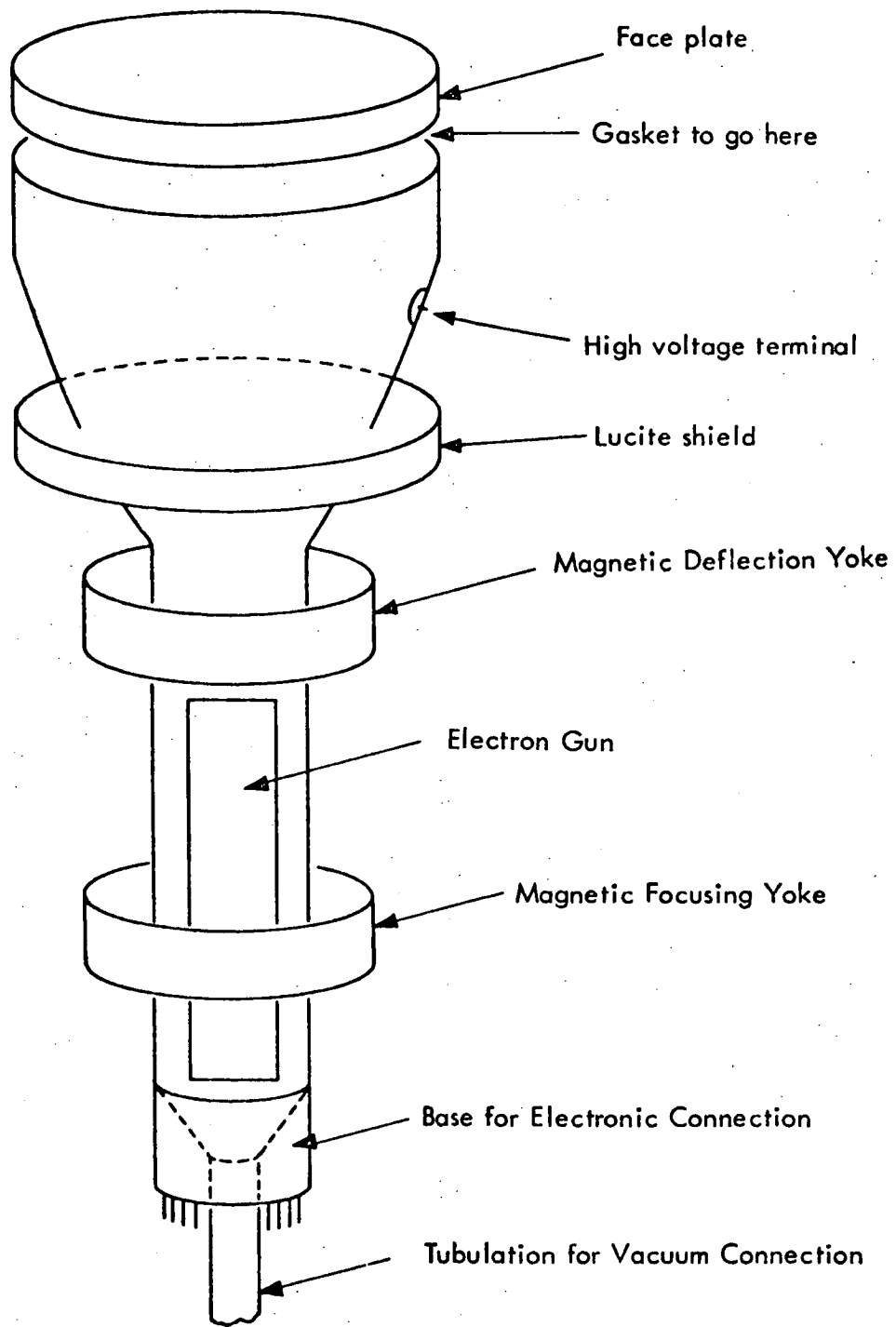computer input and laser writing applications.

A significant asset of thermochromics is the relative ease with which important properties such
as rise time and persistence can be adjusted. These properties depend, among other things, on
the heat capacities and thermal conductivities of the thermochromic and associated materials,
as well as the ambient thermal levels. Thus, by varying the choice and mass of the materials
and the ambient thermal levels, optimal conditions can be obtained.

In addition, as mentioned earlier, another advantage of thermochromics over phosphors is the
differential reflection of incident radiation rather than the emission of light. Thus, they can
be used at high ambient light levels. Also, since the transitions depend on heat the possibility
exists of inducing color changes by the use of infrared stimulation.

The existence of only two distinct thermochromic states in addition to relatively long life-
times, gives these materials an edge over phosphors in that they can lead to flicker free dis-
plays. To avoid flicker in thermochromic displays it is necessary merely to repeat the signal
before the material has had an opportunity to cool below its transition temperature. In standard
phosphor displays where the phosphor reaches peak brightness almost immediately after being
pulsed and then gradually decreases in brightness, rapid repetition values are necessary to
avoid flicker.

3.2.1 DEMOUNTABLE CRT STUDIES

The demountable CRT (Figure 16) was described in the Second Annual Progress Report[14]. It
was again used this year in evaluating thermochromics as potential CRT target materials. A
minor modification consisted of the fabrication and introduction of an aluminum support upon
which the various thermochromic samples could be mounted. This aluminum mount replaced
the wire gauze that was used in previous experiments.

Face plate

Gasket to go here

High voltage terminal

Lucite shield

Magnetic Deflection Yoke

Electron Gun

Magnetic Focusing Yoke

Base for Electronic Connection

Tubulation for Vacuum Connection

SCHEMATIC OF DEMOUNTABLE CRT

FIGURE 16

39

The CRT cathode was activated by the modified activation scheme described in the Second Annual Progress Report.[14] After the cathode was activated, the tube was evacuated continuously by a Veeco Vacuum system to which the CRT was connected by a Veeco type C Quick Connect coupling. The pressure was in the 10^{-6} to 10^{-7} Torr range as indicated by the ionization gauge in the Veeco system. Since the CRT is connected to the Veeco through narrow diameter tubing, the pressure may be an order of magnitude higher in the CRT. When a thermochromic sample was introduced, the system was flushed with dry nitrogen to protect the cathode. The faceplate was removed and the thermochromic specimen was quickly attached to the sample mount. The system was then pumped down to 10^{-6} to 10^{-7} Torr before the elctron beam was operated.

3.2.1.1 Ag_2HgI_4 IN THE DEMOUNTABLE CRT

The testing of Ag_2HgI_4 deposited upon various substrates that began during the second year of the effort was continued in an attempt to define an optimum substrate and experiment configuration. In addition, Ag_2HgI_4 was tested in various protected configurations in order to find some practical means to improve the stability of this material to high vacuum and heat.

3.2.1.1.1 Ag_2HgI_4 with Beam Incident on Nickel Backing

Metal substrates were investigated in an effort to obtain optimum color resolution and faster response times at low power levels. Earlier experiments with Ag_2HgI_4 on a 0.00035" thick nickel substrate were described in the Second Annual Progress Report in which the electron beam was allowed to strike the metal first. This produced a reversible thermochromic change at a voltage of 20 kV and a power level of 7.6 watts/cm^2. The current was 3μ amperes. The fading time was of the order of 10 seconds. Experiments were therefore performed using a thinner nickel foil (0.0001") to determine whether this would produce better resolution at lower power levels, and to observe the effects of variations in foil thickness. A 2.76 mg/cm^2 coating of Ag_2HgI_4 was sprayed on the thin

foil. A good reversible thermochromic change was achieved at a voltage of 20 kV and a beam current of 0.8μ ampere which corresponded to a power density level of 2.0 watts/cm^2. The decay time was approximately 6 seconds. Thus, the power level and decay time were superior to either the 0.00035" nickel with values given above or the 0.0033" – 0.0051" microsheet which required power density levels of 3.8 – 5.1 watts/cm^2 and decay times of approximately 10 seconds. However, the thinness of the foil and its still relatively high thermal conductivity lead to an overall temperature rise in the nickel that increases with the length of time that the beam is required to spend on the foil regardless of its position. This leads to an undesireable rapid spreading of the thermochromic color change.

3.2.1.1.2 Ag$_2$HgI$_4$ with Beam Incident on Titanium Backing

Titanium has a much smaller thermal conductivity, 0.0407 cal cm^{-1}sec^{-1} $^{\circ}$C^{-1} compared to 0.22 cal cm^{-1}sec^{-1} $^{\circ}$C^{-1} for nickel. This lower thermal conductivity value for titanium would suggest that there would be less dissipation of heat in titanium. A 2.76 mg/cm^2 coating of Ag$_2$HgI$_4$ was sprayed on 0.00025" thick titanium foil. Reversible thermochromic changes were achieved at a voltage of 20 kV and a beam current of 0.5 to 0.6 μ ampere which corresponded to a power density level of 0.3 – 1.5 watts/cm^2. However, a heat spreading problem that was very similar to the 0.0001" nickel foil was encountered. Beam spreading limits the use of this sort of metal substrate.

3.2.1.1.3 Magnesium Oxide–Ag$_2$HgI$_4$–Glass Sandwich

It was reported[15] that a reversible thermochromic transition was achieved with a MgO coated Ag$_2$HgI$_4$ glass sandwich. The low thermal conductivity value (0.001 cal cm^{-1}sec^{-1} $^{\circ}$C^{-1}) and the ability to apply variable MgO coating thicknesses by burning Mg ribbon warranted further investigation of this configuration. It was decided to repeat the previous study with a thicker coating of MgO to ensure the complete stoppage of electrons which could penetrate about 2.8 microns in the MgO according to Terrill's equation[15]. The MgO coating on this particular sample was 3.4 microns thick. At a potential of 20 kV and a power level of 2.5 –

5.0 watts/cm^2, predominantly irreversible changes of the thermochromic were noted along with some fluorescence from the MgO. It appears that there is a problem in obtaining consistent results with a MgO coating applied in this manner. If a very tight and uniform coating of MgO is not applied, the electron beam will penetrate and induce irreversible changes in the thermochromic. It became apparent also that the MgO coatings tend to flake rather easily and are ablated by the electron beam during bombardment. Thus, MgO does not appear to be a good substrate at present.

3.2.1.1.4 Saran F220 Copolymer Micro-Encapsulated Ag_2HgI_4

The National Cash Register Company micro-encapsulated samples of Ag_2HgI_4 in Saran F220 copolymer. The polymer was reported to have good vacuum and heat stability. A sample of this micro-encapsulated material was painted on thin conducting glass with a brush. Partially irreversible color changes were produced at 20 kV and 1 microampere corresponding to 2.5 watts/cm^2. The Saran F220 copolymer appeared to be decomposing under the action of the electron beam since the pressure of the system rose rapidly as long as the electron beam was allowed to impinge on the material.

The response of this system was also tested with the beam striking the conducting glass rather than the copolymer . It required 5 microamperes at 20 kV or 12.7 watts/cm^2 to produce the thermochromic transition, which was quite a bit higher than with unencapsulated Ag_2HgI_4. Color spreading was worse with the encapsulated material in this configuration.

A vacuum stability study of the encapsulated thermochromic showed a 14.5 percent weight loss over an eight day evacuation at a vacuum of 1×10^{-7} Torr to 5×10^{-7} Torr. The weight losses were continuous and permanent over this period. Also, the intensity of the color change of the sample had noticeably declined in comparison to an unevacuated sample. Therefore, the vacuum and CRT studies indicate that this encapsulated material would not be suitable in a CRT.

3.2.1.1.5 Glass-Ag_2HgI_4-Glass Sandwich

A. Glass-Ag_2HgI_4-Glass Sandwich Involving 0.0033"-0.0051" Microsheets

One possible means of stabilizing the Ag_2HgI_4 would be to prepare a sandwich of Ag_2HgI_4 between two thin conducting glass plates (0.0033" - 0.0051") and seal the edges with a vacuum stable epoxy. A sandwich was made by spraying the thermochromic on one plate and sealing to the other plate with Torr-seal epoxy. The thermochromic had a surface density of 2.7 mg/cm^2. A good reversible color change was achieved at 20 kV and 1.2 μ amperes or about 3.1 watts/cm^2. Spreading of the lines and resolution appeared to be better than for the simpler system of thermochromic on one glass plate. The decay time for the sandwich was 5 to 6 seconds. This also is an improvement on the open faced experiments.

Since the CRT and high vacuum tests of the glass sandwich sealed with the Torr-seal were satisfactory, it was decided to determine the heat stability of this configuration under moderate vacuum. The epoxy is stated to be bakeable up to 120°C. Therefore, a preliminary test was made in which the sandwich was heated at a temperature of 90 – 105°C for 1.5 hours under a moderate vacuum. The thermochromic appeared to be unchanged except for one small corner where AgI formation was indicated. A small crack in the epoxy was noted.

The epoxy sealed sandwiches were then exposed to higher temperatures. One sandwich was heated to 144°C over a period of 45 minutes and then cooled fairly rapidly. The basic color of Ag_2HgI_4 seemed to have been retained, but the sample had a striated appearance. Another sample was heated to 164°C over a period of 35 minutes and then cooled over a period of 100 minutes. The Ag_2HgI_4 appeared to be in good condition with no bubbles or color change. The epoxy, however, was discolored. The tests with regard to vacuum and thermal stability of the thermochromic in this sandwich have been good so far.

However, it is doubtful that Torr-seal epoxy could withstand the bakeout tempera-
tures required to manufacture a sealed CRT.

B.   Glass-Ag$_2$HgI$_4$-Glass Sandwich Involving 0.0020"-0.0033" Microsheets

Thinner microsheets with thicknesses in the range of 0.0020"-0.0033" were

employed to see if improved resolution could be obtained. These experiments

were conducted with the thinner microsheet as the substrate facing the beam in

each test. The thickness of the microsheet was calculated from the specific

gravity, surface area, and weight measurements of the glass. The thickness of

the second glass was obtained from micrometer measurements. The surface

density of the Ag$_2$HgI$_4$, the thickness of the microsheet and the thickness of the

second glass are tabulated in Table 7 along with CRT experimental results shown

in Table 8.

The resolution of the thermochromic on the 0.0029" glass in sample #1 appeared

to be somewhat better than the thicker microsheets. The resolution and response

times appear to improve generally with increasing thickness of the second glass

member. However, it is necessary to increase the size of the beam current with

increasing thickness. This will be a limiting factor for glass thickness. The de-

cay time for sample #2 was measured to be 5 seconds which is about the same

value obtained with previous glass sandwiches. However, the response time

generally appeared to be faster.

3.2.1.2   CRT EXPERIMENTS WITH Al$_2$O$_3$-Cr$_2$O$_3$ MIXTURES

Chromium oxide-doped aluminum oxide compositions were tested for the first time in the

demountable CRT. The materials possess very good thermal and vacuum stability. If re-

versible thermochromic change with high contrast can be achieved, several such materials

will be very promising candidates for a sealed off CRT.

TABLE 7

GLASS SANDWICHES USED FOR CRT EXPERIMENTS

Sample #	Microsheet Thickness (inches)	Thickness of Second Glass (inches)	Surface Density of Ag_2HgI_4 (mg/cm^2)
1	0.0029	0.0044	3.30
2	0.0031	0.045	4.17

TABLE 8

GLASS SANDWICH CRT EXPERIMENTS

Sample #	Voltage (kV)	Faraday Cup (Current (μa)	Beam Diameter(cm)	Power Watts / cm^2	Results
1	20	1-2	~ 0.1	2.5 to 5.0	Resolution was somewhat better than for 0.0033" - 0.0051" conducting glass sandwich referred to in the March 4, 1968, report.
2	20	3-4	~ .1	7.6 to 10.2	Resolution was very good. Response time was best in this group of samples. However, power levels are high.

R-2 and R-3 specimens which were described in section 3.1.3 were painted onto thin conducting glass from an acetone slurry using an artist brush. Since these compounds are very stable toward heat, the samples were mounted in the CRT with the chromium oxide-doped aluminum oxide material facing the electron beam. Reversible thermochromic changes were demonstrated in the CRT. The contrast in the color change was not nearly as pronounced as with Ag_2HgI_4. It was necessary to illuminate the material with a flashlight in order to enhance the observation of the thermochromic color change. The experimental results are given in Table 9. The power level at which the reversible color change was achieved in R-3 was approximately 15 watts/cm^2. The power level for R-2 was 15 – 20 watts/cm^2. No fluorescence was observed in this material.

In a subsequent set of experiments, chromium oxide-doped aluminum oxide materials, R-2 R-6, and R-3, were coated over a portion of the surface of thin conducting glass. The remainder of the glass surface was coated with yellow P-14 phosphor in an effort to provide a positive indication of electron beam position. The specimens were tested in two configurations, one in which the electron beam struck the materials first, and one in which the electron beam struck the glass substrate. It was felt that there would be more uniform distribution of heat conducted to the thermochromic in the latter configuration. The contrast in the color change in each configuration was again poor for each material. The power level, as in the previous experiments, was approximately 15 – 20 watts/cm^2.

Since the contrast for ruby type compounds was rather poor without additional direct illumination, these compounds were de-emphasized as candidate materials for the CRT.

3.2.1.3   CRT EXPERIMENTS WITH $PbI_2 \cdot 2AgI$

This system was now examined in the CRT to determine its suitability as a candidate material for the sealed off tube.

TABLE 9

Thermochromic Behavior of Cr_2O_3-Al_2O_3 Compositions In Demountable CRT

Specimen No.	Voltage (kV)	Faraday Cup Current (μa)	Beam Diameter (cm)	Comments
R-2	20	4	~ 0.1	No color change.
R-2	20	6	~ 0.1	Slight color change from red to grey green.
R-2	20	3	~ 0.1	Definite color change from red to grey green. Decay time was fast.
R-3	20	3	~ 0.1	Color change was observed if spot rested for several seconds on same area.
R-3	20	6	~ 0.1	Definite color change. Decay time was fast.

3.2.1.3.1   INITIAL EXPERIENCE WITH $PbI_2 \cdot 2AgI$ IN THE DEMOUNTABLE CRT

An initial experiment with the fired $PbI_2 \cdot 2AgI$ composition in which glass resin
Type 100 was used as a possible protection of the thermochromic against vacuum discoloration
was conducted in the demountable CRT. Glass resins are vacuum and thermally stable
materials whose properties are described in Section 3.2.2.6. A slurry of $PbI_2 \cdot 2AgI$ in a
dilute solution of glass resin in methanol was coated onto a microsheet substrate. The
sample was bombarded in the CRT with the microsheet substrate facing the electron beam.
A reversible transition from yellow to orange was observed at 20 kV and approximately 5 micro-
amperes beam current which corresponded to a power density of 13 watts/cm^2 at the usual
0.1 cm beam diameter.

Two $PbI_2 \cdot 2AgI$ samples that did not contain glass resin were also prepared on
microsheet. These samples were bombarded in the CRT with the thermochromic facing the
beam. The thermochromic was dislodged from the substrate by the electron beam before
the power level could be obtained to produce thermochromic change. It was noted that
the uncoated samples discolored in the CRT after several days. It was not known at that
time whether this discoloration was due to the action of vacuum or light.

Then, it was decided to again use the glass resin, Type 100, to bind the thermochromic with
adequate curing of the resin. The CRT faceplate was coated with a slurry of 3:1 mixture of
$PbI_2 \cdot 2AgI$ to glass resin in methanol. The glass resin was cured at $200°C$ for 10 minutes.
The faceplate was placed on the CRT and evacuated overnight. The following day it was
found that the thermochromic had badly discolored on the side facing the fluorescent
lighting in the room (through the glass). There was no noticeable discoloration on the
inner surface that was not exposed to the light. When this faceplate was allowed to stand
overnight at atmospheric pressure, the $PbI_2 \cdot 2AgI$ composition reverted back to nearly its
original color even in the presence of the fluorescent lighting.

An attempt was made to protect the thermochromic by applying two coats of glass resin over

the resin-thermochromic mixture on a microsheet substrate. The first coating of glass resin was cured before the second coating was applied. It was decided to use thin conducting glass in this experiment to prevent any space charge buildup on the glass surface. The surface density of the thermochromic was 3.2 mgs/cm^2. The thermochromic was observed to undergo good reversible color changes while curing the resin in the oven. This sample was tested in the CRT with the thermochromic facing the electron beam during the same afternoon that it was placed in the CRT. No appreciable color change was achieved at 20 kV and currents up to 10 microamperes. Some gas began to evolve as the beam current was increased to higher levels than 10 microamperes. This sample also discolored (in the same manner as previously) after overnight exposure to the vacuum. The discoloration again disappeared at atmospheric pressure. The extra coatings of glass resin did not protect the thermochromic from discoloration.

Another 3:1 mixture of thermochromic and resin on microsheet was tested in the CRT without the extra coats of glass resin. A good reversible thermochromic change was achieved with the thin conducting glass facing the electron beam. The surface density of the thermochromic was 2.5 mgs/cm^2. The transition was achieved at 20 kV and approximately 5 microamperes of current. The contrast was good. The change was more rapid than with Ag_2HgI_4. No color change was achieved with the thermochromic facing the electron beam at 20 kV and currents up to 10 microamperes.

It appeared that both light and vacuum are required to produce the discolorations in the thermochromic after a period of time. A spectrophotometric curve of the clear face-plate revealed 70 percent transmission at 3600 angstroms and 30 percent transmission at 3350 angstroms. A yellow filter was placed in front of the faceplate of the CRT while the thermochromic on microsheet was under vacuum over the weekend. There was no dis-coloration detected after this period of time. A good reversible color change was achieved at 20 kV and 5 microamperes with the microsheet facing the electron beam. Subsequently, the CRT faceplate has also been covered with aluminum foil or a black cloth which prevents discoloration of the thermochromic.

3.2.1.3.2   SUBSEQUENT EXPERIMENTS WITH $Pbl_2 \cdot 2AgI$

The inability to achieve a color change by direct bombardment of the thermochromic by the electron beam was examined in more detail. A new sample of $Pbl_2 \cdot 2AgI$ was prepared with a surface density of 3.2 mg/cm^2 on a microsheet substrate that contained approximately 3 percent glass resin Type 100. It was felt that the glass resin content of approximately 25 percent employed in previous experiments may have been too high thus interfering in the thermochromic change when the $Pbl_2 \cdot 2AgI$ is bombarded directly by the electron beam. A second microammeter was placed in the system that would enable continuous monitoring of the Aquadag current which is more or less proportional to the beam current. The thermochromic surface of this sample was then subjected to a range of voltages and beam currents in the CRT.

The results were as follows for a fixed beam diameter of approximately 0.1 centimeter. At 20 kV, a Faraday cup current of about 5μ gave an initial reversible thermochromic change. However, the change stopped almost immediately. It was noted on the Aquadag current meter that the total current in the system had dropped to about half of the original value. The current returned to its original value when the beam was moved off the thermochromic. Then the process could be repeated. If the beam current was increased, reversible change would be achieved for an instant again and then would stop. The beam current would drop simultaneously. Approximately the same effect occurred at 10 kV with a 10μa beam current and 5 kV with a 20 μa beam current.

$Pbl_2 \cdot 2AgI$ on microsheet substrates containing 1 percent and 0 percent glass resin were tested in the CRT with the thermochromic facing the beam. Surface densities were 3.0 mgs/cm^2 and 3.3 mgs/cm^2, respectively. A sample was also placed in the CRT with the microsheet facing the electron beam to act as a control. The procedure would be to achieve a thermochromic change on the sample with the glass substrate facing the beam first, and then attempt to achieve a thermochromic change by bombarding the test sample directly.

Reversible color changes were achieved fairly easily with the control sample at 20 kV and approximately 5μ a beam current at a fixed 0.1 cm diameter spot size. When the electron beam was focused on the thermochromic with 1 percent resin, thermochromic behavior would start and then cease as in the experiment with the thermochromic with 3 percent resin. The results were the same with the thermochromic that contained no glass resin.

This peculiar behavior of initial thermochromic transition followed by cessation of thermo-chromism suggests the possibility of ionization of the thermochromic with corresponding increase in electrical and thermal conductivity. This might account for the immediate change and subsequent recovery. A hybrid $P-14/PbI_2 \cdot 2AgI$ system was investigated as a solution to this problem. This system is discussed in Section 3.2.1.4.3.

3.2.1.4 P-14 PHOSPHOR SYSTEMS

Efforts were made at different times to combine P-14 with the thermochromics in various con-figurations that would be both fluorescent and thermochromic. These techniques are now discussed.

3.2.1.4.1 50-50 MIXTURE OF P-14 PHOSPHOR AND Ag_2HgI_4

A CRT test was performed on a 50-50 mixture of P-14 phosphor and Ag_2HgI_4 to determine experimentally whether phosphor fluorescence can be achieved with the electron beam striking the thin conducting glass substrate of 0.0031" thickness. Two samples were placed in the CRT. Each contained 50-50 mixtures of P-14 phosphor and Ag_2HgI_4 with surface densities of 4.00 mg/cm^2. One of the samples was mounted with the 0.0031" microsheet facing the beam. The second sample was mounted with the 50-50 mixture facing the beam. At a voltage of 20 kV and currents large enough to produce fluorescence in the sample facing the beam, no thermochromism was observed. In the sample with the microsheet facing the beam, no fluorescence could be observed.

3.2.1.4.2   50-50 MIXTURE OF P-14 PHOSPHOR AND $PbI_2 \cdot 2AgI$

A 50-50 mixture of thermochromic to P-14 phosphor was coated onto a microsheet substrate from a dilute solution of glass resin in methanol. The phosphor thermochromic material was bombarded directly by the electron beam to determine if both a thermochromic transition and fluorescence of the phosphor could be obtained. Arcing and a rise in pressure occurred in the CRT as the beam was focused on the material. At this particular time it was felt that either incompletely cured glass resin binder or decomposition of the ternary iodide might have caused this gassing.

3.2.1.4.3   HYBRID P-14/$PbI_2 \cdot 2AgI$ SYSTEM

One approach to prevention of electrical breakdown would be to protect the thermochromic with coatings of P-14 phosphor. A $PbI_2 \cdot 2AgI$ coating with a surface density of 1.6 mgs/cm^2 was prepared on a microsheet substrate. Three separate coatings of P-14 phosphor were sprayed over the thermochromic with a total surface density of 3.4 mgs/cm^2. All coats and the thermochromic layer contained approximately 3 percent glass resin. Each coating and the thermochromic layer were cured separately at approximately 210°C.

This composition was placed in the CRT with the phosphor facing the beam. The results of the tests are contained in Table 10.

Judging from the results of Table 10, the sprayed phosphor coatings are tight and thick enough to prevent penetration of the electrons through the phosphor. The energy of the beam is thereby absorbed by the phosphor and the heat generated induces the thermochromic transition without breakdown. It should be noted that an experiment with a physical mixture of P-14 and $PbI_2 \cdot AgI$ gave fluorescence but no thermochromic change.

The successful demonstration that both $PbI_2 \cdot 2AgI$ thermochromism and P-14 phosphorescence and fluorescence could be generated in a hybrid system suggested that a phosphor coated thermochromic technique can now be applied to a CRT faceplate. One 4 cm^2

TABLE 10

HYBRID P-14/$PbI_2 \cdot 2AgI$ SYSTEM IN DEMOUNTABLE CRT

Voltage (kV)	Faraday Cup Current (μa)	Beam Diameter (cm)	Comments
20	5-6	~ 0.1	A bright yellow spot of fluorescence is observed through the thermochromic which changes in about 2 seconds to a bright red spot due to thermochromic change.
20	~ 10 or greater	~ 0.3	The results were identical to above. The larger spot size made the transitions more attractive.
10	~ 8-9	0.1	Fluorescence and then thermochromic change was again achieved.
10	> 10	~ 0.3	The results were the same as above.

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section of a faceplate was sprayed with the $PbI_2 \cdot AgI$ composition and three coatings of the phosphor was applied in the same manner as previously described. Another 4 cm^2 portion of the same faceplate was first sprayed with a thin coating of the phosphor followed by a thermochromic and three phosphor coatings. No surface density measurements were made because this particular faceplate was too heavy for our analytical balances. A thin coating of phosphor was applied initially to the one section with the hope that the phosphor would be a poorer conductor of heat than the large mass of the CRT faceplate.

The results of the CRT tests showed that the two sections behaved similarly, except that the color change was better without the extra phosphor coating between the glass and the thermo-chromic. The beam currents in these tests were rather large and were measured by the meter monitoring the Aquadag current. At 10 and 20 kV and a fixed spot size of approximately 0.2 cm diameter, beam currents of approximately 50 microamperes and 30-40 microamperes, respectively were required to achieve a color change as measured by the Aquadag current meter. Although the Aquadag current reading is somewhat higher than the Faraday cup, these are somewhat large beam currents. The color change is also not as pronounced and fades very quickly. Fluorescence was again achieved, but the color was darkened somewhat by a larger amount of $PbI_2 \cdot 2AgI$ than was used in the previous experiments.

Thus, the hybrid system $PbI_2 \cdot 2AgI$ – P-14 was selected for the sealed CRT. The thermochromic has good thermal and vacuum stability. It is necessary to protect the material from light, especially at wavelengths shorter than 400 mμ after the thermochromic has been exposed to CRT vacuum conditions. It may also be necessary to have a phosphor coating to protect the thermochromic from electrical breakdown.

3.2.2 SANDWICH PREPARATION STUDIES OF Ag_2HgI_4

If there was any possibility of using Ag_2HgI_4 as the candidate material in the sealed CRT, a technique had to be developed to prevent the loss of HgI_2 at the high vacuum and heat treatment process necessary for a sealed CRT. Therefore, in addition to the effect reported

under 3.2.1 the following studies for encapsulating and protecting the Ag_2HgI_4 were conducted.

3.2.2.1 RESIN SANDWICHED THERMOCHROMIC

A weighed sample of Ag_2HgI_4 was sprayed evenly onto an ordinary glass plate. A thin coating of Dow 332 epoxy was sprayed over the thermochromic. This epoxy is used with an amine hardener and a toluene-acetone solvent. The sample was evacuated to a pressure of 10^{-7}-10^{-8} Torr at room temperature to remove the solvent. The epoxy did not protect the Ag_2HgI_4 in the high vacuum environment. The percent weight loss was 15.5 percent after approximately 24 hours and 19.9 percent after 48 hours. The sample seemed to have decomposed since predominantly the yellow color of AgI was noted.

3.2.2.2 GLASS SANDWICH SEALED BY SAUEREISEN CEMENTS

Sauereisen cements were investigated as possible materials since they are reported to be stable to $1000°C$. A Sauereisen technical representative recommended Sauereisen #31 and Insa-Lute as the most suitable of the Sauereisen cements for bonding glass-to-glass in a high vacuum system. Sauereisen #31 consists of a filler powder and a liquid binder. The cement hardens when the liquid evaporates either at room temperature or at slightly elevated temperatures. Once hardened, the cement is claimed by the manufacturer to be stable to $1000°C$.

Sauereisen #31 is rather difficult to apply since it is not very adherent to glass during the application. A sandwich configuration was made in the usual manner except that micro-sheet glass was not used. It was observed that when the cement dried at room temperature, it trapped some of the liquid binder inside the sandwich. This trapped liquid caused cracks in the glass when heat was applied. The cement was also rather brittle. Rather than continue with this material we chose to look at alternative materials.

Another sandwich was made with the Insa-Lute cement. All of the edges of the sandwich were sealed except for a small corner. The sample was pumped to evaporate any trapped solvent. Then the open corner was sealed with the cement. However, cracks appeared in the cement after it hardened. It was also found that the cement was very brittle and could be chipped easily. Because of this brittleness, Sauereisen cement will present difficulties on application.

3.2.3.3 GLASS SANDWICH SEALED BY AgCl CEMENT

Attempts were also made to seal glass with Ag Cl as the cement. AgCl is a powder that bonds to the glass at its melting point (455°C). Microsheet is more convenient in these experiments since the AgCl fusion temperature is more easily achieved and controlled through microsheet than thicker glass.

However, it was still difficult to heat the edges of the microsheet to the high fusion temperature of the AgCl without overheating the interior of the glass where the thermo-chromic would be deposited. There was also a tendency of the microsheet to crack under localized high temperatures. It was also noted that upon melting, the AgCl tended to contract into a non-uniform layer that might prevent a tight vacuum seal.

3.2.2.4 GLASS SANDWICH SEALED BY PYROCERAM FUSION

Attempts were made to seal the edges of two thin conducting glasses by fusing the glass with a gas-oxygen microtorch. At the temperatures hot enough to fuse the glass, the glass would crack upon cooling even when metal heat sinks were used. These conducting glasses or microsheets are very difficult to fuse together according to a Corning Glass representative. He recommended matching the coefficient of expansion of the microsheet with a mixture of Corning cements called "Pyroceram". These cements which are a sort of ground glass in a vehicle would have a lower softening point than the microsheet (720°C).

Fusion bonding of the microsheet with Pyroceram was attempted with the microtorch. The glass cracked under the localized heat. A more controlled method of heating was

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attempted in which steel blocks were heated by a flame to a temperature $480^{\circ}C$, which is above the melting point of Pyroceram and below the strain point of the microsheet. The temperature was measured by a surface thermometer which was accurate to about ± 2 percent. This thermometer was more satisfactory than the Tempilaq points which had been tried as temperature indicators. The microsheet sandwich was placed between the two heated steel blocks in an effort to fuse the Pyroceram. The Pyroceram melted, but the glass cracked upon cooling. A Corning technical representative stated that the microsheet could crack at these temperatures which were below the strain point. There are definite problems in trying to prevent the microsheet from cracking under the temperature gradients that occur in this process.

3.2.2.5 GLASS RESIN, TYPE 650

Glass resins are thermosetting silicones that are stated by the vendor to be stable up to $450^{\circ}C$ with little or no outgassing under vacuum. However, the bond strength is only about 1/10 that of an epoxy. Also, resin coatings thicker than 1 mil tend to be somewhat brittle. It is necessary to heat the resin in order to properly cure it. The cure is a function of both time and temperature. The cure cycles recommended by Owens-Illinois are followed as closely as possible, but there is the limitation imposed by the thermal instability of Ag_2HgI_4.

The first configuration in which this resin was tested was designed to determine if the resin alone could prevent decomposition of the thermochromic. A mixture of 2 parts Ag_2HgI_4 to 1 part of the resin by weight in butanol which is a solvent for the resin was sprayed onto thin conducting glass. Butanol was selected as the solvent for spraying because of its relatively high viscosity and density which would tend to produce good dispersions of Ag_2HgI_4. The sample was air and vacuum dried at room temperature. Then a partial cure was attempted by heating the sample at $80^{\circ}C$ under vacuum for about 15 minutes. The coating appeared to be fairly hard upon cooling to room temperature. The sample was again heated under vacuum at gradually increasing temperatures. Noticeable decomposition involving about a third of the area occurred at $80 - 90^{\circ}C$. There was a total loss of the HgI_2 at approximately $110^{\circ}C$ over a period of 2 1/2 hours.

Two sandwich configurations were made of the resin-thermochromic mixture. The first sandwich was made by sealing with the resin the edges of the glass substrate containing the mixture, described above, to another glass plate. Preparation of the second sandwich involved dipping the glass plate coated with the resin-thermochromic mixture into the resin solution. The edges were then sealed with the glass resin. Some curing of the resin was performed at the appropriate stages during the preparation. It was done to prevent any continuous passageways produced by the evaporation of the butanol through which HgI_2 might escape. However, the one mil thickness limits the number of coatings that can be applied. There was appreciable decomposition of the Ag_2HgI_4 upon heating to 120 - 130°C under vacuum in both samples over a period of 1 1/2 hours. Since the results were not very promising with the Type 650 resin, it was decided to next look at the Type 100 resin.

3.2.2.6 GLASS RESIN TYPE 100

Ag_2HgI_4, encapsulated in Owens-Illinois glass resin polymer Type 100, was prepared at NASA/Electronics Research Center for testing in the CRT. Reversible thermochromic changes were achieved in the thinner sections of this sample in the CRT but not in the thicker sections. Thin films of the resin-thermochromic mixture are needed for further testing. Various ratios of resin to thermochromic in different solvents were therefore prepared.

Three samples of a 1:1 mixture of thermochromic and resin deposited from a butanol dispersion were prepared. An attempt was made to cure one sample by placing it in a 150°C oven. The Ag_2HgI_4 decomposed in about 20 minutes. A second sample was placed in a 100°C oven for overnight curing which also produced decomposition of the Ag_2HgI_4. The third sample was made into the sandwich configuration and cured overnight at 100°C. Decomposition of Ag_2HgI_4 occurred only in a corner of the sandwich indicating a pinhole leak. A further treatment of the sandwich at 164°C for 1 hour produced further decomposition only in this corner.

2:1 mixtures of resin to thermochromic were prepared in butanol and also in methanol. The methanol was used because of its relatively high evaporation rate. One coating of the

mixture from each solvent was cured overnight at 100°C. Ag_2HgI_4 decomposed in each coating. Then a sandwich was made from each solvent. There was no decomposition in either sandwich after overnight curing at 100°C. Further heating of each sandwich at 164°C for about 1 hour produced no decomposition of the Ag_2HgI_4.

A 3:1 mixture of resin to thermochromic was prepared in methanol solvent. Ag_2HgI_4 again decomposed upon overnight curing at 100°C. A sandwich configuration of the same composition was again stable at the 100°C curing temperature and also at 164°C for several minutes.

10:1 mixtures were prepared in methanol and also in ethanol. It was found that at higher concentrations increasingly poorer coatings were being obtained with methanol as solvent. The methanol mixture was approximately 50 percent decomposed after overnight curing at 100°C. The coating had numerous cracks also. Since it was felt that this may be due to too rapid evaporation of the methanol during spraying, ethanol was tried as a solvent. Better coatings were obtained with ethanol.

A fast cure as described by Owens-Illinois was attempted with the ethanol mixture. The sample was dried after spraying in a procedure similar to that described in "The Technology of Solvents and Plasticizers" by A. K. Doolittle.[17] The sample was then cured at 200°C for 15 minutes. Ag_2HgI_4 decomposed under these conditions. There are definite difficulties in this technique.

3.2.2.7 PARYLENE SEALANT

A new series of polymers, based on poly(p-xylene), which have the generic name of Parylene have been developed by Union Carbide Corporation. It is an unusual system in that the monomer polymerizes as it condenses from the vapor state and coats any substrate. This method of film deposition would presumably enable one to obtain a coating free of pin-holes and also practically free of low molecular weight volatiles. It is also stated by the manufacturer that this polymer forms a conformal coating with a very low permeability to gases.

A sample of Ag_2HgI_4 was prepared on a glass substrate. A two mil thick coating of Parylene C, a poly(monochloro-p-xylene), was deposited as a film coating the thermochromic. Parylene C formed a transparent coating, but the adhesion was poor. The film could be pulled off the thermochromic fairly easily.

3.2.3 COMPUTER INPUT APPLICATION

Ag_2HgI_4 was evaluated for a novel computer input application. It was planned to take advantage of the unique electrical properties of silver mercuric oxide in a combination display-computer input device. The device is similar to the Rand Tablet[18] in that it is a two-dimensional graphic input tablet. Basically, the Ag_2HgI_4 serves as a writing surface in conjunction with a heating stylus (instead of a light pen). A color change occurs along the path of interaction between heat given off by the stylus and the writing surface. This should cause a sharp increase in the electrical conductivity through the thermochromic [1]. Signal differences could be detected by means of an electronic scan to measure resistivity changes.

3.2.3.1 CONCEPTS

Several configurations for an input tablet have been considered. These included the utiliza-tion of bulk as well as surface conductivity in Ag_2HgI_4. Figures 17 a and 17 b show schematics of tablets based on bulk conductivity in Ag_2HgI_4. The configuration shown in Figure 18 makes use of the surface conductivity in the thermochromic.

In Figure 17 the thermochromic material is sandwiched between a plate of conducting glass and a spaced parallel array of conducting paths. Each of the conducting paths, as well as the conducting glass, are connected to a power supply and an electronic scan mechanism. Thus, a signal corresponding to any of the conducting lines can be detected when a short circuit between the conducting path and the conducting glass occurs (by heating of the thermochromic in between).
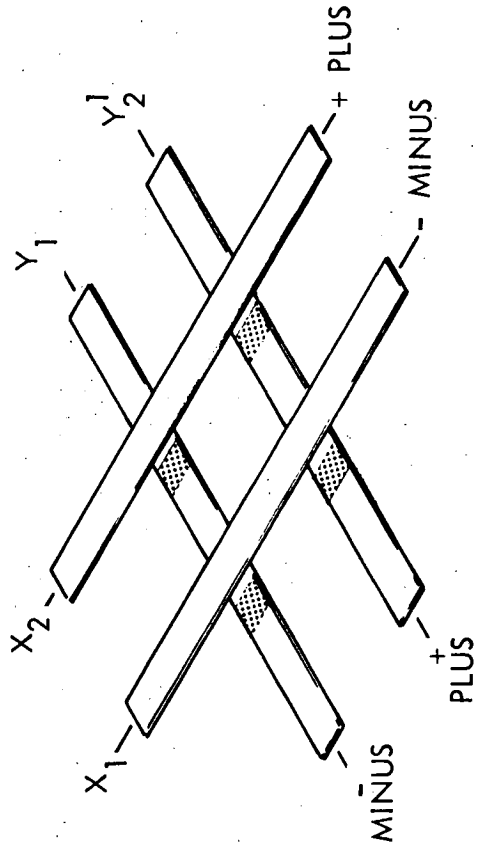
FIGURE 17

SCHEMATIC OF COMPUTER INPUT TABLET
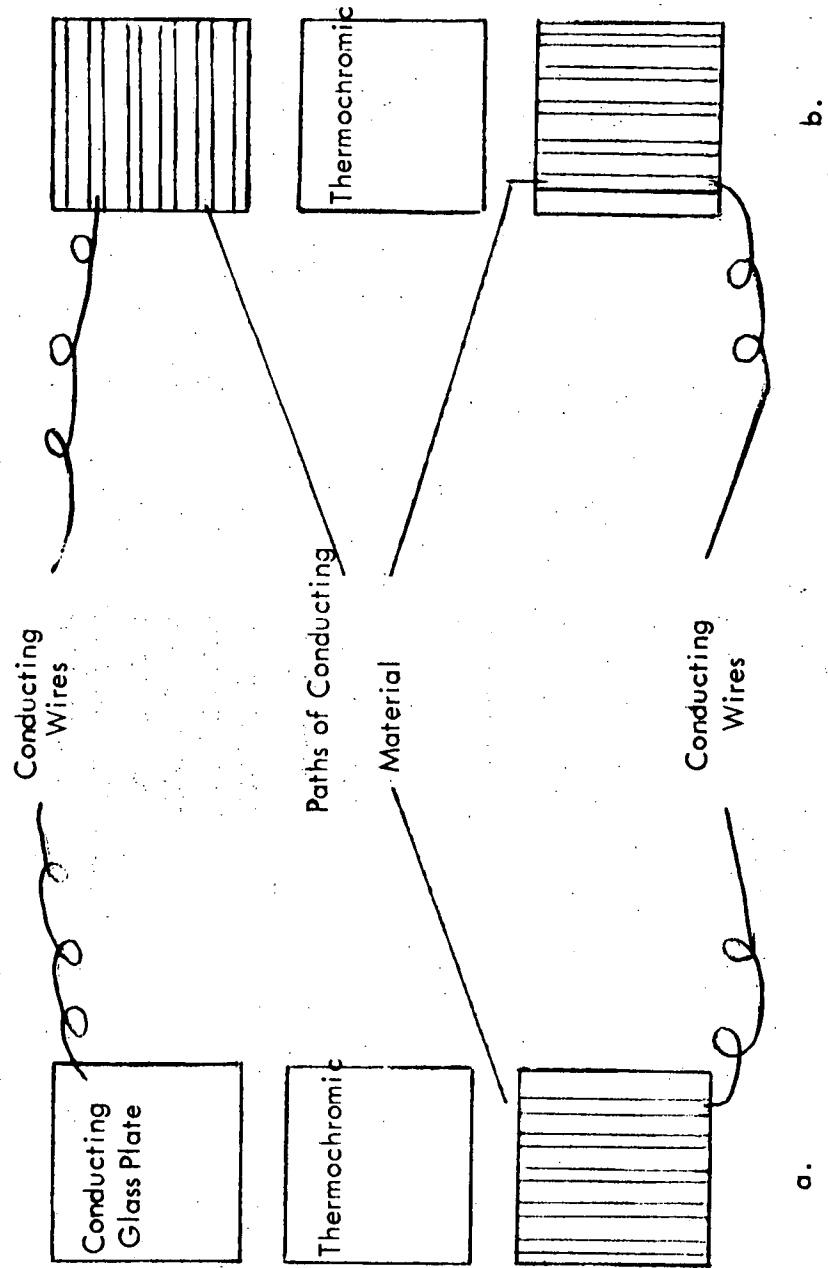
FIGURE 18

COMPUTER INPUT

The configuration shown in Figure 17 b should enable one to locate a point (both X and Y coordinates) in a plane. Here the thermochromic material is sandwiched between parallel arrays of conducting paths that are perpendicular to each other. All the other features in this configurations are similar to those described for Figure 17a.

In Figure 18 the Ag_2HgI_4 is embedded between conducting lines X_1, X_2, Y_1, Y_2, with complete isolation between the X_1X_2 and Y_1Y_2 planes. Thus, X_1 and X_2; Y_1 and Y_2 are connected only via the thermochromic material. When the material is heated there is a lowering in resistance between X_1 and X_2, and Y_1 and Y_2 thus, enabling the detection of the coordinates of the hot spot. This configuration can, of course, be expanded in a larger structure.

3.2.3.2 CONCEPT EVALUATION

Before any computer input prototype device is built it is important to test the workability of principles involved on a simple "one cell" configuration. Important factors to be considered in preparing any prototype include the type of electrodes to be used to make good electrical contact to the thermochromic, as well as the thickness of the thermochromic layer.

Several materials were considered as electrodes for both sandwich and nonsandwich configurations. These included: aluminum, gold, conducting glass, and graphite.

Combinations of materials and method outlined in the previous paragraphs were utilized in attempting to build a simple "one cell" configuration of the computer input tablet. Conducting glass was used as one of the electrodes in all the sandwich configurations investigated, and also as a protective means for the thermochromic. The Ag_2HgI_4 was sprayed onto the glass in all the experiments. The thermochromic material was heated through the glass with a soldering iron; resistivity measurements were made by means of an ohmeter.

The following observations were made based on the results obtained from the experimental "one cell" configurations.

o   It was found that when aluminum or gold were used as electrodes a resin had to be incorporated into the thermochromic to obtain good electrical contact.

o   Vapor deposition of the electrodes was   far superior to painting or spraying methods in that better uniformity was obtained.

o   Aluminum was found to be unsuitable as an electrode due to its high chemical reactivity. A battery effect was probably obtained between the aluminum electrode and the silver mercuric iodide.

o   Since the thermochromic and binder are heated to a high temperatures when electrodes are vapor deposited on them, it is essential that the binder had previously undergone proper curing. It was found that improper curing of the binder led to discolored Ag_2HgI_4 in vapor deposition processes.

o   Experiments performed with painted graphite as the second electrode did not yield the desired effect – the thermochromic discolored at the area of contact with the graphite. Since this process involved heating, the discoloration, again, may be attributed to improper curing of the resin.

o   Gold appears to be the material most useful as a second electrode, mainly because of its inertness. However, experiments involving gold did not yield the expected results of a sharp rise in the electrical conductivity upon heating of the thermochromic. The fault here

probably lies in the experimental techniques employed. Resistivity measurements should be carried out by means of gold rather than copper probes, since the latter probably produce a contact resistance with gold electrodes. Unsuccessful results could also be attributed to the unintentional heating of the electrodes, in addition to the thermochromic, which would have the effect of raising resistivities.

3.2.4 CONTRAST ENHANCEMENT AND WRITING

An attempt was made to demonstrate enhancement in the color contrast in thermochromic $PbI_2 \cdot 2AgI$ composition with the aid of appropriate filters. It should be noted, however, that $PbI_2 \cdot 2AgI$ gives very good contrast without filters, comparable to Ag_2HgI_4 and that these experiments serve to suggest ways to approach maximum contrast at the expense of brightness. Filters selected included Corning 4-72 glass and Wratten gelatin filters 21, 22, and 23A. A plot of the transmission characteristics of Corning 4-72 along with the reflectance spectra of hot and cold forms of $PbI_2 \cdot 2AgI$ is shown in Figure 19. Transmission characteristics of the Wratten filters are shown in Figure 20. The band edge for all four filters cuts sharply across the change in reflectance of the thermochromic.

No contrast enhancement was noted with the Corning 4-72 or Wratten 23A, but to the naked eye contrast enhancement was noted through Wratten filters 21 and 22. Color pictures were made of the transition through Wratten 21, 22 and 23A, but these had not been processed in time for this report.

Direct laser writing was attempted on the $PbI_2 \cdot 2AgI$ fired composition. The unfocused beam, 3/16" in diameter of a neodymium glass laser was used in this experiment. The output of the laser was at 1.06μ at an estimated 0.5 joules for a duration of $500\,\mu$sec. The flash input consisted at 5000 joules. The fired mixture with a 3 percent resin content was sprayed onto a glass plate and mounted six inches away from the laser, with the thermochromic facing the beam. No change in color was observed in the thermochromic upon exposure to the beam.

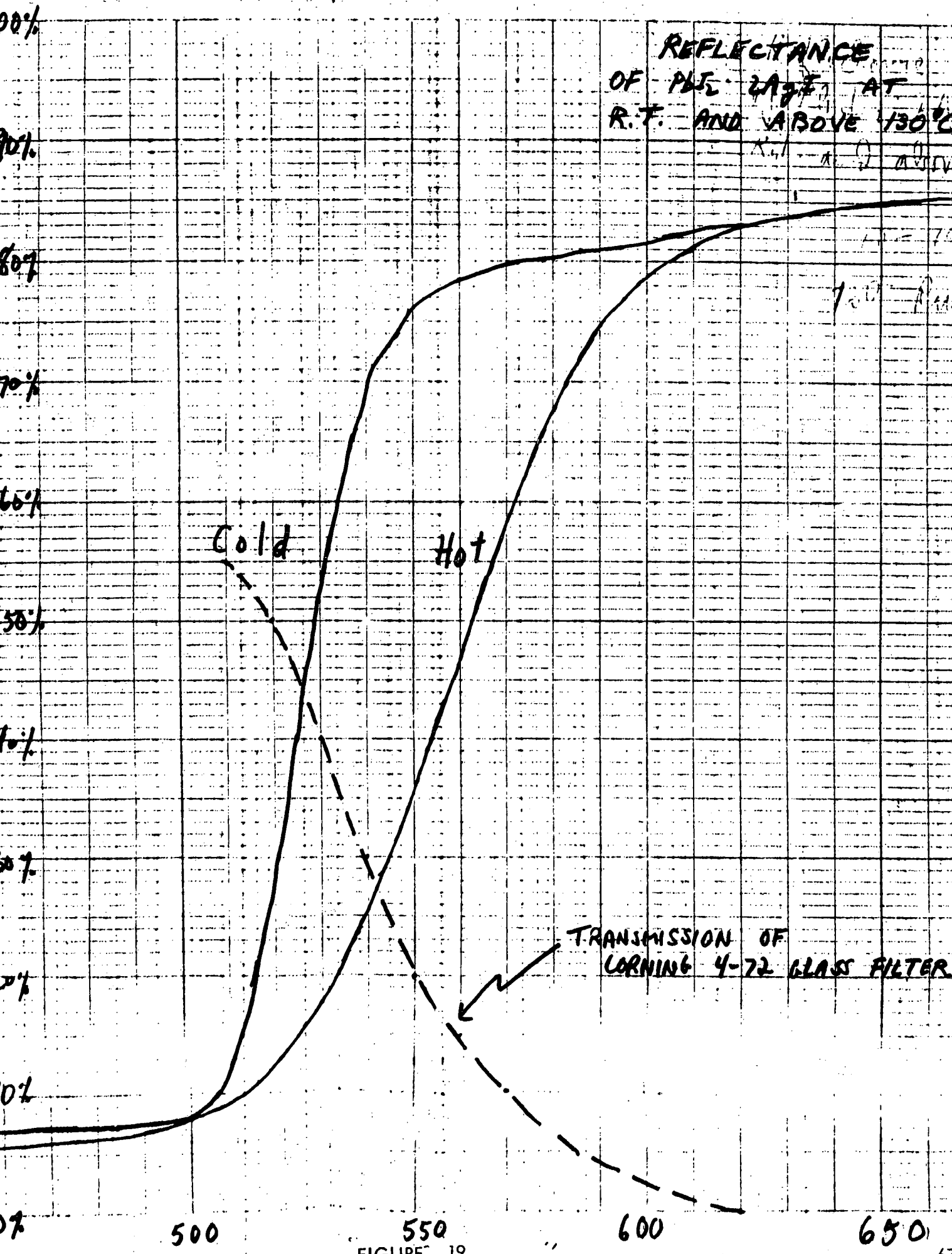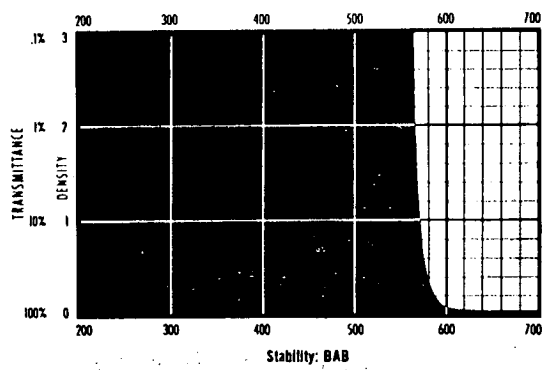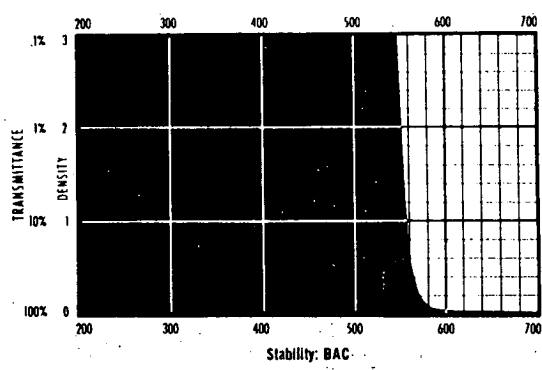REFLECTANCE
OF $PbI_2 \cdot 2AgI$ AT
R.T. AND ABOVE +30°C

Cold   Hot

TRANSMISSION OF
CORNING 4-72 GLASS FILTER

500   550   600   650

FIGURE 19

Stability: CBB

Stability: BAC

Stability: BAB
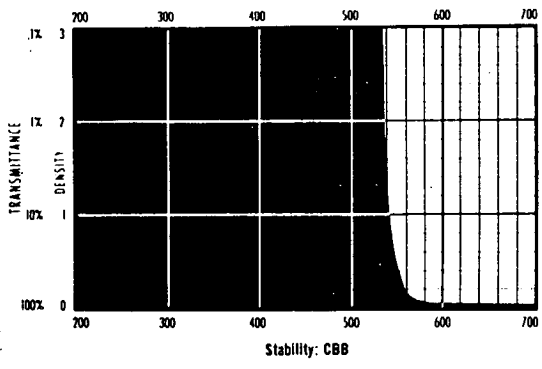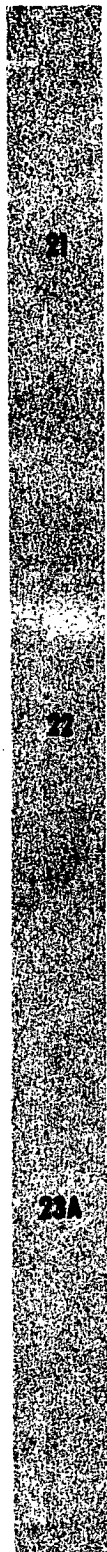
WAVE LENGTH	PERCENT TRANSMITTANCE		
	No. 21	No. 22	No. 23A
400			
10			
20			
30			
40			
50			
60			
70			
80			
90			
500			
10			
20			
30			
40	2.50		
50	29.0	0.25	
60	65.0	19.0	
70	80.6	60.0	11.0
80	85.4	81.0	47.0
90	87.3	87.0	69.6
600	88.1	88.5	82.7
10	88.7	89.0	85.8
20	89.0	89.5	87.2
30	89.5	89.8	87.9
40	89.9	90.0	88.5
50	90.2	90.1	89.0
60	90.4	90.2	89.4
70	90.5	90.3	89.6
80	90.5	90.4	89.8
90	90.6	90.5	90.0
700	90.6	90.6	90.2
Luminous Transmit.	45.6	35.8	25.0
Dominant Wave Lgth.	588.9	595.1	602.7
Excitation Purity	99.9	99.9	100.0

FIGURE 20

4.   CATHODE RAY TUBE (CRT) FABRICATION

Arrangements were made to deliver to Fairchild-Dumont, a manufacturer of electron tubes, four glass envelopes coated with $PbI_2 \cdot 2AgI$ on the glass faceplate and a second coating of P-14 phosphor over the thermochromic. Fairchild-Dumont could then introduce the electron gun, proceed with a modified conventional bakeout and seal the tubes.

It was planned that one of the tubes would have an aluminized coating above the phosphor for possible enhancement of the fluorescence and thermochromism. The sealed cathode ray tubes should fluoresce at low beam currents and constant high voltage. The same tube should also produce a thermochromic change with the fluorescence at higher beam currents.

4.1   PREPARATION OF THE THERMOCHROMIC AND PHOSPHOR COATINGS ON THE CRT ENVELOPES

In the preparation of the sealed CRT, it was planned to prepare the $PbI_2 \cdot 2AgI$ and P-14 phosphor coatings by separate depositions from liquid slurries. Coatings with a good physical appearance of the thermochromic material were obtained by depositing onto a demountable CRT faceplate from either a methanol slurry or a xylene slurry. The supernatant liquids were evaporated on a hot plate. Although the physical appearance of the coatings were about the same from solutions of at least 60 ml in volume, there was a deterioration in the color contrast during the thermochromic change especially from the methanol solvent. Since the glass resin which was 3 percent by weight ratio to thermochromic is soluble in methanol, and is only slightly soluble in xylene, a solvent mixture was suggested. Therefore, it was decided initially to use 75 percent xylene and 25 percent methanol mixture in the first coating process.

An approximately 60 ml slurry that contained about one gram of $PbI_2 \cdot 2AgI$ was poured through a glass tube into each of four glass envelopes furnished by Fairchild-Dumont. The glass envelopes had been placed previously in a large oven which could be heated gradually up to above $200^\circ C$. Air flow was introduced through a small copper tubing to aid in the

evaporation of the solvent since the oven had only two small openings to the atmosphere.

It proved to be very difficult to remove the last traces of xylene even after heating up to 200°C in this particular oven. A small amount of solvent appeared to be trapped in the resin that also may not have cured properly due to incomplete removal of solvent. When the P-14 phosphor was applied in the same manner, the thermochromic and phosphor coatings blistered badly during the glass resin curing cycle. This may have been due to trapped solvent.

Butyl alcohol (b.p. = 118°C) was then substituted for xylene (b.p. = 137 - 139°C). The thermochromic produces a very good slurry with butanol which has a fairly high viscosity. However, the problem of evaporation without blistering the coating still remained.

The process that Fairchild-Dumont uses in applying their phosphor coatings was observed. Fairchild ball mills their phosphors in a water slurry, if necessary, to achieve a particle size of 15 - 20 microns. This slurry is diluted with 150 cc of water and a 15 cc solution of potassium silicate. The slurry is further diluted with 350 cc of a solution referred to as gel that contains acetone and alcohol. The resultant mixture is poured into the glass envelope through a thistle tube and allowed to settle for half an hour. The glass envelope containing the solution is clamped on top of an automatic pouring table. After the settling process is completed, the supernatant liquid is poured automatically out of the envelope. The coating is then air dried and baked. If the particle size is larger than 15 - 20 microns, the coating will pull away from the faceplate during the decanting process.

This technique was attempted with the thermochromic material. The supernatant liquid was poured off manually, however. The thermochromic pulled away from the faceplate during the pouring process. P-14 phosphor was substituted for the thermochromic with no success. One of the problems is the difficulty in duplicating the same sort of decantation manually that is achieved automatically. It was then decided to siphon off the supernatent liquid with a gentle vacuum. The coating was subsequently air dried at room temperature. The dried

thermochromic coating appeared to have AgI color. When the coating was heated, the transition temperature occurred at approximately 150°C and the color change was similar to AgI. It was noted that the potassium silicate produced an immediate color change with $PbI_2 \cdot 2AgI$ in acetone when volatile solvent systems were being tested.

Methanol was tried again as the solvent. Methanol produces a good slurry with the thermochromic and is easily evaporated under a gentle air stream. Although the quality of the thermochromic change may not be quite as good after using methanol, the other advantages outweigh this. A slurry was prepared that contained one gram of thermochromic in approximately 60 ml of methanol. There was approximately 5 percent resin to thermochromic which ensured good adhesion to the faceplate during the addition of the phosphor. A half hour was allowed for the thermochromic to settle before the supernatant liquid was siphoned off. The coating was air dried at room temperature. The resin was cured at approximately 215°C for about 15 minutes. The phosphor slurry was then added in the same manner. A fairly good coating was achieved in three of the tubes. The four tubes were delivered.

4.2 TUBE SEAL-OFF AND ACTIVATION

The tubes were prepared as 5 FP cathode ray tubes. These are magnetic deflection and magnetic focusing cathode ray tubes that are capable of developing an anode current of 200 microamperes focused to a spot size of 0.020". The operating conditions and physical dimensions for the 5FP are identical to those described for the 5FPA cathode ray tube[14].

A modified conventional bakeout was used in the processing of these tubes. Normally these tubes are baked out at approximately 420°C for 1 - 2 hours. In this case the unaluminized tube was baked at a maximum of 250°C for about 2 1/2 hours. The aluminized tube was baked at a maximum temperature of 280°C for 2 1/2 hours. One of the tubes was ruined during the aluminizing process.

The cathodes were activated prior to the seal-off of the tubes in the conventional manner by Fairchild. Barium getter material was flashed from a small container connected to the electron gun onto the walls of the tube by RF heating to trap small amounts of residual

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gas. Since one tube was not coated very well initially and one was ruined during aluminization, two tubes were produced for testing.

4.3 TESTING OF CRT'S

Two tubes, one aluminized and one unaluminized were tested as to their operating condition at Fairchild-Dumont. Both tubes operated at voltages up to 10 kV and currents of approximately 25 microamperes. The aluminized tube was operated at 20 kV, but there was some arcing at this voltage. The beam was programed to scan rapidly over an area of at least two square inches at these voltages and currents. Therefore, the power density per unit area was small.

Fluorescence of the phosphor was achieved in both tubes, but the thermochromic coating may have been too thick and   reduced the phosphor brightness. Since approximately one gram of the thermochromic was used in the coating process, the surface density was estimated to be 9 mgs/cm^2. This is approximately the weight of material that Fairchild-Dumont uses for their phosphors to ensure a good faceplate coating.

The tubes were then transferred and tested at our facility. Fairly large beam currents of approximately 50 – 60 microamperes were obtained at 10 – 12 kV over a fairly large spot size. There was fluorescence of the phosphor. However, when the spot size was reduced to approximately 0.1 cm in the aluminized tube, the beam current dropped off rapidly from gassing of the tube. A thermochromic change was achieved with the unaluminized tube at 50 – 60 microamperes Aquadag current, 0.1 cm spot size and 12 kV. However, there was a rapid drop in current in this tube also. After the current dropped off, there was a bluish glow in the tube near the cathode indicative of a poor vacuum. Apparently there is gassing in the tube at the high power density levels required to produce a thermochromic change. Also, the initial vacuum in the tube was not too good according to Fairchild-Dumont.

The aluminized tube was reactivated by Fairchild-Dumont by flashing more Barium getter on the walls of the CRT. Also, the cathode was reactivated. The fluorescence of this tube was demonstrated at the Electronics Research Center on December 16, 1968. The appearance of

the tubes and associated apparatus are shown in Figures 21, 22, and 23.

Additional sealed tubes are now being processed. The bakeout temperature for these tubes will be at least 325°C and over a longer period of time. The tubes will be tested with the faceplate heated to nearly the transition temperature in order to reduce the beam power requirements.
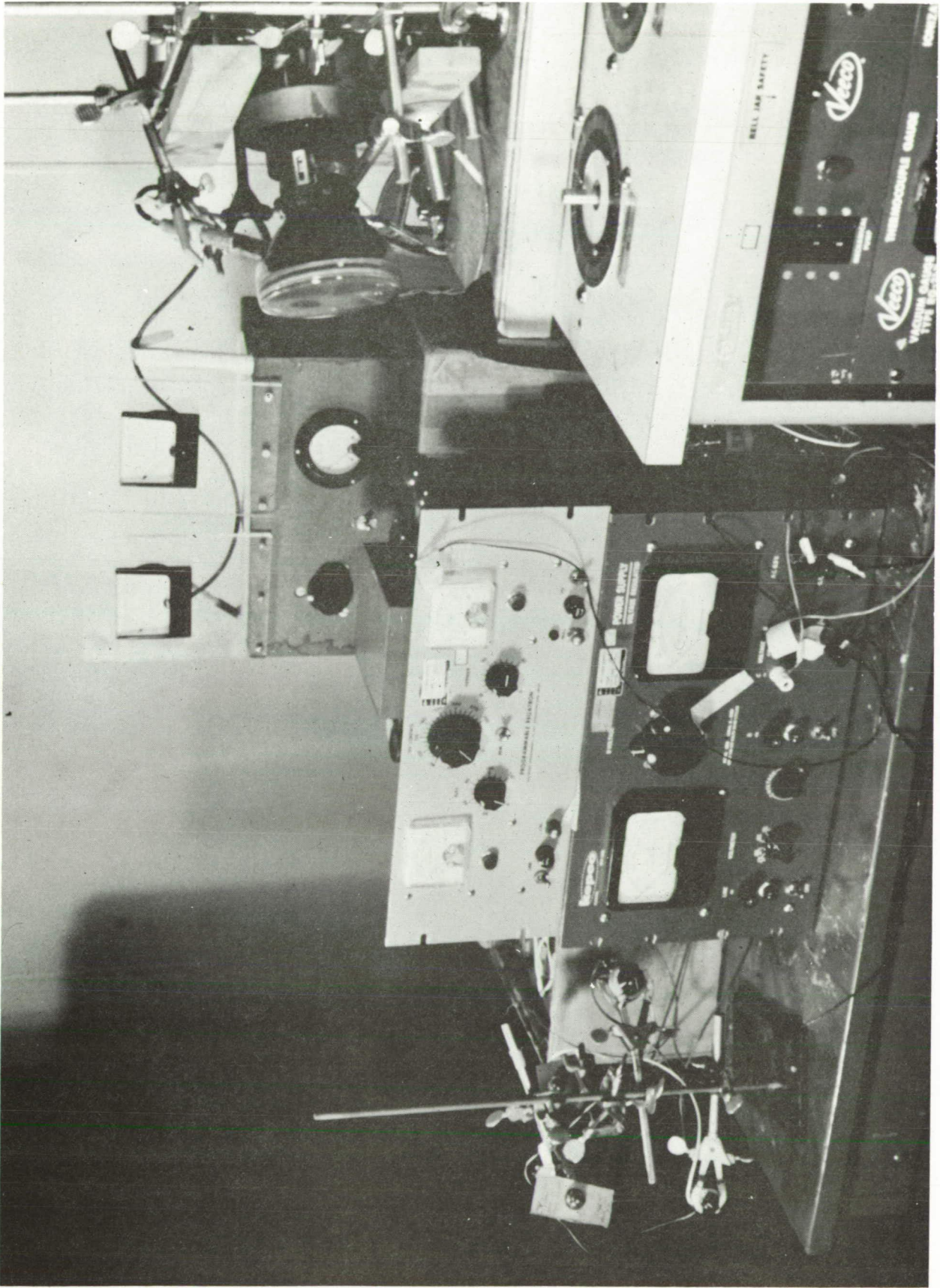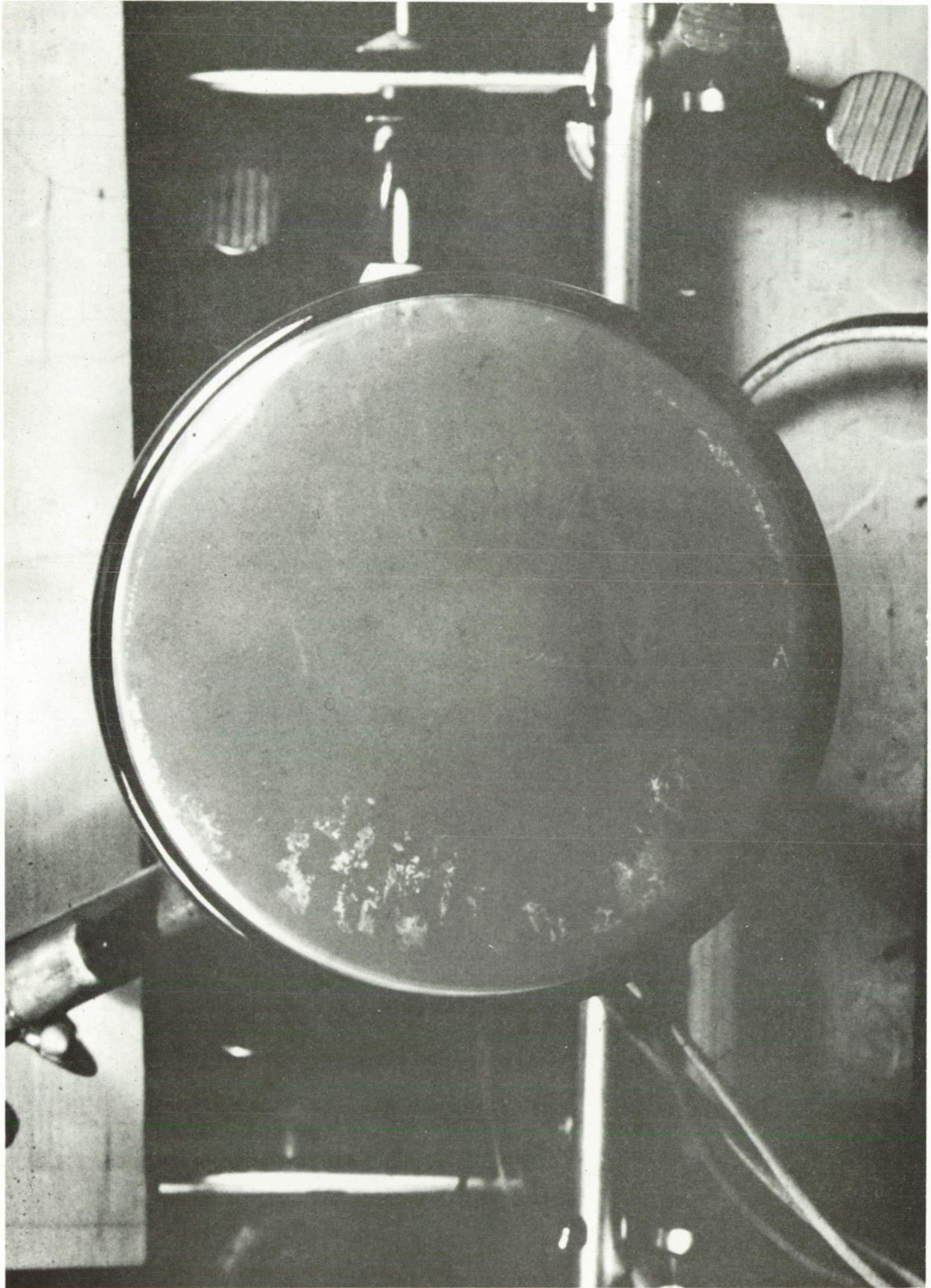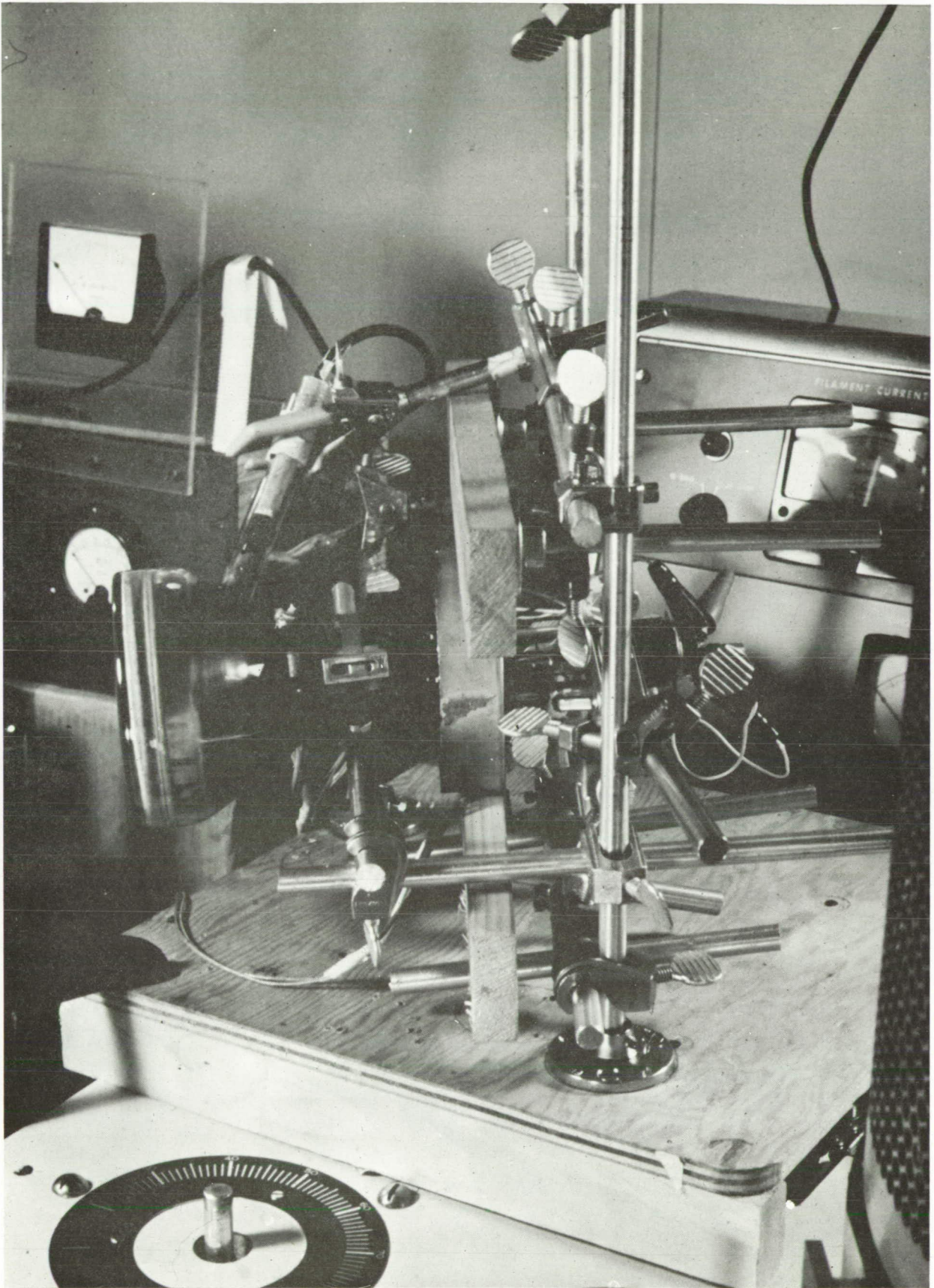
FIGURE 21

FIGURE 22

FIGURE 23

5. SUMMARY AND RECOMMENDATIONS

The main purpose of the program was the synthesis of thermochromic materials suitable for a wide range of display applications. In view of the applications investigated, the materials had to meet certain requirements, the most important of which included pronounced changes in color at convenient temperatures accompanied by sharp changes in electrical conductivities. For application to a conventional CRT technology, the materials had to possess high stabilities to vacuum and heat environments.

None of the previously described thermochromic materials possessed the necessary combination of stabilities and properties. Many compositional variations were synthesized. Although color transitions associated with order-disorder transitions were very sharp over narrow temperature ranges, the group as a whole tended to thermal and vacuum instabilities. Al_2O_3-Cr_2O_3 compositions which change color by expansion of the lattice were found to have poor color contrast over large temperature ranges, thus making them unsuitable for the applications investigated during this program.

A new composition, a $\sim$ 33 percent solid solution of PbI_2 in AgI, was developed which met all of the important physical requirements for a good candidate thermochromic material. It was found to be thermochromic with a sharp reversible color change from yellow to orange at $\sim$ 130°C. Weight loss studies showed no loss in weight under a vacuum of 10^{-7} Torr at room temperature for 80 days. In addition, this composition was found to be stable up to its melting point + $\sim$ 375°C. The phase diagram of this chemical system is surprisingly complex.

The only drawback in the $PbI_2 \cdot$ AgI composition was the tendency of some compositions to discolor when under high vacuum in room light. Discoloration took place to a lesser extent at room lighting under atmospheric pressure. However, this drawback is not considered to be serious and circumvention should be possible. In order to circumvent this phenomenon, a more intensive investigation of the material is necessary. Studies should include:

1. Further phase diagram and structural analyses.
2. The study of the effect of varying wavelength and composition on the tendency to discoloration.
3. Determination of the mechanism of discoloration.

Initially, two sealed cathode ray tubes were fabricated with faceplates containing a coating of $PbI_2 \cdot 2AgI$ thermochromic followed by a coating of P-14 phosphor. One tube also contained an aluminized coating over the phosphor for enhancement of the color change. These tubes were designed to produce phosphor fluorescence when the electron beam strikes the phosphor. Fluorescence and phosphorescence should be seen through the thermochromic. In addition, at higher beam energies, the energy of the beam absorbed by the phosphor should generate enough heat to induce a thermochromic transition in the $PbI_2 \cdot 2AgI$.

The tubes were tested. Phosphor fluorescence was obtained in each tube. The thermochromic coating was probably too thick since the phosphor brightness was relatively weak. Thermochromic transitions were achieved at high beam currents in the unaluminized tube. However, there was a rapid drop in current due to gassing of the tube. The high power density necessary to achieve the thermochromic transition could not be achieved in the aluminized tube because of rapid gassing of the tube.

It is apparent that both tubes were gassy because the initial bakeout temperature was not sufficiently high for thorough outgassing. It is recommended that a higher bakeout temperature and perhaps a longer bakeout time period be employed in fabricating new tubes. The limiting factor , of course, is the stability of the thermochromic material.

The large beam currents that are required to heat $PbI_2 \cdot 2AgI$ up to its transition temperature creates the possibility of overheating the areas exposed to the beam. The heat capacity of the glass faceplate substrate is responsible to a large extent for the high beam current requirements.

In order to reduce the power requirement somewhat, the faceplate may be heated by a separate power source to a temperature close to the transition temperature. This could reduce the beam current requirements. Another possibility would be to put a material between the faceplate and the thermochromic that is transparent and also possesses a lower thermal conductivity than glass.

Additional tubes are now being processed and will be exposed to higher bakeout temperatures. the thermochromic coating thickness will be reduced which will enable the phosphor fluorescence to appear brighter. These new tubes will be tested with a heated faceplate.

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