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

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SINGER
KEARFOTT DIVISION

THERMOCHROMIC DISPLAY MATERIALS FOR USE UNDER WIDE
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Contract NAS 12-89

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ABSTRACT

This report documents the results of a three-year program to synthesize inorganic thermochromic 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 substitutions 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 electroluminescent 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 application is based upon the differential electrical conductivity of the high and low temperature 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 $\text{PbI}_2\text{-AgI}$ 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 $\text{PbI}_2\text{-2AgI}$ 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 $\text{PbI}_2\text{-2AgI}$.

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ADMINISTRATIVE INFORMATION

This 36-month program was sponsored by the NASA-Electronics Research Center, Cambridge, Massachusetts under Contract NAS 12-89. The NASA monitoring scientist was Mr. E. H. Hilborn. The Project Supervisor at the Singer-General Precision, Inc. Aerospace Research Center was Dr. Daniel Grafstein and the Principal Investigators were Dr. Jehuda Menczel and Mr. William L. Flint. Contributors to the first 24-month effort also included: Dr. Raymond P. Borkowski, Dr. Marvin J. Kornblau and Dr. Lies N. Finnie. Acknowledgements are also due to the following: Alfred Brauer for his assistance in the CRT work, Donald Yee and William M. Benko for their DTA analyses.

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 $Ag_2Hg_{1-x}Cd_xI_4$ ($x=0-0.40$), $Ag_2Hg_{4-x}Br_x$ ($x=0.17-1.40$) 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 $\text{Ag}_2\text{Hg}_{1-x}\text{Cd}_x\text{I}_4$ As A Function of X

<u>X</u>	<u>Transition Temperature Range ($^{\circ}\text{C}$)</u>
0	$47^{\circ} - 51^{\circ}$
0.05	$48^{\circ} - 55^{\circ}$
0.10	$48^{\circ} - 58^{\circ}$
0.15	$52^{\circ} - 63^{\circ}$
0.20	$51^{\circ} - 65^{\circ}$
0.25	$56^{\circ} - 67^{\circ}$
0.30	$62^{\circ} - 77^{\circ}$
0.35	$64^{\circ} - 82^{\circ}$
0.40	$68^{\circ} - 88^{\circ}$

TABLE 2

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

<u>Thermochromic</u>	<u>T_{trans} $^{\circ}\text{C}$</u>
Ag_2Hgl_4	50.5
$\text{Ag}_2\text{Hgl}_{15/4}\text{Br}_{1/4}$	43 ± 1
$\text{Ag}_2\text{Hgl}_{15/4}\text{Cl}_{1/4}$	43 ± 1
Cu_2Hgl_4	69.5
$\text{Cu}_2\text{Hgl}_{15/4}\text{Br}_{1/4}$	50 ± 1
$\text{Cu}_2\text{Hgl}_{15/4}\text{Cl}_{1/4}$	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.

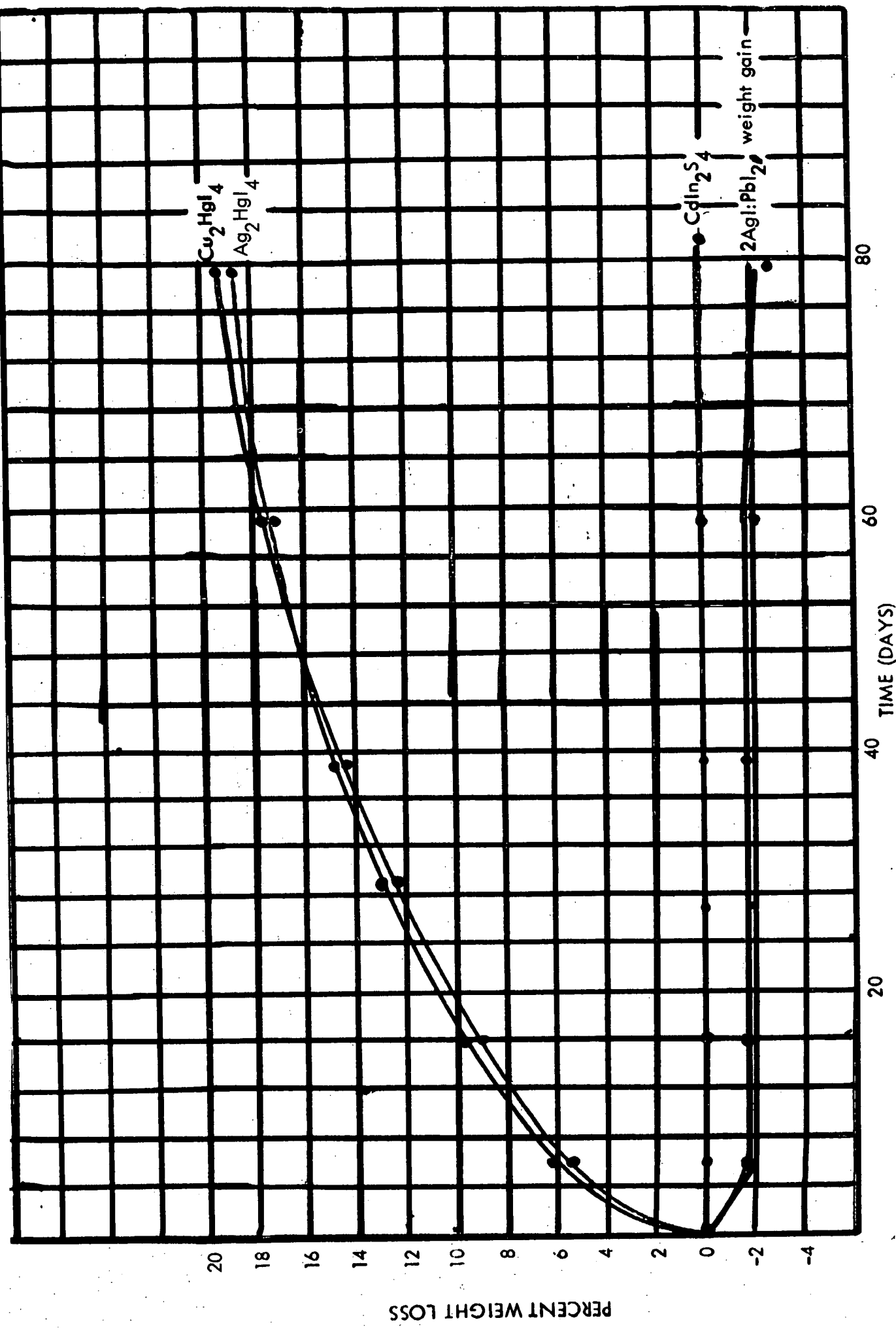
Stability tests of Ag_2HgI_4 and Cu_2HgI_4 ⁽⁴⁾ have shown that both are unstable with respect to vacuum and heat by evolving HgI_2 . Thus, it was reasoned that by substituting a different element completely for Hg, stability might be induced in the thermochromic. We substituted Pb for Hg and conducted 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 $\text{MM}'_2\text{X}_4$ where here $\text{M}=\text{Zn, Cd, or Hg}$; $\text{M}'=\text{Ga, In, Al}$ and $\text{X}=\text{S, Se or Te}$ 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°C and tends to change color from dull-orange to orange-red at $95\text{--}100^\circ\text{C}$ ⁽⁶⁾. The shift in the reflection spectrum was about $500\text{\AA}$. The color change, however, was too gradual and the visual contrast too weak for this material to be of practical use.



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

FIGURE 1

TABLE 3

DESCRIPTION OF TERNARY CHALCOGENIDES

Compound	Color	X-ray	Reflectivity Shift($\text{\AA}$)
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)	-----	----
$\text{ZnGa}_2\text{S}_3\text{Se}$	yellow-green	Tetragonal	75

n.d. = not determined

(a) = color obtained from literature

--- Attempts to prepare these compounds were unsuccessful

2.2 CRT EXPERIMENTS

It was calculated that it was possible to achieve a thermochromic change in materials such as Ag_2Hgl_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_2Hgl_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_2Hgl_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_2Hgl_4 was exposed directly to the electron beam. It tended to decompose. It was concluded that in order to use Ag_2Hgl_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 nichrome 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°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.

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 $\text{PbI}_2 \cdot \text{AgI}$ compositions. These will be discussed independently.

3.1.1 SUBSTITUTION COMPOUNDS

Numerous substitution compounds were prepared. Substituted iodides were synthesized by firing at $400\text{--}500^\circ\text{C}$ 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 $\text{PbI}_2 \cdot \text{AgI}$ 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 convenient transition temperatures ($100 - 140^\circ\text{C}$) from yellow to orange, depending on composition. 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 $\text{AgI} \cdot \text{PbI}_2$ compositions ranged from 15 hours to 4 days over temperatures of $400 - 600^\circ\text{C}$. 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 $\text{AgI} \cdot \text{PbI}_2$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ (33 mole percent PbI_2).

TABLE 4

DESCRIPTION OF SUBSTITUTION
COMPOUNDS

Nominal Compositions *	Color Change		Temperature	Remarks
1. $\text{ZnI}_2 \cdot 2\text{AgI}$	Green-yellow	→ brange-yellow	150-180°C	Poor color contrast
2. $\text{ZnI}_2 \cdot 2\text{CuI}$	No change		-----	Light sensitive
3. $\text{ZnI}_2 \cdot \text{AgI} \cdot \text{AgBr}$	No change		-----	-----
4. $\text{ZnI}_2 \cdot \text{CuI} \cdot \text{CuBr}$	Grey	→ green	~ 150°C	Poor color contrast
5. $\text{ZnI}_2 \cdot \text{AuI} \cdot \text{AgI}$	Greenish-yellow	→ dark green	Continuous	Irreversible change, accompanied by evolution of iodine.
6. $\text{ZnI}_2 \cdot \text{CuI} \cdot \text{AuI}$	No change		-----	-----
7. $\text{CdI}_2 \cdot 2\text{AgI}$	Yellow	→ yellow-orange	~ 250°C	Poor color contrast. Light sensitive
8. $0.05\text{AgBr} \cdot 1.95\text{AgI} \cdot \text{CdI}_2$	Yellow	→ orange	Continuous	Poor color contrast. Light sensitive.
9. $0.10\text{AgBr} \cdot 1.90\text{AgI} \cdot \text{CdI}_2$	Yellow	→ orange	Continuous	Poor color contrast. Light sensitive.
10. $\text{CdBr}_2 \cdot 2\text{AgBr}$	Yellow	→ orange	Continuous	Poor color contrast.
11. $0.05\text{AgI} \cdot 1.95\text{AgBr} \cdot \text{CdBr}_2$	Yellow	→ orange	Continuous	Poor color contrast. Light sensitive.
12. $\text{AgBr} \cdot \text{AgI} \cdot \text{CdI}_2$	Pale yellow	→ yellow	~ 150°C	Poor color contrast.
13. $\text{CdI}_2 \cdot 2\text{CuI}$	Green-yellow	→ orange	180 - 220°C	Poor color contrast. Light sensitive.
14. $0.05\text{CuBr} \cdot 1.95\text{CuI} \cdot \text{CdI}_2$	Green-yellow	→ orange	181 - 210°C	Poor color contrast. Light sensitive.
15. $0.10\text{CuBr} \cdot 1.90\text{CuI} \cdot \text{CdI}_2$	Green-yellow	→ orange	168 - 208°C	Poor color contrast. Light sensitive.
16. $\text{CdBr}_2 \cdot 2\text{CuBr}$	No change		-----	-----
17. $0.05\text{CuI} \cdot 1.95\text{CuBr} \cdot \text{CdBr}_2$	No change		-----	Light sensitive.

18.	$0.10\text{CuI} \cdot 1.90\text{CuBr} \cdot \text{CdBr}_2$	No change	-----	Light sensitive.
19.	$\text{CdI}_2 \cdot \text{CuI} \cdot \text{CuBr}$	Tan → green	~ 150°C	Color change irreversible.
20.	$\text{AgI} \cdot \text{CdI}_2$	Tan → yellow	60 – 90°C	Poor color contrast. Light sensitive.
21.	$\text{AgI} \cdot 2\text{CdI}_2$	Pale yellow → bright yellow	130 – 170°C	Poor color contrast. Light sensitive.
22.	$\text{CuI} \cdot \text{CdI}_2$	Yellow-green → orange	190 – 200°C	Poor color contrast. Light sensitive.
23.	$\text{CuI} \cdot 2\text{CdI}_2$	Yellow-green → orange	180 – 200°C	Poor color contrast. Light sensitive.
24.	$0.16\text{AgBr} \cdot 1.84\text{AgI} \cdot \text{PbI}_2$	Yellow → orange	~ 120°C	-----
25.	$\text{PbBr}_2 \cdot 2\text{AgBr}$	No change	-----	-----
26.	$\text{PbI}_2 \cdot 2\text{AgBr}$	Pale yellow → dark yellow	160 – 190°C	-----
27.	$\text{PbI}_2 \cdot \text{CuI} \cdot \text{CuBr}$	No change	-----	-----
28.	$\text{PbI}_2 \cdot 2\text{AuI}$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
29.	$\text{AuI} \cdot \text{AgI} \cdot \text{PbI}_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
30.	$1.5\text{AuI} \cdot \text{PbI}_2 \cdot 0.5\text{AgI}$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
31.	$\text{CuI} \cdot \text{AuI} \cdot \text{PbI}_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
32.	$\text{AgI} \cdot \text{AuI} \cdot \text{CdI}_2$	No change	-----	Decomposes with the evolution of iodine upon slow heating.
33.	$\text{AuI} \cdot \text{CuI} \cdot \text{CdI}_2$	Grey → green	~ 140°C	Gradual transition. Poor color contrast.
34.	$\text{AuI} \cdot \text{AgI} \cdot \text{PbBr}_2$	No change	-----	Decomposes with the evolution of iodine. Light sensitive.

*Based on materials charged.

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.

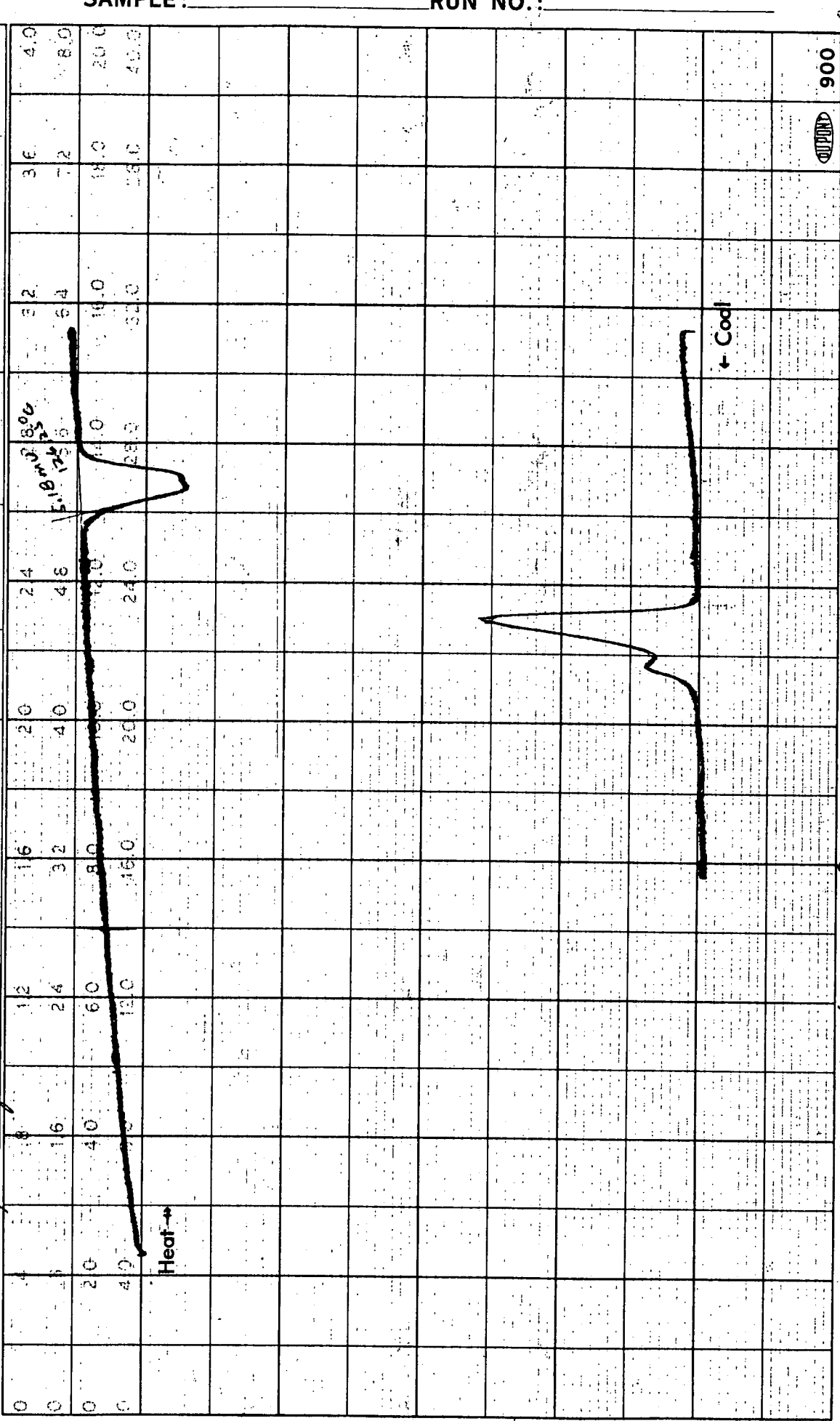
Figures 3 and 4 show DTA thermograms of two initially fired $\text{PbI}_2 \cdot 2\text{AgI}$ compositions in the horizontal furnace. DTA thermograms of an unfired mechanical mixture of identical composition (Figure 5) and of the two components PbI_2 (Figure 6) and AgI (Figure 7) are also shown. In every 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: Spel #9
161-2 Agi
 Components fired at 450°C
 for 2 days.

SIZE 7.230 mg
 REF. Empty Pan
 PROG. MODE Heat
 RATE 2.0 °C/min START 230°C

ATM. 0.8 160 MM
 T 0.8 0.000 0.000 0.000 0.000
 SCALE 0.8 0.000 0.000 0.000 0.000
 SHIFT 0 IN. Greg'd IN.
 BASE LINE SLOPE 0.000

ORIGIN: L. Flint / J. Henry



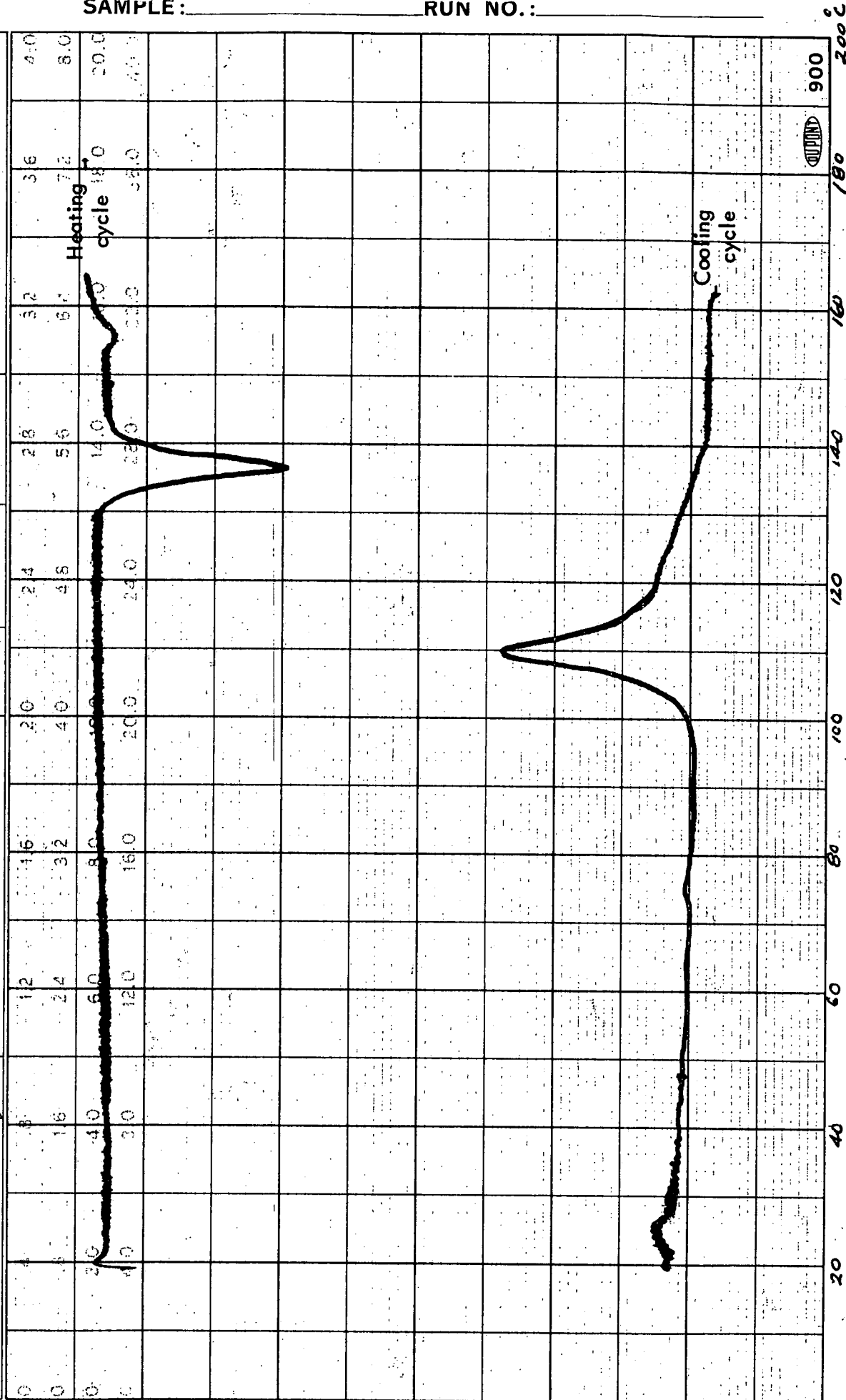
SAMPLE: _____ RUN NO.: _____

SAMPLE: Sample 14
PbI₂:2AgI components fired at
450°C for 15 hours.

SIZE 15.633
REF.
PROG. MODE Heat
RATE 2° START 250°C.

ATM. N₂ 760 MM RUN NO. 68-67
T ΔT
SCALE 0.8 MV IN. 0.001 MV IN.
SHIFT 0 IN. Accq'd IN. BASE LINE SLOPE

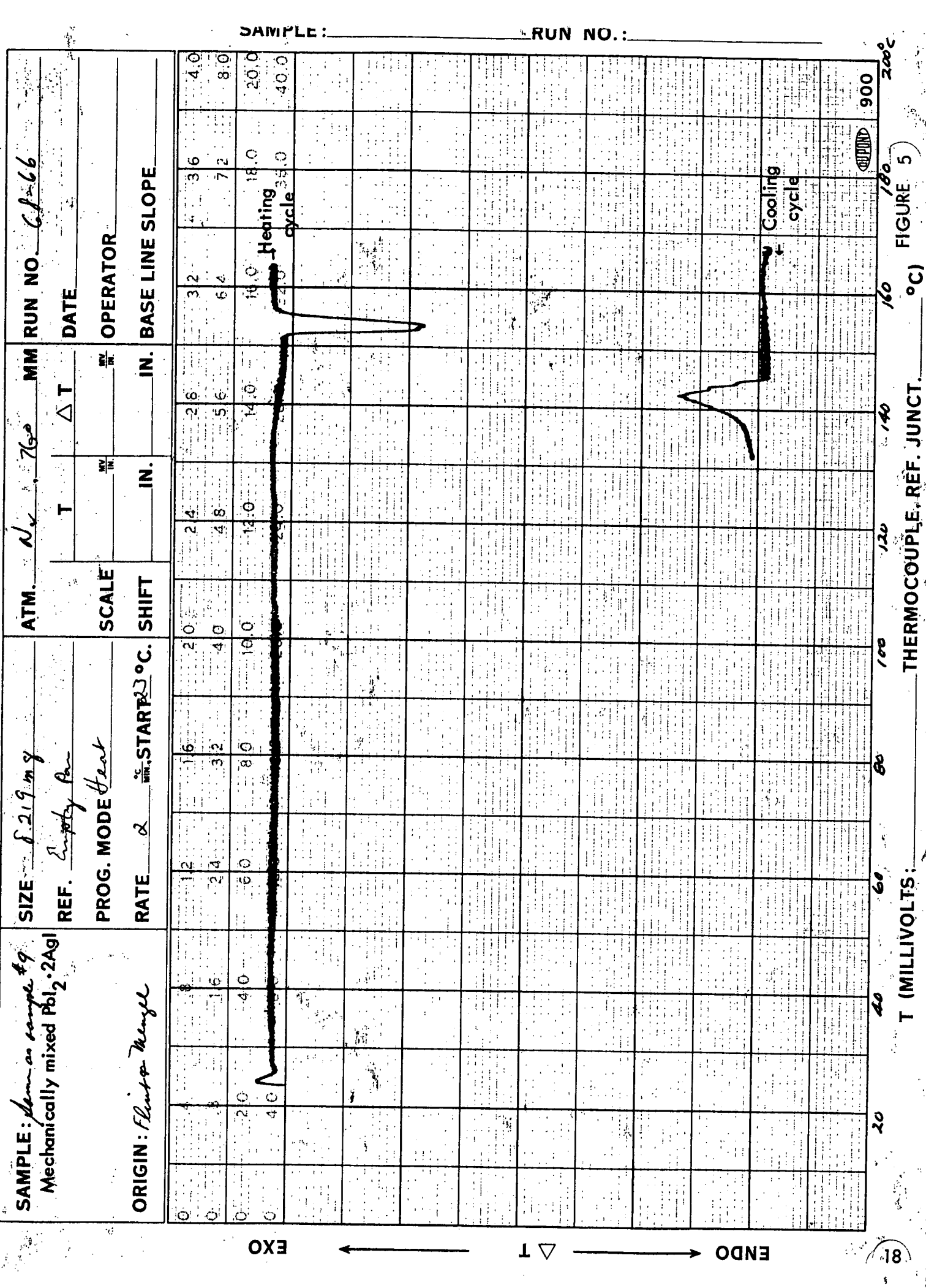
ORIGIN: Flint and Mangel



SAMPLE:

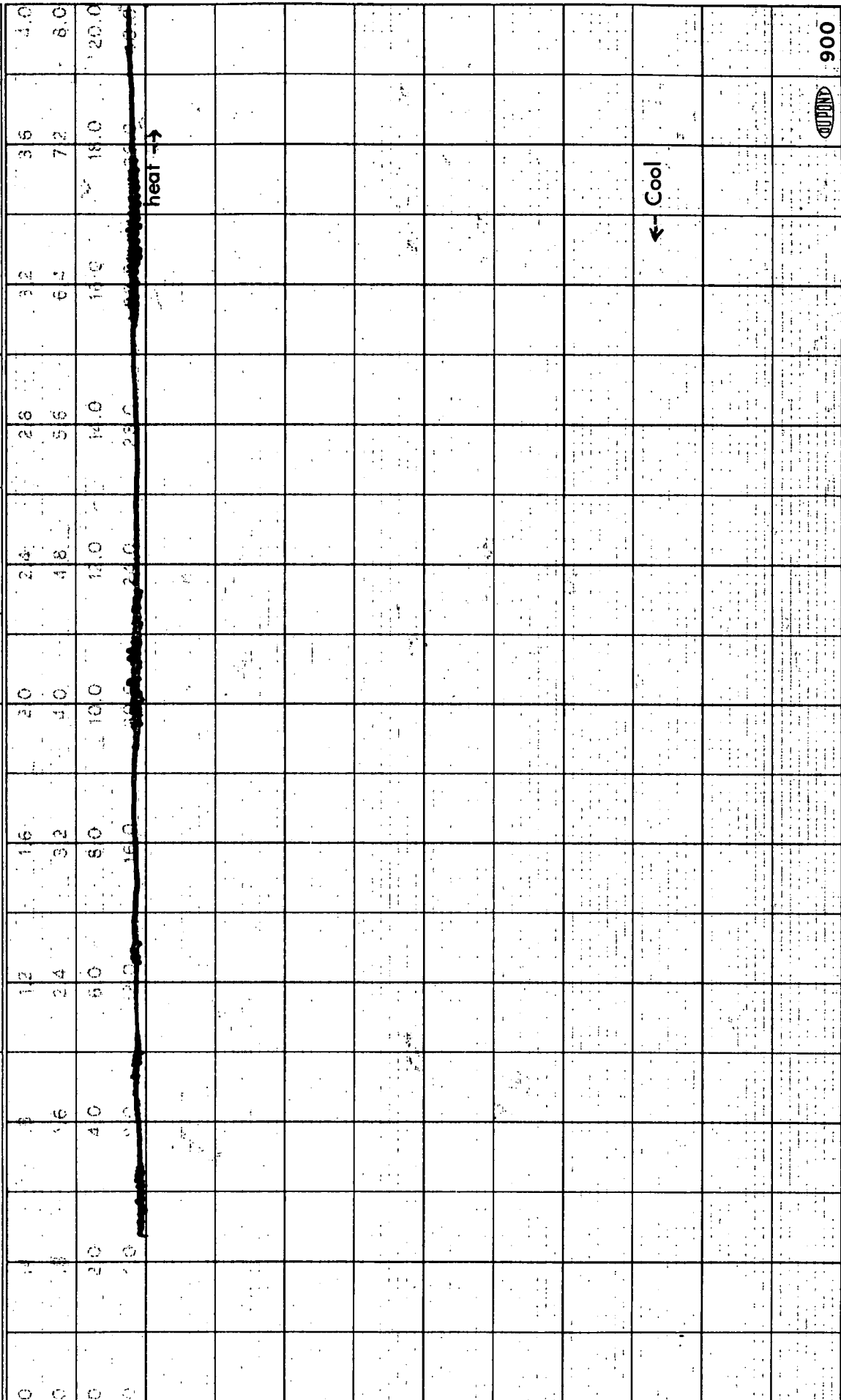
RUN NO.:

THERMOCOUPLE, REF. JUNCT. °C) FIGURE 4



SAMPLE: _____ RUN NO.: _____

SAMPLE: <u>LEAD IODIDE</u>	SIZE _____	ATM. <u>12</u>	MM <u>16</u>	RUN NO. <u>69</u>
	REF. _____	T _____ Δ T _____		DATE <u>8/22/69</u>
	PROG. MODE <u>Heat</u>	SCALE <u>0.0/2.0</u> $\frac{mV}{IN}$	SHIFT <u>0</u> IN. <u>6.1994</u> IN.	OPERATOR _____
	RATE <u>2/20</u> $\frac{min}{min}$ START <u>30</u> °C.	BASE LINE SLOPE _____		
ORIGIN: <u>Menazet</u>				



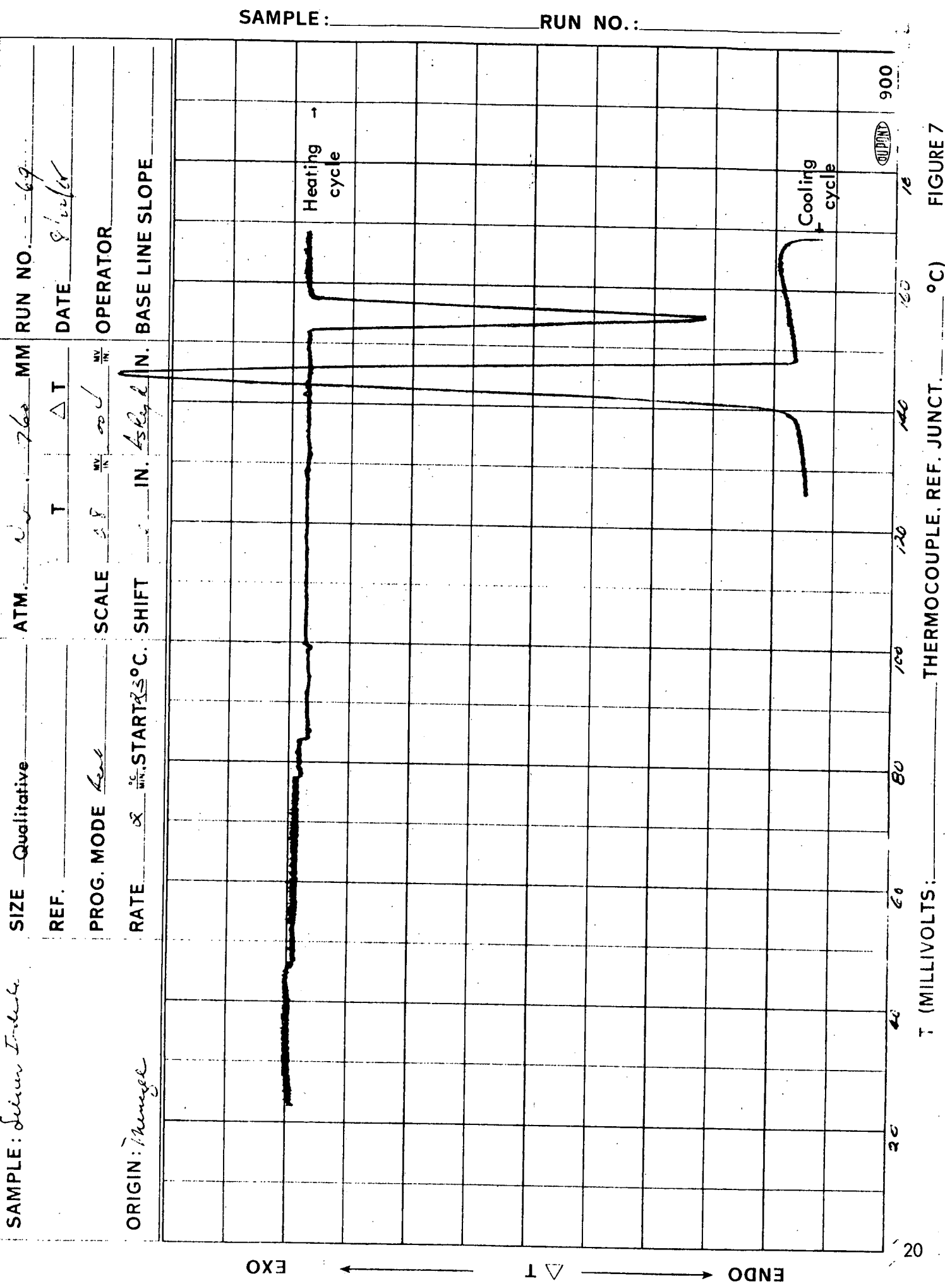


FIGURE 7
THERMOCOUPLE, REF. JUNCT. °C

SAMPLE: # 9 PbI_2 : 2.45 g COMPONENTS FIRED AT 450°C FOR 2 DAYS ORIGIN: 19211221	SIZE 16828 mg REF. 4T Run PROGRAM MODE Heat RATE 5 $\frac{^\circ C}{MIN}$. START 23 $^\circ C$	ATM. N_2 760 T ΔT SCALE 50 $\frac{^\circ C}{IN}$ 0.1 $\frac{^\circ C}{IN}$ SETTING	RUN NO. 83 DATE 9/5/68 OPERATOR JH
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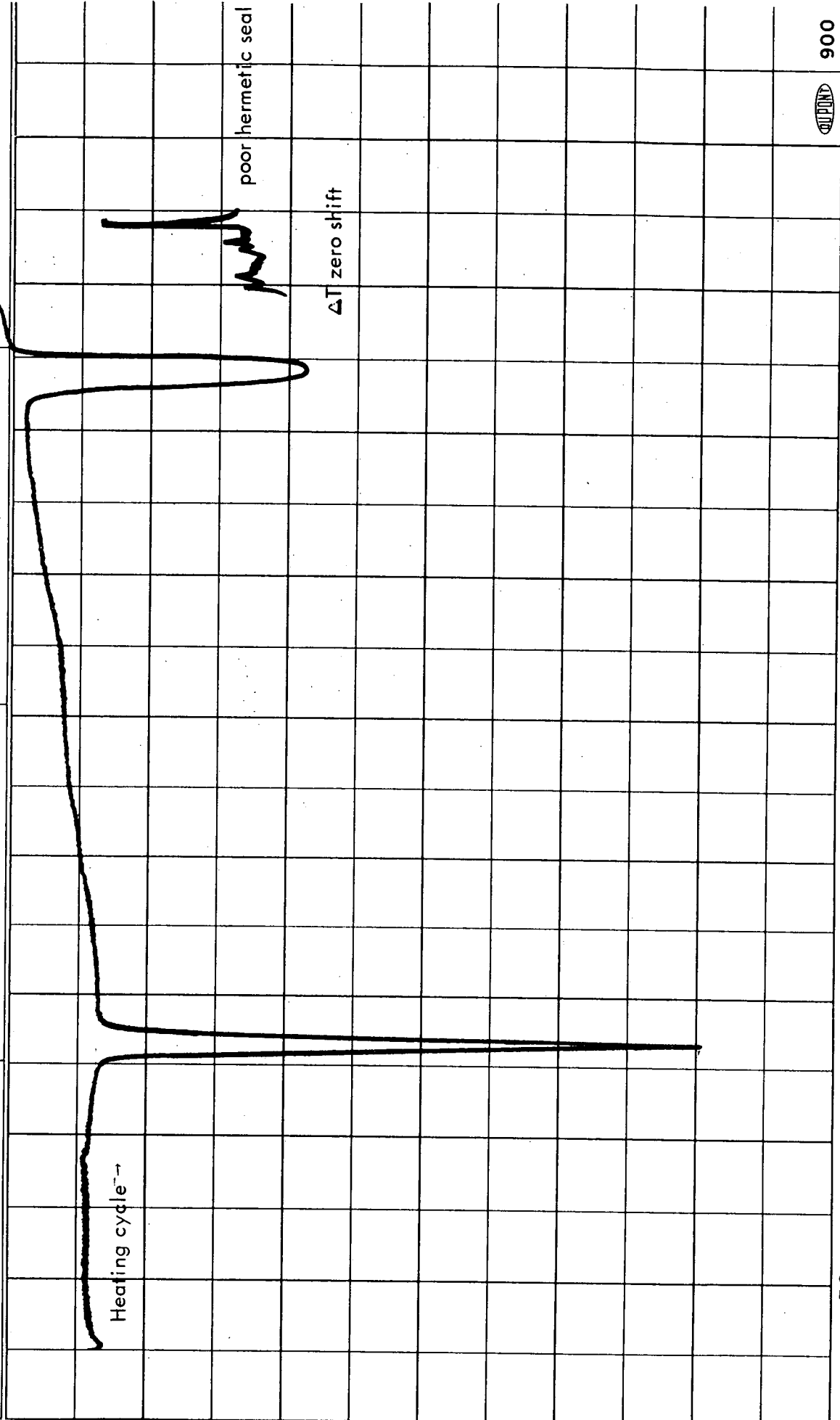
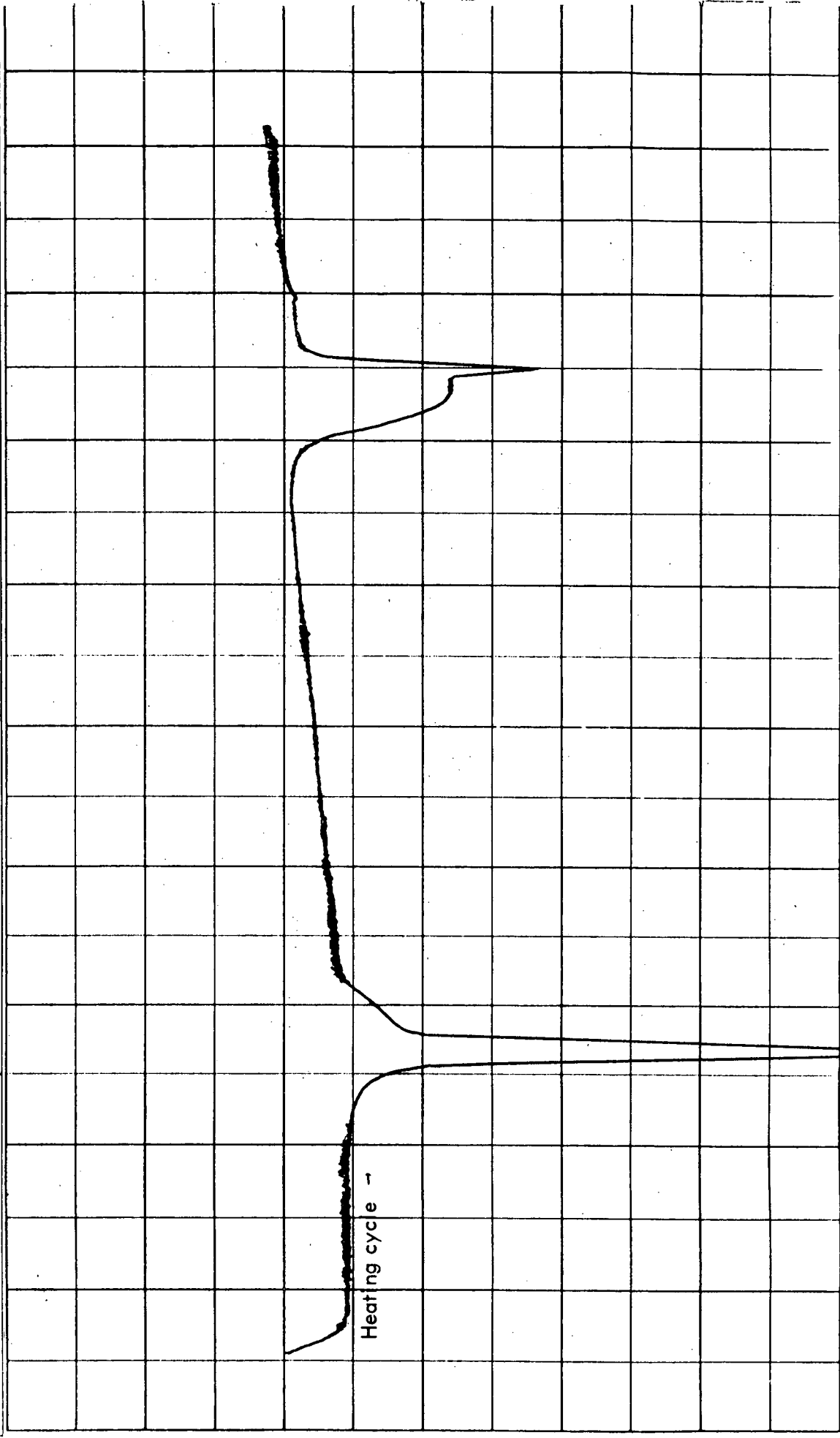


FIGURE 8
T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

SAMPLE: # 14 2AgI: PbI ₂ COMPONENTS FIRED AT 450°C FOR 15 HOURS ORIGIN: FLINT/MENZEL	SIZE <u>15.898 mg</u>	ATM. <u>N₂</u> <u>760</u>	RUN NO. <u>68-78</u>
	REF. <u>MT Pan</u>	T <u>Δ T</u>	DATE <u>8/30/68</u>
	PROGRAM MODE <u>Heat</u>	SCALE <u>50</u> <u>°C</u> <u>IN</u>	OPERATOR <u>D. Yee</u>
	RATE <u>15</u> <u>°C</u> <u>MIN</u> START <u>25</u> <u>°C</u>	SETTING	



- 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 transition 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 $\text{PbI}_2 \cdot 2\text{AgI}$ composition 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{AgI} \cdot \text{PbI}_2$ mixed composition was undertaken. According to Weiss, et al ⁽⁹⁾, PbI_2 is miscible in AgI only to the extent of five mole percent; 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 $\text{PbI}_2 \cdot \text{AgI}$. A simple diagram was indicated with a eutectic composition at $\text{PbI}_2 \cdot 4\text{AgI}$. The eutectic had a reported melting point at 395°C. No comment was made about thermochromism in these references, but a $\beta \rightarrow \alpha$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$

Using the DTA curves, the heat of the thermochromic phase transition (at 130°C) of the $\text{PbI}_2 \cdot 2\text{AgI}$ fired composition was evaluated. The relationship is given by:

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

E = calibration coefficient, mcals/°C-min.

A = peak area, sq in.

ΔT_s = Y-axis sensitivity setting, °C/in

T_s = X-axis sensitivity setting, °C/in

M = sample mass, mg.

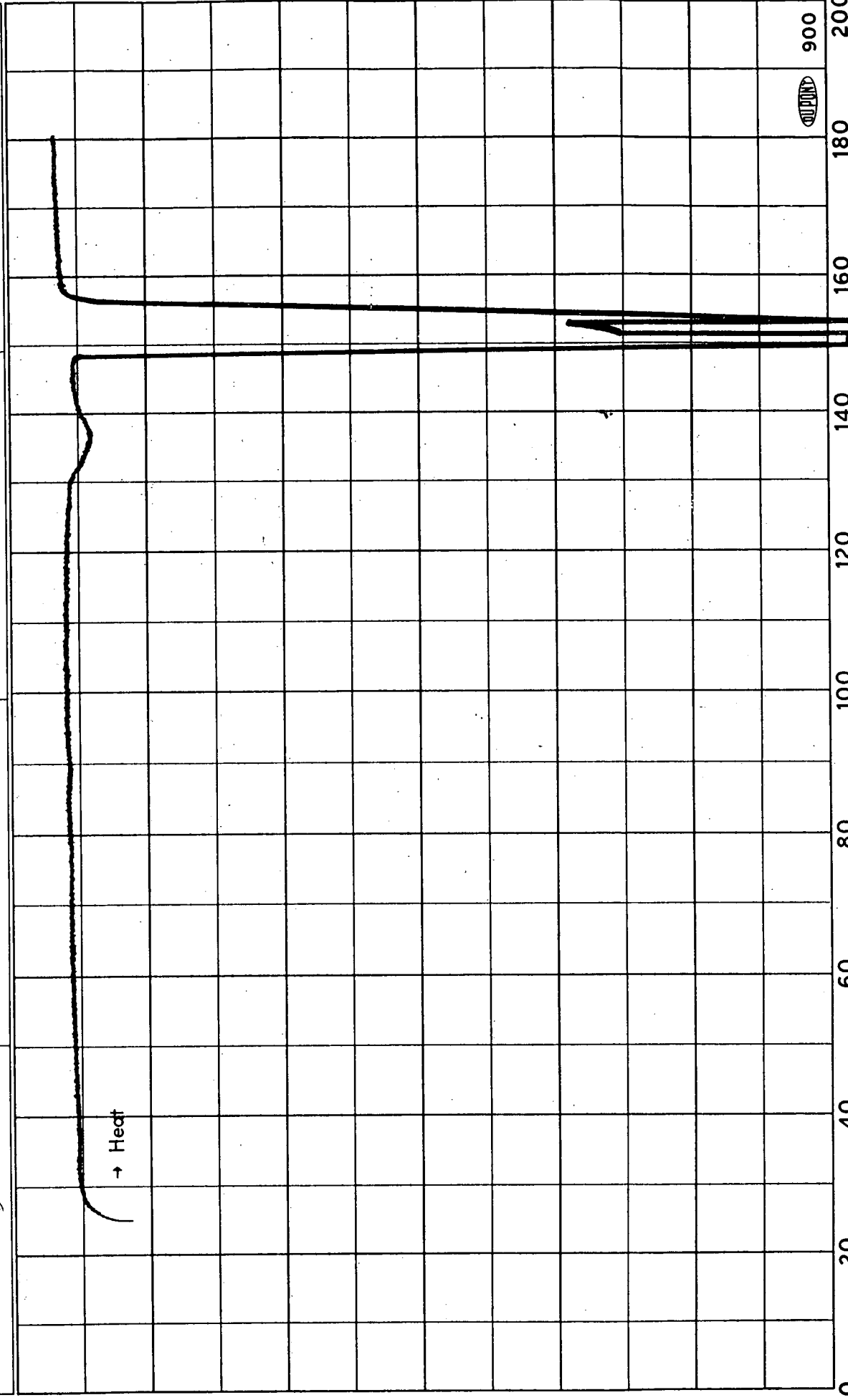
a = heating rate, °C/min.

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

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

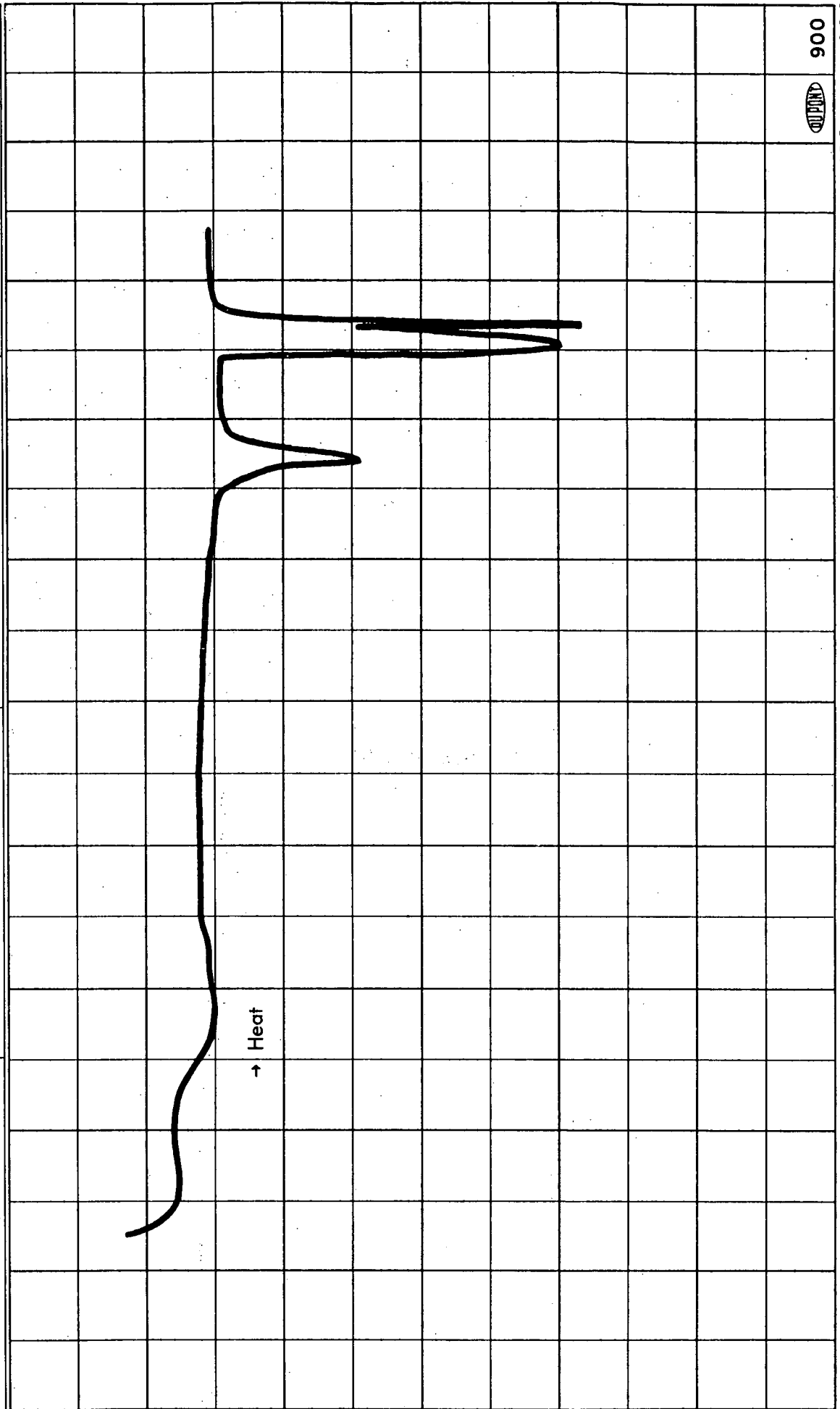
In comparison, the heat of transition for Ag_2HgI_4 was found to be 1.55 mcals/mg⁽¹¹⁾.

SAMPLE: 5% PbI ₂ in Sty I ORIGIN: Manganese	SIZE <u>Small</u> REF. <u>PT 2.0</u> PROGRAM MODE <u>Heat</u> RATE <u>10</u> $\frac{^{\circ}\text{C}}{\text{min}}$ START <u>25</u> $^{\circ}\text{C}$	ATM. <u>N₂</u> <u>760</u> T <u>Δ T</u> SCALE <u>20</u> $\frac{^{\circ}\text{C}}{\text{in}}$ SETTING <u>0.1</u> $\frac{^{\circ}\text{C}}{\text{in}}$	RUN NO. <u>103</u> DATE <u>10-1-63</u> OPERATOR <u>DJ</u>
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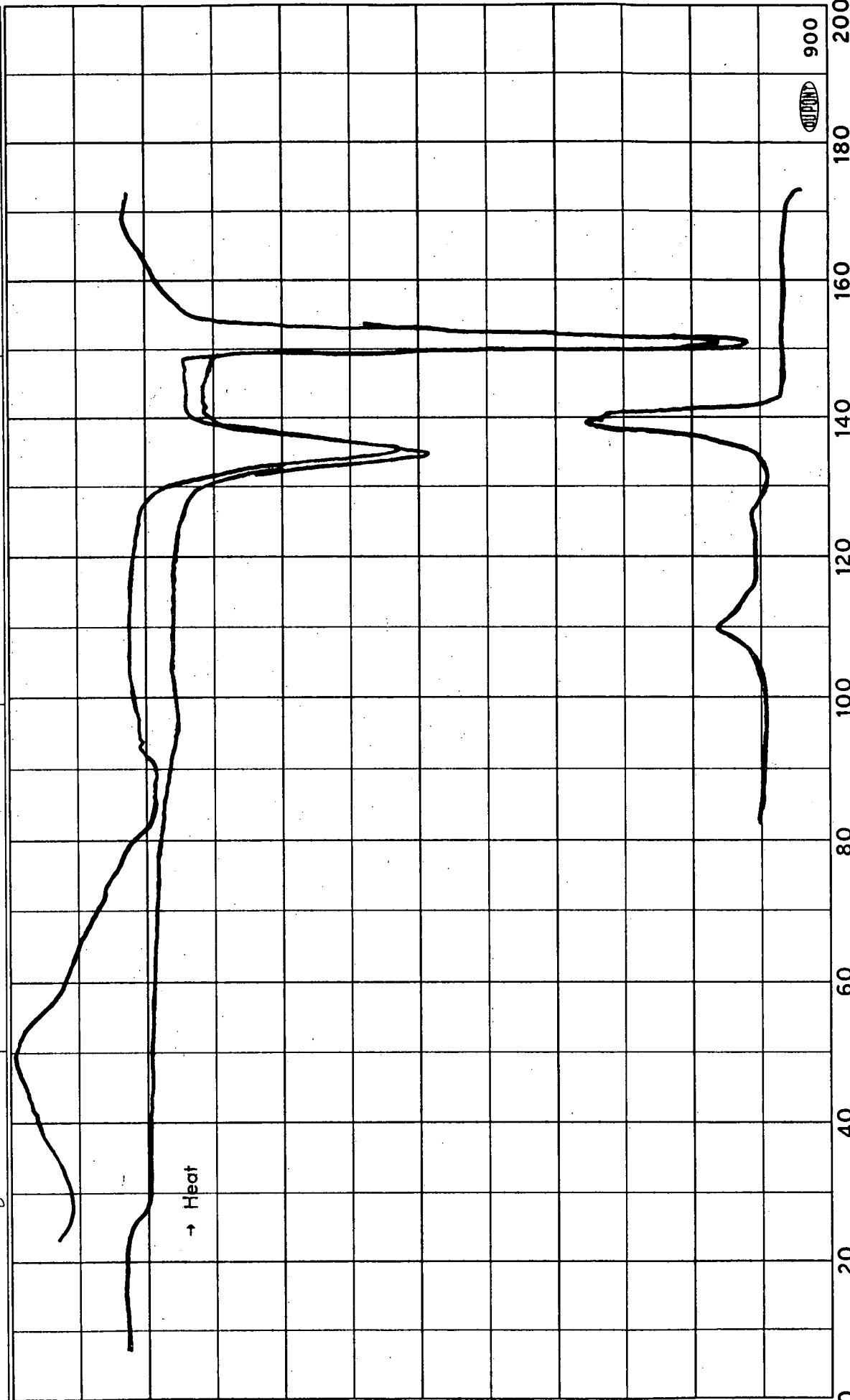
T °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES) FIGURE 10

SAMPLE: $10\% \text{ PbI}_2$ in AgI 500, 1 mg	SIZE 2.989 mg	ATM. Air 760	RUN NO. 115
	REF. Lead 107.194	T ΔT	DATE 10/8/68
	PROGRAM MODE Heat	SCALE 20 $\frac{^\circ\text{C}}{\text{IN}}$	OPERATOR J. J. J.
	RATE 15 $\frac{^\circ\text{C}}{\text{MIN}}$, START 27 $^\circ\text{C}$	SETTING 0.2 $\frac{^\circ\text{C}}{\text{IN}}$	
ORIGIN: Methyl			



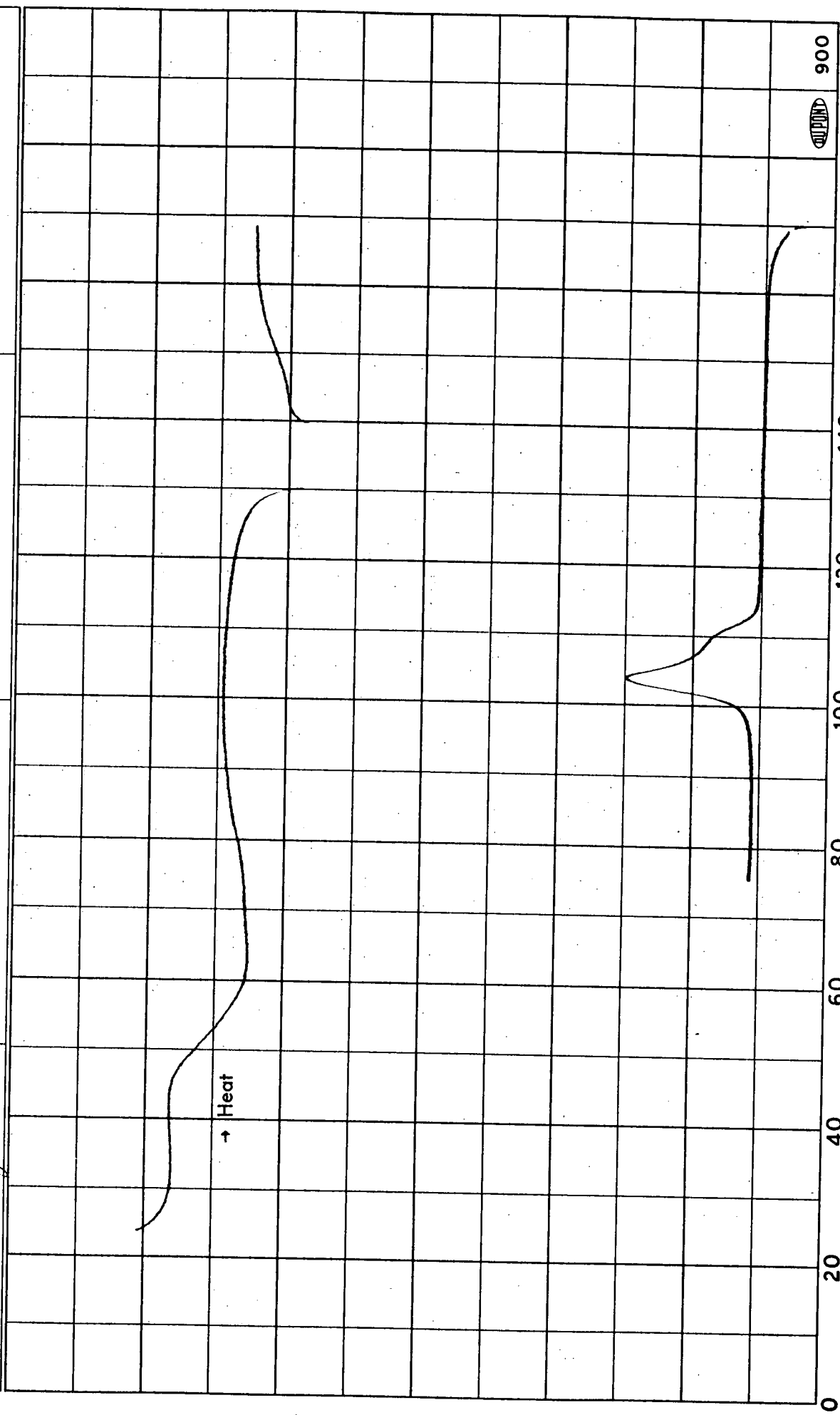
T. $^\circ\text{C}$ (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES) **FIGURE 11**

SAMPLE: 2.5% PbI ₂ in AgI 600', 1 day	SIZE	16.988mg	
	REF.	47 Pan	
	PROGRAM MODE	Heat	
	RATE	10 °C/min, START 25 °C	
ORIGIN: Menage	ATM.	Ali 760	
	T	Δ T	
	SCALE	20	0.2
	SETTING	°C/in.	
	RUN NO.	118	
	DATE	10/9/68	
	OPERATOR	D.J.	



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

SAMPLE: 30% PbI ₂ in AgI (600°, 1 day)	SIZE	17 10/16 mg	ATM.	Am	760	RUN NO.	116
	REF.	147 Pwr	T	Δ T		DATE	10/9/68
	PROGRAM MODE	Heat	SCALE	20	°C IN.	OPERATOR	D. J. M.
	RATE	10	°C MIN	START	127	°C	
ORIGIN: Manganese							



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

Attempts were also made to determine heat capacities of $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$) 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 $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) 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 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: <u>PbI₂ 2 AgI</u> <u>Sample in beaker</u> ORIGIN: <u>J. Menzies</u>	SIZE <u>11.003 mg</u> REF. <u>MT Pan</u> PROGRAM MODE <u>Heat</u> RATE <u>10</u> $\frac{^{\circ}\text{C}}{\text{MIN}}$ START <u>29</u> $^{\circ}\text{C}$	ATM. <u>Air</u> <u>760 mm</u> T <u> </u> Δ T <u> </u> SCALE <u>20</u> $\frac{^{\circ}\text{C}}{\text{IN}}$ <u>0.2</u> $\frac{^{\circ}\text{C}}{\text{IN}}$ SETTING	RUN NO. <u>160</u> DATE <u>12/2/68</u> OPERATOR <u>Dyer</u>
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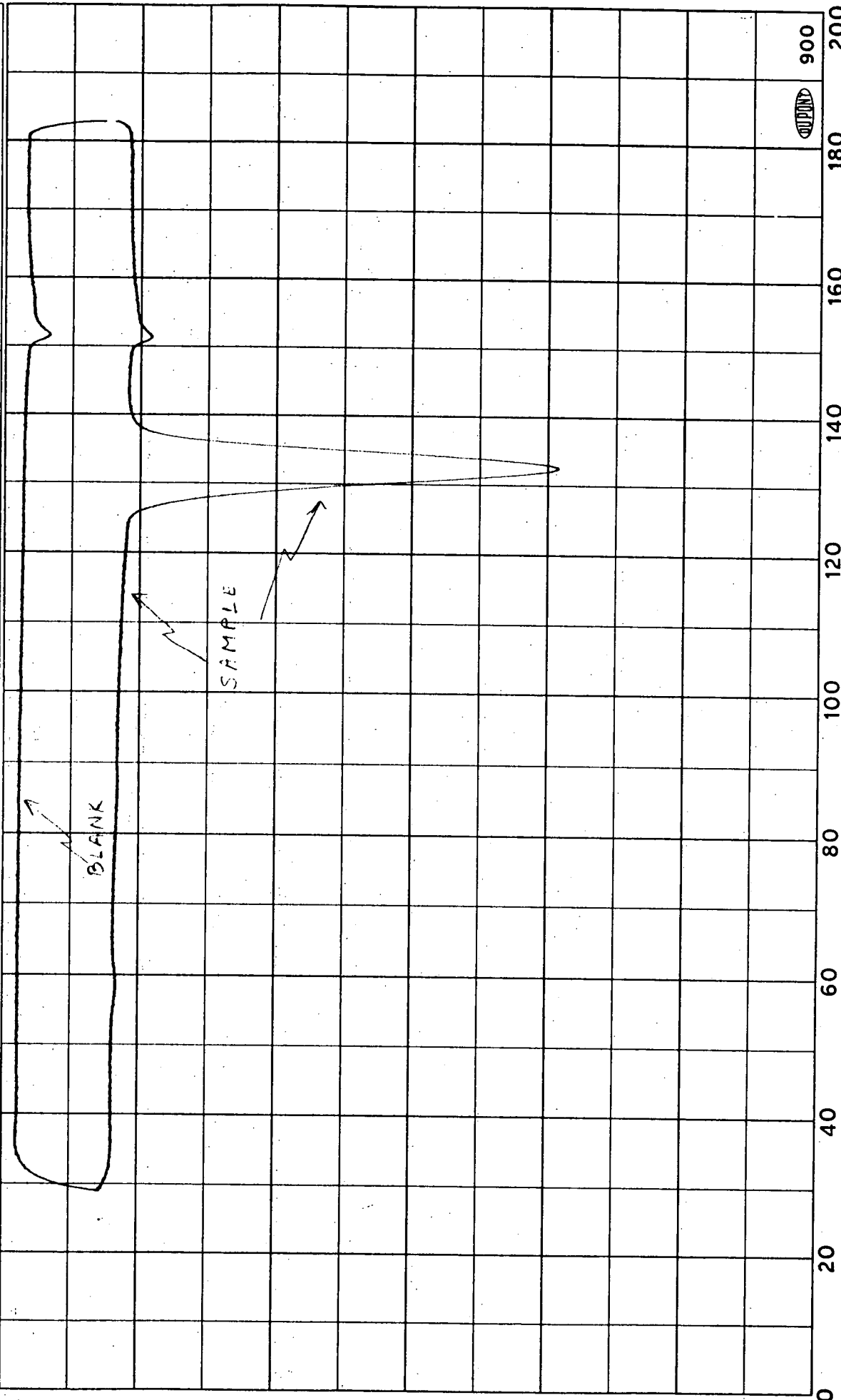


FIGURE 14
T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

X-RAY POWDER PATTERNS

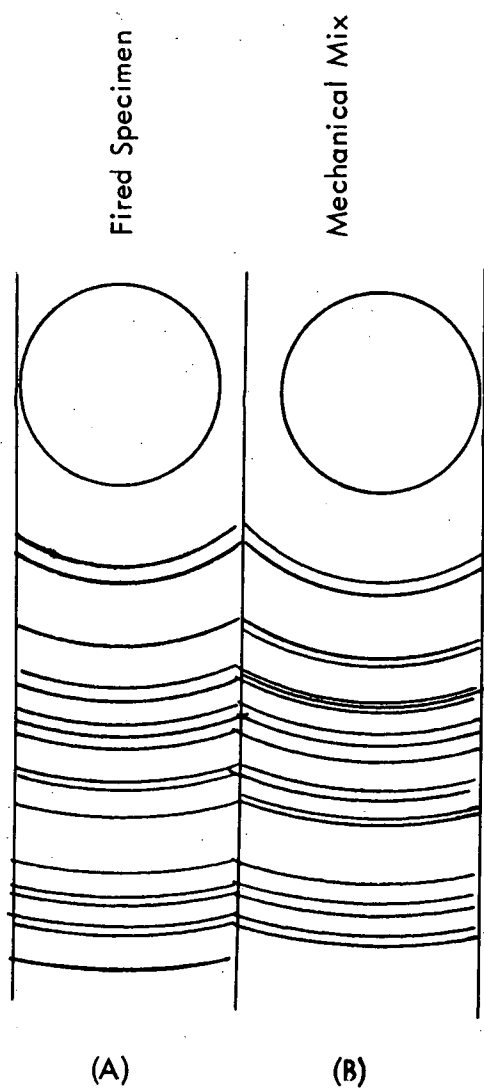


FIGURE 15

TABLE 5
X-RAY DIFFRACTION SPECTRUM FOR $\text{PbI}_2 \cdot 2\text{AgI}$ SYSTEMS

<u>1)</u> <u>d(hkl)</u>	<u>2)</u> <u>d(hkl)</u>	<u>γ-AgI</u>	<u>3)</u> <u>(hkl)</u>	<u>4)</u> <u>PbI_2 (hex.)</u>	<u>(hkl)</u>
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 - C8627 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, $a=6.495\text{\AA}$, Space Group F43 m.
- 4) d spacings as reported by N.B.S. (circular 539, V, p.35) Lattice constants $a=4.557\text{\AA}$, $C=6.979\text{\AA}$ Space Group $\overline{P}5m1$.

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 $\text{PbI}_2 \cdot 2\text{AgI}$ SOLUBILITY STUDIES

Efforts were made to identify the chemical nature of the $\text{PbI}_2 \cdot \text{AgI}$ fired compositions by solubility studies. The solubility of PbI_2 in water at 100°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 $\text{PbI}_2 \cdot \text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ (about equal weights) were accurately weighed into round-bottom flasks, containing 50 ml of water and refluxed at 100°C . Three determinations were made with the following results.

First Determination

	<u>Initial Weight</u>	<u>Undissolved Residue</u>
Reflux Time: 7 hours		
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

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

Third Determination

	<u>Initial Weight</u>	<u>Undissolved Residue</u>	<u>Solute Residue</u>
Reflux Time: 20 hours			
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°C (PbI_2). The residue of the unfired mixture revealed only one peak at 150°C (AgI), whereas three peaks appeared in the thermogram for the fired mixture. These peaks showed up at 130°C , 150°C , and 375°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°C and 150°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°C , Cr_2O_3 at 2435°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 $1350 - 1500^\circ\text{C}$. 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 $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ COMPOSITIONS

Specimen Number	Mole % Cr_2O_3	Mode of Preparation	R.T. Color After Firing	Approx. Temp. Change to Grey, °C	Pronounced Temp. Change to Green, °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 conjunction 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.

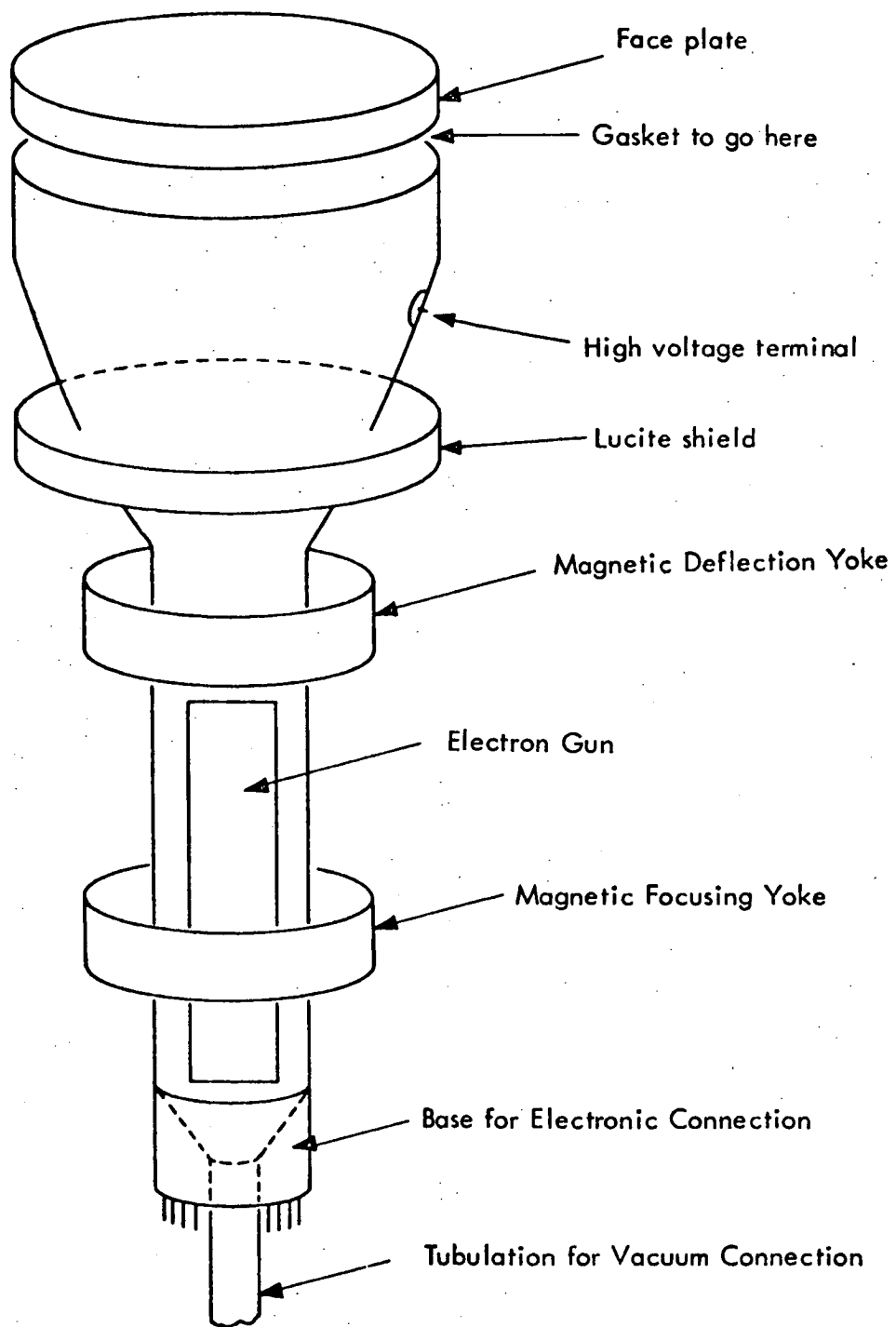
A significant asset of thermochromics is the relative ease with which important properties such as rise time and persistence can be adjusted. These properties depend, among other things, on the heat capacities and thermal conductivities of the thermochromic and associated materials, as well as the ambient 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 lifetimes, gives these materials an edge over phosphors in that they can lead to flicker free displays. 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.



SCHEMATIC OF DEMOUNTABLE CRT

FIGURE 16

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 electron beam was operated.

3.2.1.1 Ag_2Hgl_4 IN THE DEMOUNTABLE CRT

The testing of Ag_2Hgl_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_2Hgl_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_2Hgl_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_2Hgl_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/cm². 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/cm² coating of Ag_2Hgl_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 $3.8 - 5.1 \text{ watts/cm}^2$ 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 undesirable rapid spreading of the thermochromic color change.

3.2.1.1.2 Ag_2Hgl_4 with Beam Incident on Titanium Backing

Titanium has a much smaller thermal conductivity, $0.0407 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ compared to $0.22 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ 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_2Hgl_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 0.6μ ampere which corresponded to a power density level of $0.3 - 1.5 \text{ watts/cm}^2$. 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_2Hgl_4 -Glass Sandwich

It was reported⁽¹⁵⁾ that a reversible thermochromic transition was achieved with a MgO coated Ag_2Hgl_4 glass sandwich. The low thermal conductivity value ($0.001 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$) 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/cm², 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 Ag₂HgI₄

The National Cash Register Company micro-encapsulated samples of Ag₂HgI₄ 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/cm². 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/cm² to produce the thermochromic transition, which was quite a bit higher than with unencapsulated Ag₂HgI₄. 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-Ag₂Hgl₄-Glass Sandwich

A. Glass-Ag₂Hgl₄-Glass Sandwich Involving 0.0033"-0.0051" Microsheets

One possible means of stabilizing the Ag₂Hgl₄ would be to prepare a sandwich of Ag₂Hgl₄ 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/cm². A good reversible color change was achieved at 20 kV and 1.2 μ amperes or about 3.1 watts/cm². Spreading of the lines and resolution appeared to be better than for the simpler system of thermochromic on one glass plate. The decaytime 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 Ag₂Hgl₄ 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 Ag₂Hgl₄ 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 temperatures required to manufacture a sealed CRT.

B. Glass- Ag_2Hgl_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_2Hgl_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 decay 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_2O_3 - Cr_2O_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 reversible thermochromic change with high contrast can be achieved, several such materials will be very promising candidates for a sealed off CRT.

TABLE 7GLASS SANDWICHES USED FOR CRT EXPERIMENTS

<u>Sample #</u>	<u>Microsheet Thickness (inches)</u>	<u>Thickness of Second Glass (inches)</u>	<u>Surface Density of Ag_2Hgl_4 (mg/cm^2)</u>
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 ² Watts / cm	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_2Hgl_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 $15 - 20 \text{ watts/cm}^2$. 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 $15 - 20 \text{ watts/cm}^2$.

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 $\text{Pbl}_2 \cdot 2\text{AgI}$

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

TABLE 9Thermochromic 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 $\text{PbI}_2 \cdot 2\text{AgI}$ IN THE DEMOUNTABLE CRT

An initial experiment with the fired $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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_2Hgl_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 faceplate 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 discoloration 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 $\text{PbI}_2 \cdot 2\text{AgI}$

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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 10μ a beam current and 5 kV with a 20μ a beam current.

$\text{PbI}_2 \cdot 2\text{AgI}$ 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 thermochromism 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/ $\text{PbI}_2 \cdot 2\text{AgI}$ 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 configurations 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_2Hgl_4

A CRT test was performed on a 50-50 mixture of P-14 phosphor and Ag_2Hgl_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_2Hgl_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 $\text{PbI}_2 \cdot 2\text{AgI}$

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/ $\text{PbI}_2 \cdot 2\text{AgI}$ SYSTEM

One approach to prevention of electrical breakdown would be to protect the thermochromic with coatings of P-14 phosphor. A $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot \text{AgI}$ gave fluorescence but no thermochromic change.

The successful demonstration that both $\text{PbI}_2 \cdot 2\text{AgI}$ 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 10HYBRID P-14/PbI₂·2AgI SYSTEM IN DEMOUNTABLE CRT

<u>Voltage (kV)</u>	<u>Faraday Cup Current (μa)</u>	<u>Beam Diameter (cm)</u>	<u>Comments</u>
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.

section of a faceplate was sprayed with the $\text{PbI}_2 \cdot 2\text{AgI}$ 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 thermochromic. 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 $\text{PbI}_2 \cdot 2\text{AgI}$ than was used in the previous experiments.

Thus, the hybrid system $\text{PbI}_2 \cdot 2\text{AgI}$ - 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 $400 \text{ m}\mu$ 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_2Hgl_4 were conducted.

3.2.2.1 RESIN SANDWICHED THERMOCHROMIC

A weighed sample of Ag_2Hgl_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_2Hgl_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 thermochromic 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

attempted in which steel blocks were heated by a flame to a temperature 480°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°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_2Hgl_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_2Hgl_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_2Hgl_4 . The sample was air and vacuum dried at room temperature. Then a partial cure was attempted by heating the sample at 80°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 $80 - 90^{\circ}\text{C}$. There was a total loss of the Hgl_2 at approximately 110°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 $120 - 130^\circ\text{C}$ under vacuum in both samples over a period of $1\frac{1}{2}$ 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_2Hgl_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_2Hgl_4 .

A 3:1 mixture of resin to thermochromic was prepared in methanol solvent. Ag_2Hgl_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_2Hgl_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_2Hgl_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_2Hgl_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_2Hgl_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 utilization of bulk as well as surface conductivity in Ag_2Hgl_4 . Figures 17 a and 17 b show schematics of tablets based on bulk conductivity in Ag_2Hgl_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

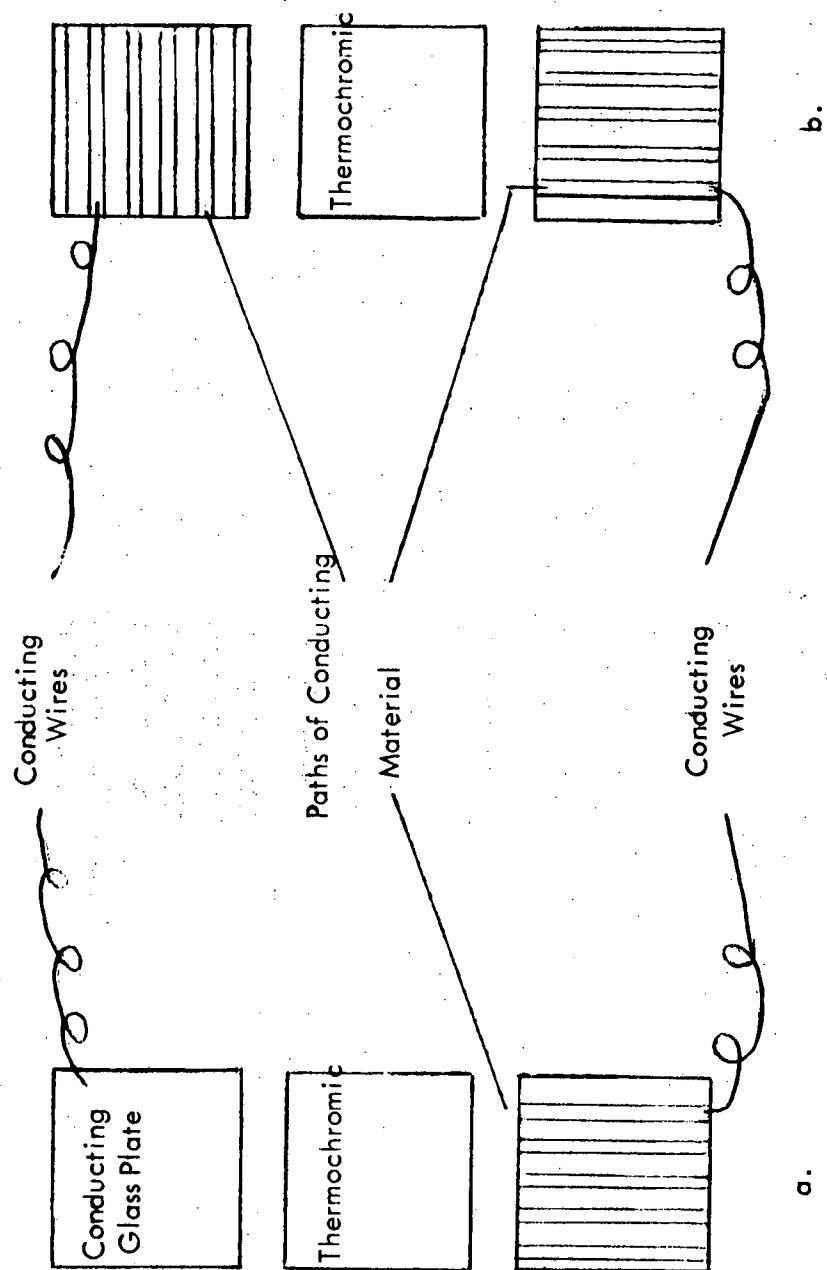
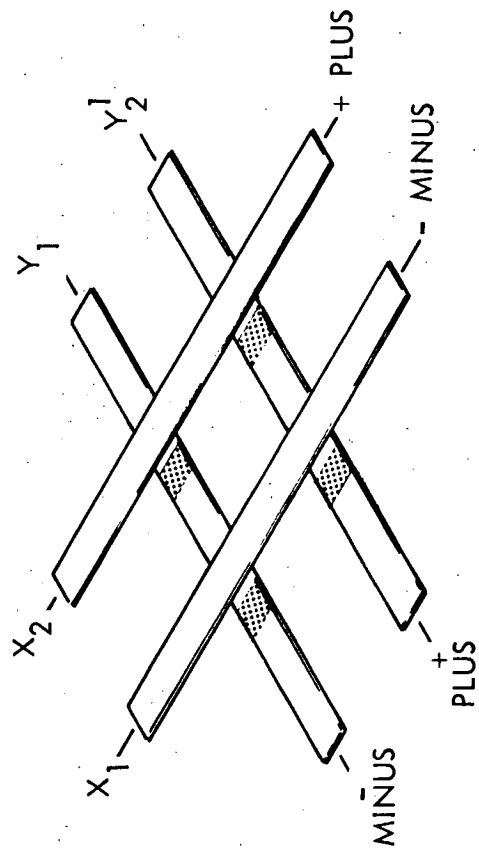


FIGURE 18

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 17 a.

In Figure 18 the Ag_2Hgl_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_2Hgl_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 ohmmeter.

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 temperature 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_2Hgl_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 $\text{PbI}_2 \cdot 2\text{AgI}$ composition with the aid of appropriate filters. It should be noted, however, that $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 μ 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 PLT. 2A3E AT
R.T. AND ABOVE 130°C

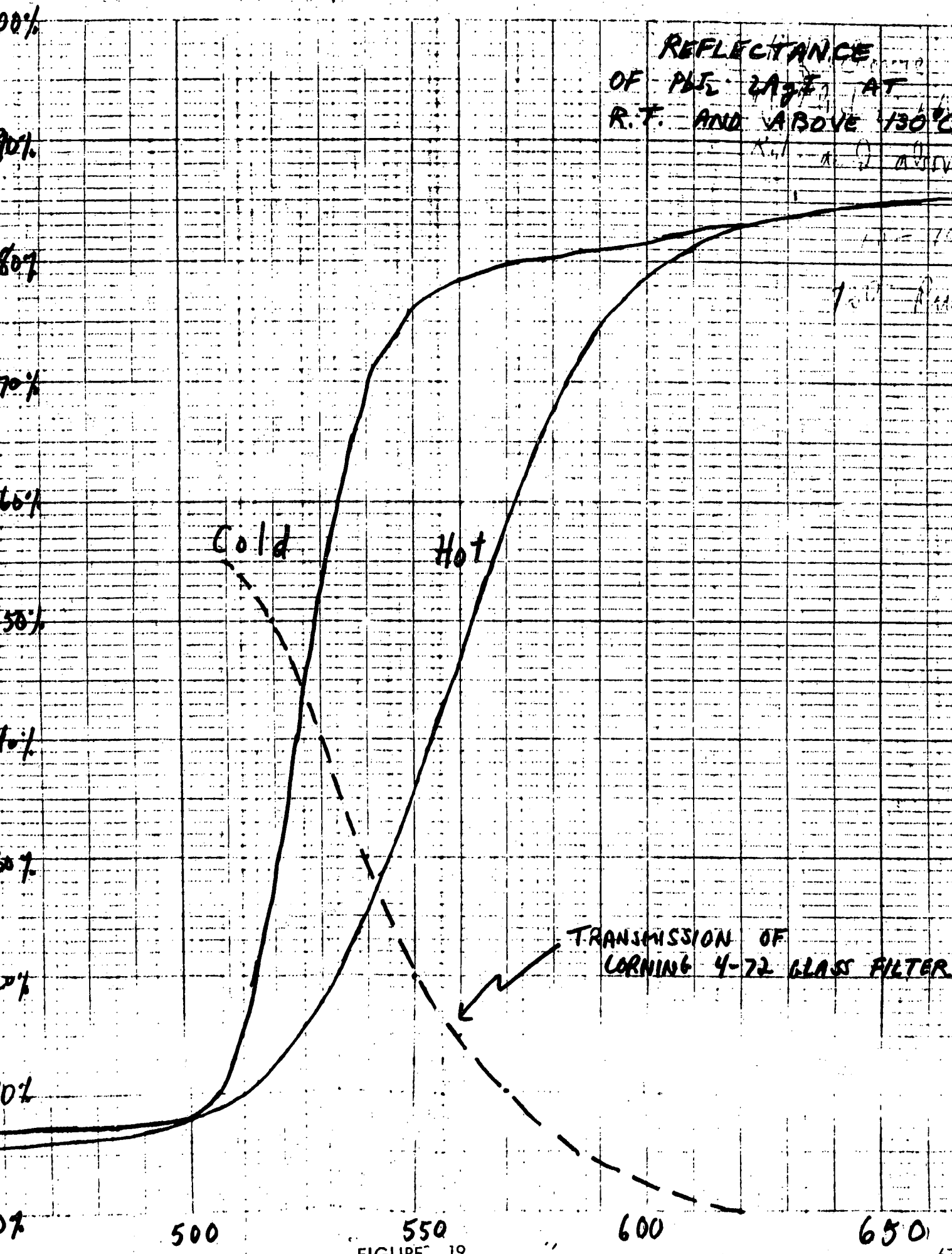
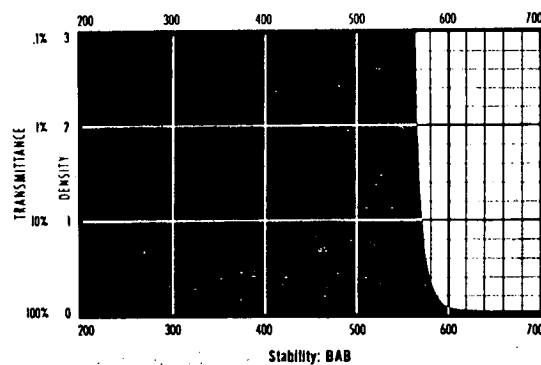
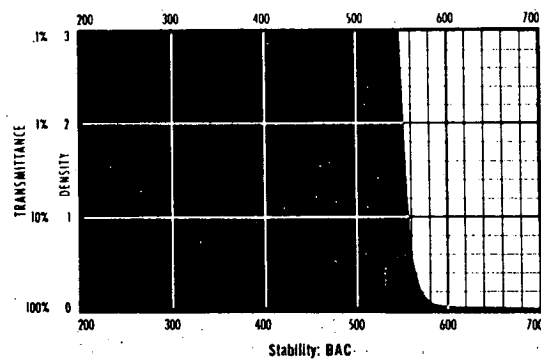
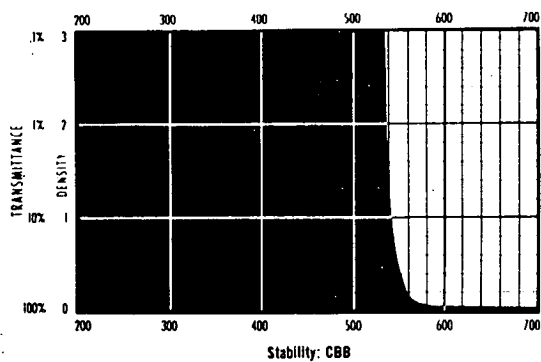


FIGURE 19



WAVELENGTH	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 Transmitt.	45.6	35.8	25.0
Dominant Wave Lth.	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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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°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 supernatant 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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

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.

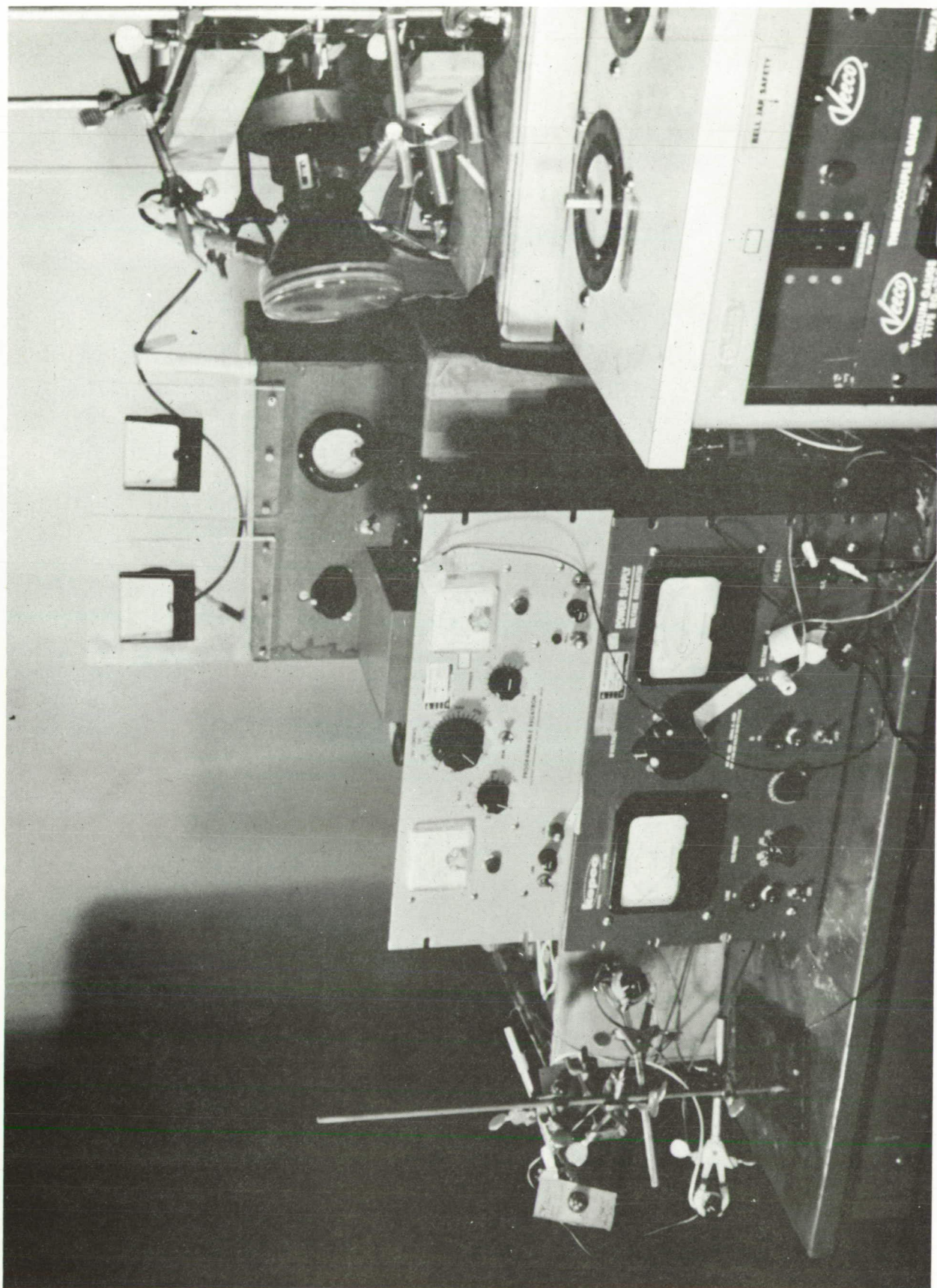


FIGURE 21

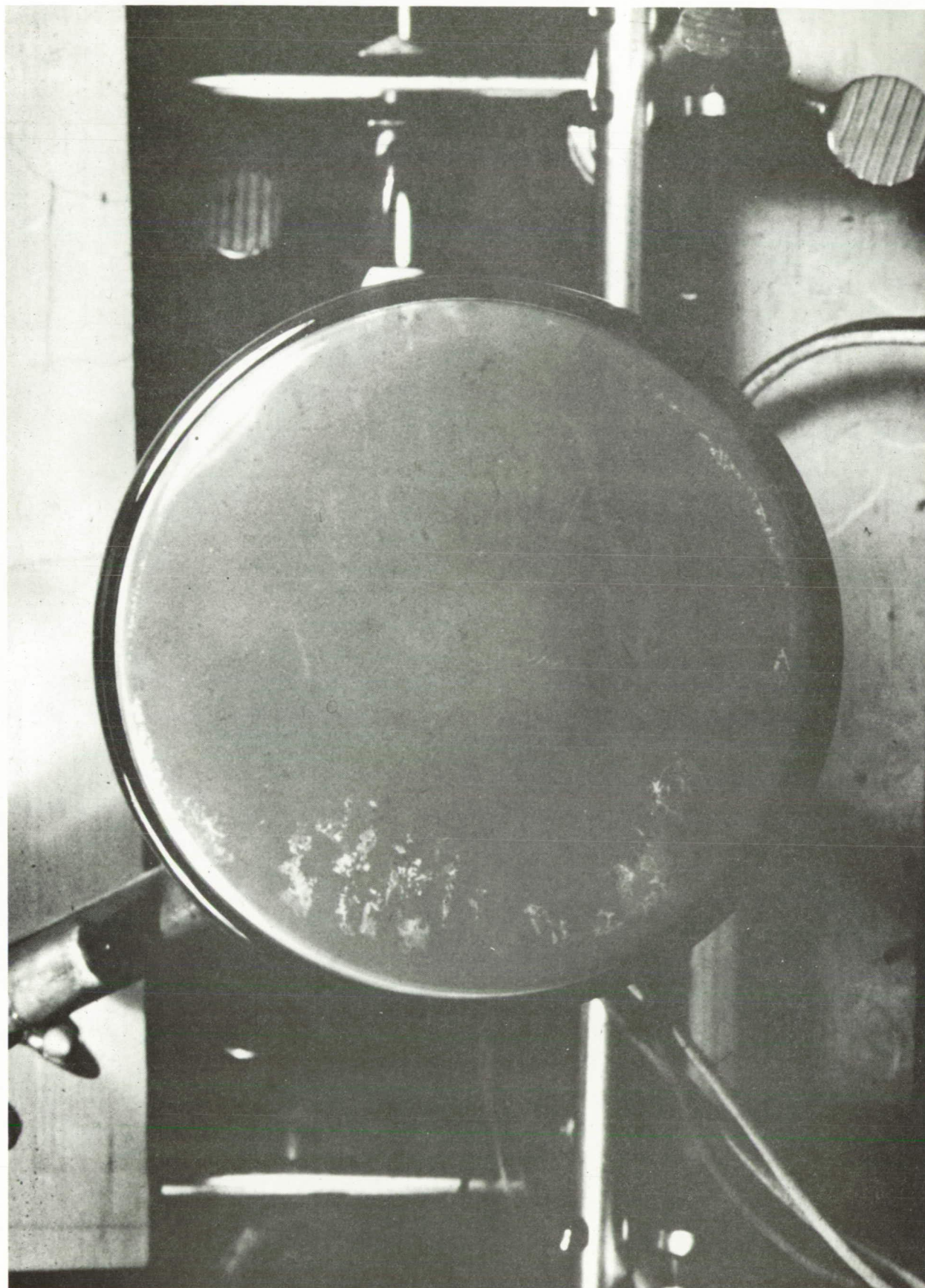


FIGURE 22

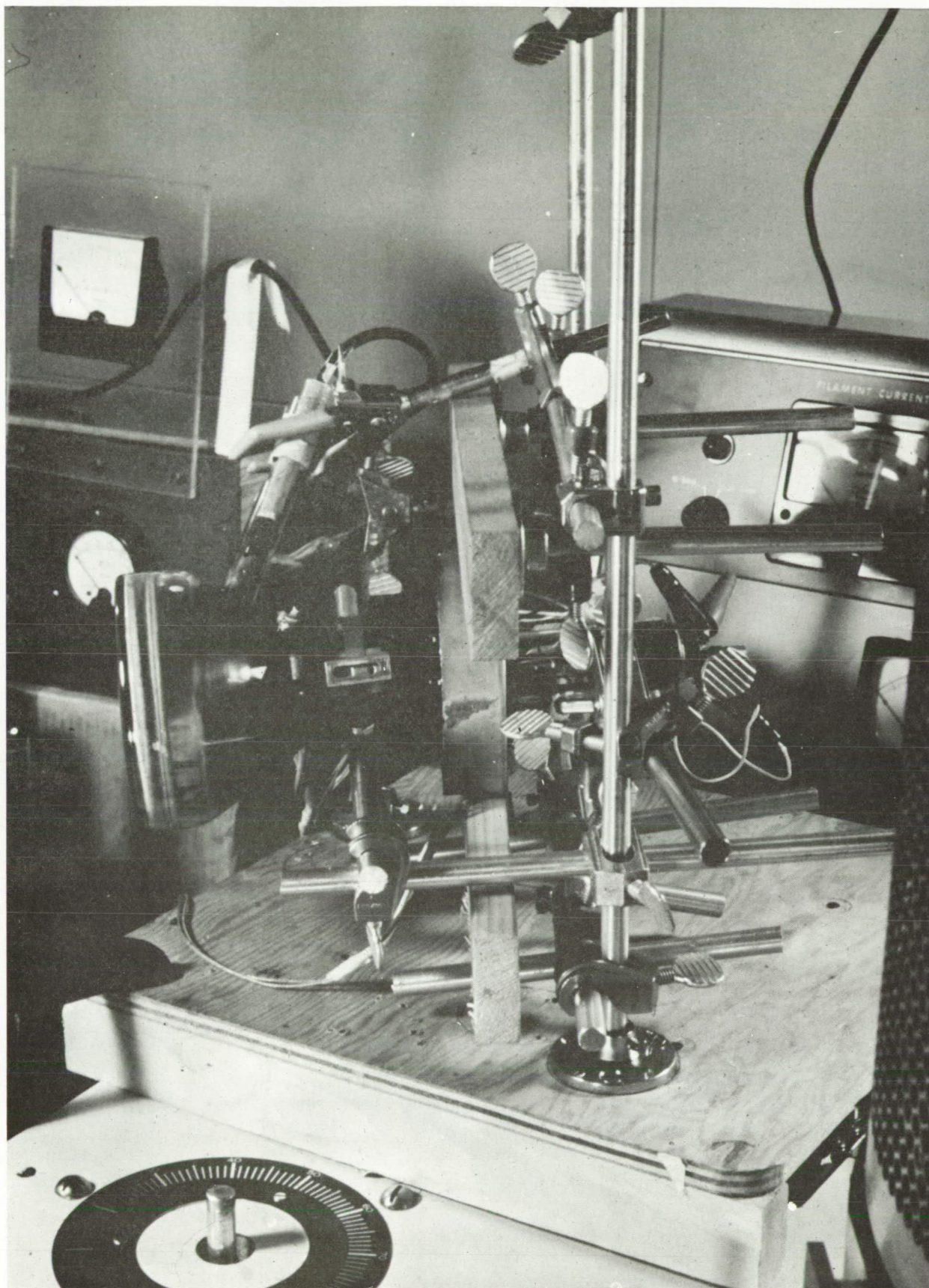


FIGURE 23

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. $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ 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 ~ 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 $\sim 130^\circ\text{C}$. 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 $\sim 375^\circ\text{C}$. The phase diagram of this chemical system is surprisingly complex.

The only drawback in the $\text{PbI}_2\text{-AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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 $\text{PbI}_2 \cdot 2\text{AgI}$.

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 $\text{PbI}_2 \cdot 2\text{AgI}$ 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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