Aerospace Research Center

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

Contract NAS 12-89

First Annual Progress Report

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GENERAL
PRECISION
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ABSTRACT

This is the first annual technical progress report under Contract NAS 12-89. It presents the results obtained on the first phase of our investigation of the feasibility of using thermochromic materials in display devices. These materials change color when heated and revert back to their original color when cooled. The observation of the color change depends on the change in reflection and not on the emission of light, as is the case in electroluminescent materials. Thus, displays utilizing thermochromic materials are visible under wide ranges of ambient illumination.

Prototype numeric display devices were constructed in which two of the known thermochromic compounds, silver mercuric iodide (Ag_2HgI_4) and copper mercuric iodide (Cu_2HgI_4), were used as the display materials. These prototypes gave high contrast images and demonstrated the feasibility of using these materials in devices of this kind. In addition, a number of other potential device applications for these materials were conceived. Two of these potential applications were considered briefly during this phase of the program. These included using thermochromic materials along with electroluminescent phosphors in an hybrid device, and as a substitute for the phosphor in a cathode ray tube.

Various new thermochromic materials were synthesized. These included substitutional formulations of the known thermochromic ternary iodides and certain ternary chalcogenides. Some of the more important properties of these thermochromic materials such as their transition temperature, reflectance spectra, thermal stability and electrical conductivity were determined.

ADMINISTRATIVE INFORMATION

This is the first annual technical progress report under Contract NAS 12-89 which was sponsored by the NASA-Electronics Research Center, Cambridge, Massachusetts. The work reported on herein covers the period December 1, 1965 through November 30, 1966. The NASA monitoring scientist was Mr. E. H. Hilborn. The Project Supervisor at the General Precision Aerospace Research Center was Dr. Daniel Grafstein. The Principal Investigators on this program included Dr. Marvin J. Kornblau, Dr. Raymond P. Borkowski and Dr. Lies N. Finnie. Dr. Finnie left the program as of June, 1966. Mr. William Benko aided in the vacuum sealing of the quartz ampoules. Mr. Clifford Whitmore gave technical assistance in the electronic circuitry for the thermochromic-CRT studies.

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I. INTRODUCTION

This study is directed toward the design and evaluation of displays suitable for use under wide variations in ambient illumination levels and applicable to aircraft and space vehicles, in addition to central command rooms. In aerospace vehicles particularly, visual displays may be subject to variations in illumination levels encompassing a range of five orders of magnitude. The more traditional displays which incorporate mechanical movements, such as the dials of meters, are usable under these extremes of ambient, but they suffer from the disadvantages of moving parts and catastrophic failure. Their more modern non-mechanical counterparts, for example, electroluminescent displays or cathode ray tubes, saturate at brightness ranges far too low to allow their use in high ambients. An electroluminescent display can be operated at the required brightness levels but only at the expense of increased power and reduced life. These are both critical factors in aerospace applications. In addition to the low brightness output and poor lifetimes, these devices are also limited by the mechanism by whence they are made visible. These devices become visible by emission of light (luminescence) rather than by selective reflection of the ambient illumination. Because of this, high ambient illumination can wash out the visibility of an electroluminescent or cathodoluminescent device. On the other hand a device which displays information by selective reflection of light does not suffer from this limitation and can be utilized in conditions of high ambient. It is the objective of this program to develop new materials that undergo visible color changes that can easily be seen in high ambient conditions and which are compatible with the aerospace environment. Furthermore, these materials should be capable of being utilized in a display device which contains no moving parts or elements that can fail catastrophically.

The concept developed at General Precision is to display information using thermochromic materials which change color upon activation by heat and revert to their original color when cooled. The observation of the color change in these materials is due to a differential reflection of the ambient light by the two different colored forms.

This study is specifically concerned with the synthesis of new thermochromic materials, an evaluation of their thermochromic properties and the determination of the feasibility of using these materials in display devices. A device based on such materials would have no moving parts, would not fail catastrophically and, would operate best under a high light ambient.

1.1 Thermochromism

Thermochromism is a change in the color of a material as a result of a change in temperature in that material. The color response to the temperature change may be slow or fast, sharp or gradual, depending on the mechanism that causes the color change. Thermochromism has been observed in a variety of organic and inorganic materials, and the mechanism has been found to vary with the molecular structure of the material. The type of mechanism invoked to explain the thermochromic activity has included equilibrium between two molecular species, broadening of a near ultraviolet absorption curve, ring opening, thermal achievement of a triplet state configuration, formation of free radicals and order-disorder phenomena. This list by no means exhausts the mechanisms by which thermochromism can occur. Many of these mechanisms, however, involve the breaking of chemical bonds and/or the migration of chemical species. In such systems the rate of the color change with temperature of the material is relatively slow. Thus, such materials would not find utility for display devices.

There are other organic materials, particularly cholesterol and its derivatives, which were not considered for different reasons. Recently these materials have found some uses in medical research such as monitoring the variation in the skin temperature of the body. Thermochromism in these materials involves the formation of "liquid crystals" and as such have several deficiencies for device use. First of all these materials are colored over only a very narrow temperature range (5 - 6°C) and show extreme sensitivity to change in temperature (fractions of a degree) in this range. They are colorless above and below this temperature range. These materials also have low refractive indices and as such observation of the color is a critical function of the viewing angle. These factors, narrow temperature range, extreme sensitivity to changes in temperature and dependence on viewing angle made these materials unsuitable for any display device consideration. Apart from these liquid crystals, organic materials rarely show sharp transition temperatures (1)*. Also, there are inorganic thermochromic materials whose color change depends on an actual chemical reaction equilibrium, such as hydration. These usually display broad ranges of transition temperatures and tend to have very slow response times. These types of materials would also be unsuitable for display device application.

For information display applications, the color changes must be fast and result in a sharp contrast of one color on another. Since both maintenance and power requirements are also important factors in device considerations, especially in aircraft and spacecraft, the materials should also show good thermal stability and require low power when they are incorporated into the device. No attempt was made to optimize the power requirements during this study since these would depend on the actual material selected and the device configuration used. The most interesting thermochromic materials, which satisfy the above conditions, are those that involve a rearrangement of cations in a close-packed anion crystal lattice where no breaking of chemical bonds occurs. Theoretically, there appears to be no upper limit to the rate at which such transitions, often called order-disorder reactions can occur. Thus, these transitions are intrinsically rapid and take place at a definite temperature.

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* (1) References are given at the end of the report.

When this program began all of the known compounds that exhibited thermochromic order-disorder transitions possessed the general formula $M_2M'I_4$, where M was either Ag^{1+}, Cu^{1+}, or Tl^{1+} and M' was either Hg^{2+} and Cd^{2+}. The two best known examples are silver mercury iodide and copper mercury iodide. The color changes are vivid and reversible and occur at a specific transition temperature.

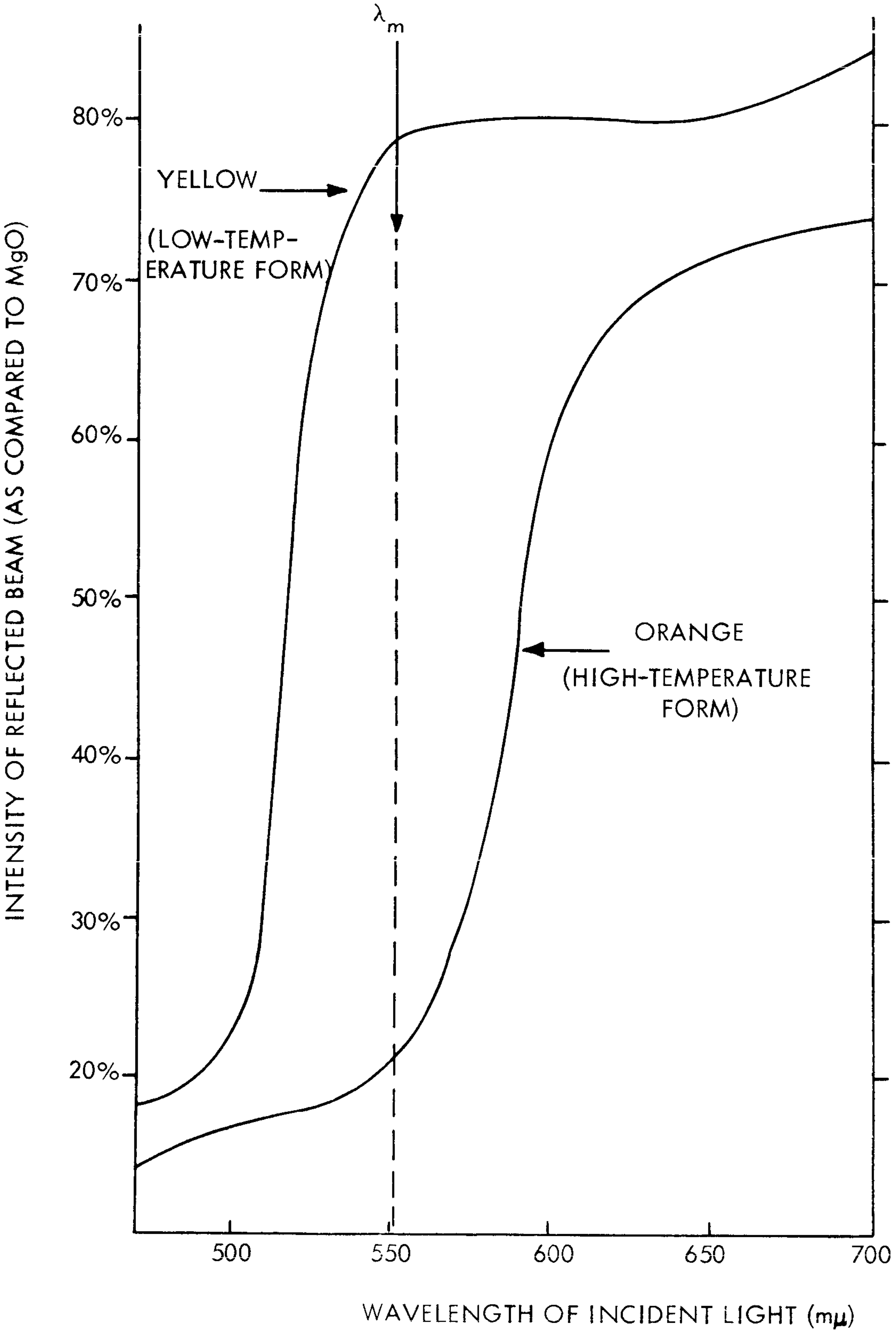
Two possible approaches were available at the start of this program. One approach would involve taking the known ternary mercuric iodides and incorporating them in display devices. The emphasis would be placed on optimizing the device characteristics such as power requirements and overall device configuration. The second approach would be to synthesize new thermochromic materials which undergo this order-disorder transformation so that materials with different transition temperatures, different color changes and improved stability could possibly be obtained. The latter course was chosen because the known ternary mercuric iodides were expected to be reasonably volatile and might possibly be thermally unstable.

1.2 Properties Of Previously Known Inorganic Thermochromic Materials

Prior to the start of this program a number of thermochromic iodides were known. As was mentioned earlier, they had the general chemical formula $M_2M'I_4$ and the mechanism for their thermochromic change was via an order-disorder reaction. A summary of these compounds and their pertinent properties are presented below.

Silver Mercuric Iodide (Ag_2HgI_4)

Silver mercuric iodide was studied by Ketelaar(2, 3, 4). The low-temperature form is a bright yellow. Its color changes reversibly to red-orange at 50.5°C. Reflectance spectra of both the yellow and orange forms were measured in our laboratory and are shown in Figure 1. Ketelaar interpreted the phenomenon as follows: The



REFLECTANCE CURVES FOR Ag_2HgI_4 AT TWO TEMPERATURES

FIGURE 1

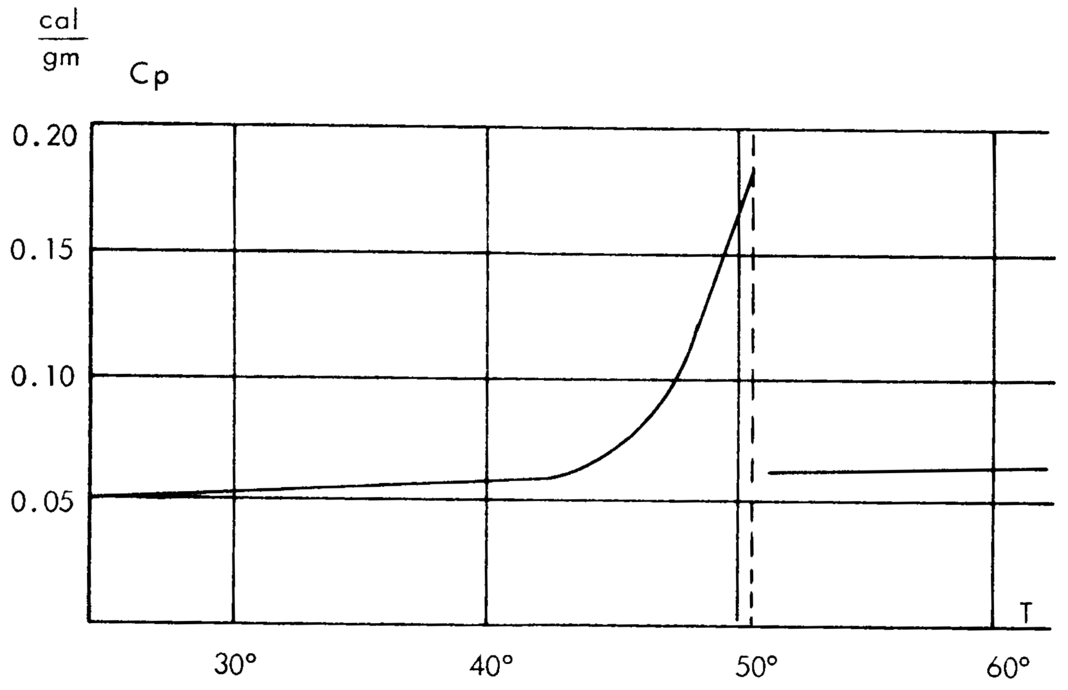
lattice is built up of a cubic close-packed frame of large iodide ions. Between these ions there are eight tetrahedral holes for every four iodide ions. Only three of these holes are occupied by silver $^{1+}$ and mercury $^{2+}$ ions. The crystal structure of the yellow form has been confirmed by Hahn et al $^{(5)}$. There are five available vacant cation sites in each Ag_2HgI_4 unit. In the yellow (β) form the vacancies and cations are ordered, while in the orange (α) form they are randomly distributed among the available tetrahedral positions. The phenomenon of the color change can therefore be described as an order-disorder movement of cations in a fixed lattice of close-packed iodide ions. This mechanism is favorable for fast response since the iodide lattice stays unaltered and only the smaller and more mobile cations change their positions. In order to prove this hypothesis, Ketelaar measured the specific heat $^{(3)}$ and the electrolytic conductivity $^{(4)}$ of Ag_2HgI_4. The data he obtained are useful for device applications of the phenomenon. The specific heat at 20°C is 0.05 cal/gm; above 37°C it rises abnormally and reaches three times its normal value at 50°C (see Figure 2). The experimental values are given by the equations.

$$Cp\ (\alpha,\ \text{orange}) = 0.0609 + 0.00021\ (t-50)$$

$$(t = \text{temp}\ ^{\circ}C)$$

$$Cp\ (\beta,\ \text{yellow}) = 0.0454 + 0.00024\ t$$

From these values the total transition energy has been calculated to be 1.43 Kcal/mole$^{(4)}$, or 5.9×10^{-4} BTU/in.^{2} (for a 0.001-inch-thick specimen). These numbers are for the pure chemicals only and do not include the effects of the binder and the substrate. The latter data along with heat losses are needed before actual power requirements of a device can be determined. The electrical conductivity of α (orange)



SPECIFIC HEAT OF Ag_2HgI_4 AS A FUNCTION OF TEMPERATURE

FIGURE 2

Ag_2HgI_4 is about a thousand times better than that of any other ionically conducting solid substance in the temperature range of 51 - 140°C. The major restraint to free movement of cations is the activation energy to surmount the potential barriers separating the different points of the lattice. In the α structure both Ag^+ and Hg^{++} are mobile, but only 6 percent of the charge is transferred by Hg^{++} ions. The conductivity of α-Ag_2HgI_4 is given by $K = Ce^{-A/RT}$, where $C = 4 \times 10^2$ and $A = 8600$ cal/atom (see Figure 3).

Copper Mercuric Iodide (Cu_2HgI_4)

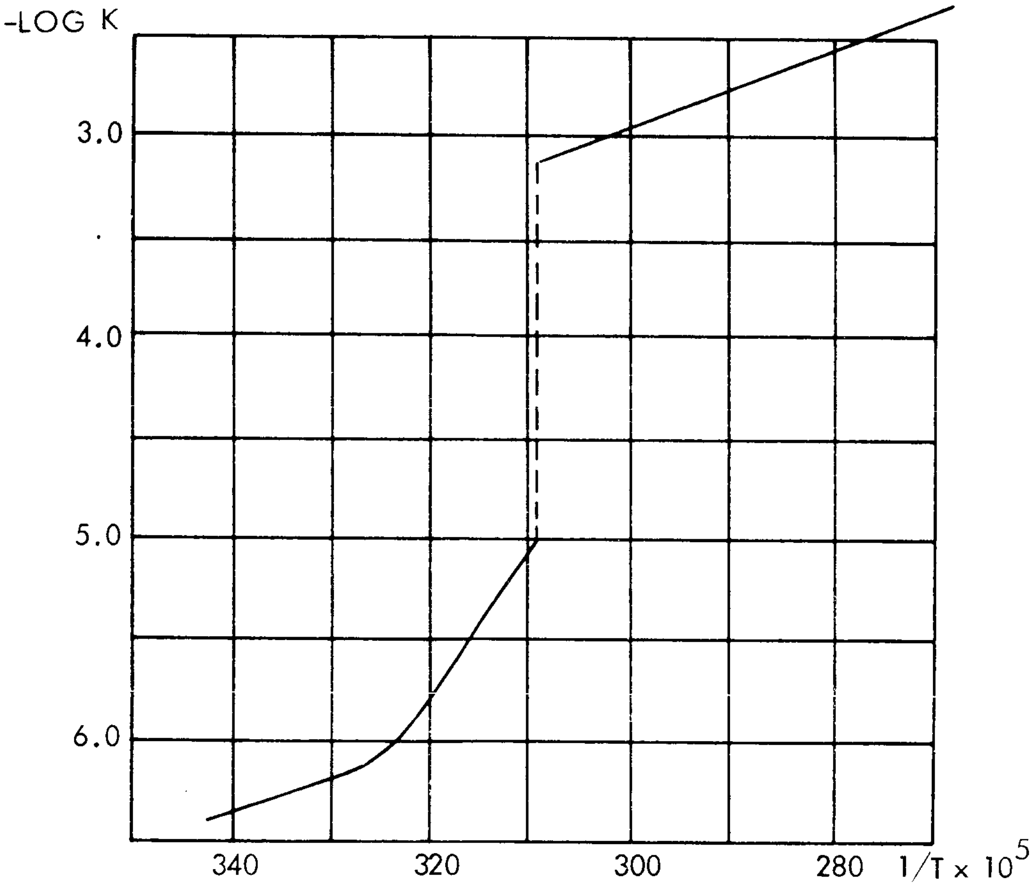
Tammann and Veszi (6) studied the copper analog of silver mercuric iodide. Copper mercuric iodide (Cu_2HgI_4) turns from red to black at 69.5°C, with a fast response. The mechanism appears to be the same as for Ag_2HgI_4. No other thermodynamic data have been reported on this compound.

Mixed Copper and Silver Mercuric Iodides

Suchow and Keck (7) prepared solid solutions of Ag_2HgI_4 and Cu_2HgI_4. They found that a compound $Ag_{1.14}Cu_{0.86}HgI_4$ was formed which underwent a transition from orange to red at 34°C. Figure 4 gives the phase diagram for the Ag_2HgI_4 - Cu_2HgI_4 system. The mechanism for the color change is presumed to be the same as for the pure ternary compounds.

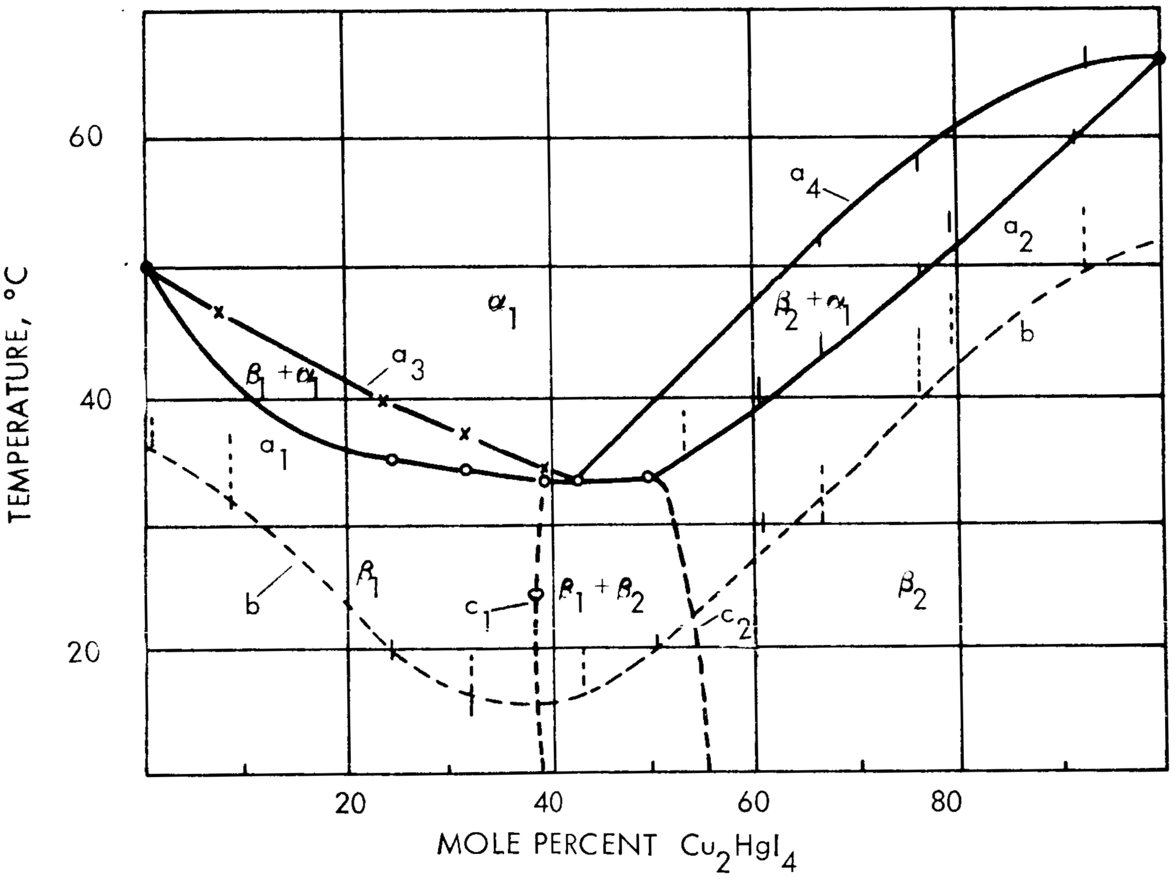
Thallium Mercuric Iodide (Tl_2HgI_4)

Another compound of the $M_2M'I_4$ type, Tl_2HgI_4, has been found to change from orange to red at 116.5°C by Asmussen and Anderson (8). However, it decomposes at 130°C. Because the decomposition temperature is so close to the color transition temperature and also because of the toxicity of thallium compounds, the uses for this compound would appear to be minimal.



ELECTRICAL
CONDUCTIVITY OF Ag_2HgI_4 AS FUNCTION OF 1/T

FIGURE 3



PHASE DIAGRAM FOR THE SYSTEM Ag_2HgI_4-Cu_2HgI_4: O, sharp color transition observed upon increasing temperature; I, range of gradual color transition observed upon increasing temperature; X, color transition observed only upon cooling; ⁞, range of gradual color transition observed upon cooling; o, limit of heterogeneous range as determined by X-ray diffraction; α_1, solid solution of α-Cu_2HgI_4 and α-Ag_2HgI_4; β_1, solid solution of β-Cu_2HgI_4 in β-Ag_2HgI_4; β_2, solid solution of β-Ag_2HgI_4 in β-Cu_2HgI_4.

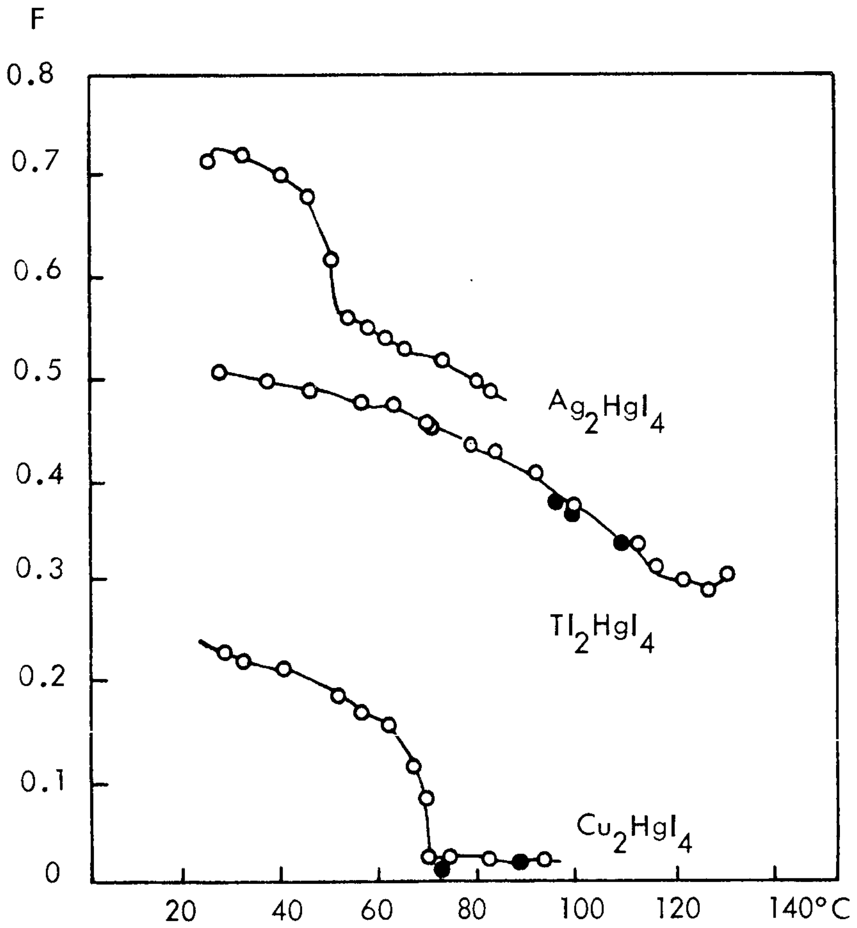
FIGURE 4

Copper Cadmium Iodide (Cu_2CdI_4)

The compound copper cadmium iodide was prepared in this laboratory. It undergoes a color change from pale yellow to rust brown at approximately 140°C. The color change is gradual rather than sharp.

Other Measurements

Asmussen and Anderson(8) measured reflectance as a function of temperature for Cu_2HgI_4, Ag_2HgI_4, and Tl_2HgI_4. The results are illustrated in Figure 5. The temperature at which the slope of the curve is greatest represents the transition temperature for each material. Both Ag_2HgI_4, and Cu_2HgI_4 have a rather narrow temperature region over which the sharp reflectance change occurs, whereas the transition region is much broader in the case of Tl_2HgI_4. The Cu_2HgI_4 had the color change with the greatest contrast.



REFLECTANCE F OF THE COMPOUNDS Cu_2HgI_4 AND Tl_2HgI_4 PLOTTED AGAINST THE CELSIUS TEMPERATURE. The "black" points represent F-values measured at decreasing temperatures.

FIGURE 5

2.0 DISCUSSION

2.1 The Approach

The results of some early studies in our laboratory on the thermal stability of Ag_2HgI_4 and Cu_2HgI_4 at 110°C had shown that these compounds decomposed presumably giving off HgI_2. Thus, it might be expected that any display device, which utilized any of the ternary mercuric iodides discussed previously, would have limited lifetime if it were maintained at elevated temperatures for too long a duration. The results of these thermal stability experiments therefore necessitated a search for new thermochromic materials. These new materials would be expected to undergo an order-disorder transition involving the migration of cations in a fixed anion crystalline lattice at a specific temperature, such as occurs with the ternary mercuric iodides. These new materials should also be more thermally stable above their transition temperature than the ternary mercuric iodides.

The first characteristic is necessary in order that the mechanism of the thermochromic change is not the limiting factor for the rate of display of information of the device. The second characteristic is necessary in order that the device have an appreciable lifetime.

2.2 Basis For Selection Of Substitutional Iodides

The selection of substitutional iodides as systems for study was based on the results of some experiments in which new compounds similar to Ag_2HgI_4 and Cu_2HgI_4 were prepared. In these compounds all or part of the mercury ions were replaced by cadmium ions. These new compounds were thermochromic but appeared to have a gradual rather than a sharp color change. The compound Cu_2CdI_4, which was mentioned earlier, changes color from pale yellow to a rust brown at approximately 140°C. The expected product from the thermal decomposition of Cu_2CdI_4, CdI_2, has a lower vapor pressure at 150°C than HgI_2 has at 80°C. This latter temperature is approximately 10°C above the transition temperature for Cu_2HgI_4 (69°C). Thus, Cu_2CdI_4 would be expected to be more thermally stable at 150°C than Cu_2HgI_4 is at 80°C. It seemed likely therefore that the thermal stability could be improved and the transition temperature be changed in ternary mercuric iodides by appropriate ionic substitution.

2.3 Basis For Selection Of Ternary Chalcogenides

The selection of chalcogenides as candidates for investigation is based on the similarity between their crystal structure and the crystal structure of the ternary mercuric iodides. It was pointed out by Hahn et al(9) that in the group of 27 compounds of the formula MM'_2X_4, where M = Zn, Cd or Hg, M' = Al, Ga or In, and X = S, Se or Te, many had the crystal structure S_4^2 and D_{2d}^{11} like $Ag_2Hg_2I_4$ and Cu_2HgI_4. The S, Se or Te anions were placed in exactly the same positions as the iodide anions, while the metal cations had similar arrangements as the Ag, Cu, and Hg cations in the known thermochromic compounds. It seemed very likely therefore 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 also usually more thermally stable than the corresponding iodides.

2.4 Thermochromic Property Measurements

In addition to the material preparation phase of the program, it was necessary to perform some physical property measurements on those which exhibited thermochromic activity. Each material that was prepared was subjected to a qualitative test for thermochromism, which consisted in heating the material on a hot plate. If a change in color was observed on heating which reverted to the original color on cooling, the material was considered for further study. Otherwise, it was discarded. The physical properties chosen for study were the reflectance spectra, the color transition temperatures, the electrical conductivity, the heat capacity and thermal conductivity.

The reflectance spectrum provides information about the color of the material which may be followed as a function of temperature. From a comparison of the reflectance spectra of the high and low temperature forms of the material, some indication about the contrast could be obtained. The transition temperature is the temperature at which the largest change in color takes place.

Since Ag_2HgI_4 and Cu_2HgI_4 showed large increases in their electrical conductivity at their respective transition temperatures, the electrical conductivity of the most promising thermochromics was determined. This large increase in the electrical conductivity could possibly be utilized in a switching operation.

Since the thermochromic change depends on heat it is important to determine the thermal properties of the material such as heat capacity and thermal conductivity, in order to assess the power requirements of a particular device configuration. It should be emphasized, however, that the importance of these data depends on the actual device configuration in which they will be utilized. Any device configuration that one can visualize would necessarily have the thermochromic material supported on a substrate. Since under these conditions the substrate would contribute importantly to the heat requirements of the device, a knowledge of the thermal properties of the thermochromic materials themselves would not appear to be as important as the thermal properties of the composites. Thus, measurements of the heat capacity and thermal conductivity were not performed during this study.

Another important property of the thermochromic is its thermal stability because the lifetime of operation of any device in which it would be incorporated is dependent on it. Two types of stability tests were conducted: a static test and a cycling test. In the static test the material was maintained at 10°C above its transition temperature. The weight loss of the material was followed as a function of time. In the cycling tests the thermochromic was continuously cycled above and below its transition temperature at a constant rate. The purpose of this test was to determine whether there was any fatigue associated with the color change. Before the experimental results are presented, however, the potential device applications for thermochromics that were considered on this program and the prototype numeric display device which was constructed using some of the known ternary mercuric iodides, will be discussed first.

3.0 POTENTIAL APPLICATIONS OF THERMOCHROMICS

Before discussing specific device areas it would be worthwhile to point out generally the advantages which thermochromics offer in display. One of the first advantages would be the absence of moving parts. Secondly, and more importantly, since observation of the color change depends on reflected rather than emitted light, it is possible to display information under high ambient illumination. The visibility of the display will not be washed out under high ambient illumination as is the case with electroluminescent devices. A third advantage is the inherent persistence of this type of material. This advantage is important for display media driven repetitively such as a cathode ray tube. Thus, a flicker-free display is possible, even with low repetition rates. A standard phosphor, even one having so-called long persistence, reaches peak brightness almost immediately after being pulsed, and then gradually decreases in brightness. Thus, fairly rapid repetition rates are necessary, if objectionable flicker is to be avoided. Thermochromics are essentially two state materials. If raised above the color transition temperature there is little change in the color even if the temperature is carried appreciably higher. For a repetitively driven display then, it is necessary merely to repeat the signal before the material has cooled down to the transition temperature in order to obtain a completely flicker-free display. This could be quite slow with appropriate materials and configuration. This becomes important particularly when the displayed information is being derived from a computer, since it permits the use of a slower, cheaper computer and reduces the size of the computer memory which might be required. The fourth advantage is that the persistence of the display which uses thermochromics can be readily controlled by a combination of three methods: (1) selection of a thermochromic with a given transition temperature, (2) determination of how far above the transition temperature the thermochromic will be carried when heated and (3) selection of the mass and thermal conductivity of the substrate on which the material is applied. With other display media there is either no persistence, or in the case of phosphors, a persistence which is strictly a function of the chemical composition of the display medium. Fifthly, since thermochromics do not emit light, but rather differentially reflect incident light, we are not limited by the usual energy transfer relationships where emission occurs at longer wavelengths than the energy which produced it. With thermochromics for example, a change in color from yellow to orange can be produced by infra-red stimulation. Finally because of the difference in electrical conductivity between the high-temperature and low-temperature forms an added storage mechanism is available particularly if they could be combined with electroluminescent materials.

The main disadvantage of thermochromics is that the color change depends on heat. This implies possibly high power consumption and relatively low rates of display of information. However, the time response of the eye is such that milliseconds are available to remain within the realm of "instantaneous" display. Furthermore, the amount of "written" information to be displayed is a small proportion of the display area, so that an analytical study is necessary for true assessment of the power requirement. No such analytical study was performed on this program. Such an analytical study requires that one have a particular device configuration in mind. Rather than concentrate on a particular device it was decided to look into the feasibility of using thermochromics for a number of different applications. On this program these applications included a numeric display device, an electroluminescent thermochromic hybrid device and a cathode ray tube device in which a thermochromic was substituted for the phosphor. Each of these particular applications are discussed in succeeding paragraphs. First of all the concept of a numeric display device is presented.

3.1 Concept Of A Thermochromic Display Device

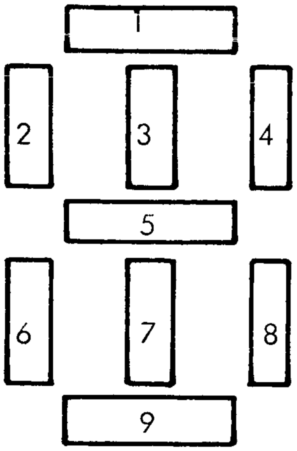
In perhaps its simplest form a thermochromic display could consist of a panel on which is applied a thin layer of the thermochromic compound encapsulated in a transparent medium. Behind the thermochromic layer there may be a certain configuration of thin resistance wires that can be heated in selected separate sections, such as in an alphanumeric arrangement, a reference map, or a set of fixed dial positions. The heated wire will produce a line of the high-temperature color of the thermochromic material against a background of the low-temperature color of that same material. Switching off the power to the heating wire will be followed by a rapid fading of the contrasting line. In principle, the visibility of such a device would be a function of the level of ambient illumination; i.e. the higher the light level, the better the contrast. Other techniques for generating the hot color form could also be considered. For example, an external energy source such as an electron beam or a laser may be used to heat the thermochromic. However, for the initial study, the hot wire technique was utilized exclusively. Numeric display devices, which incorporated either of the known thermochromics, silver mercury iodide or copper mercury iodide, were constructed and successfully demonstrated. A description of these devices is presented in the next section of this report. Such a device could be used in a command room.

The type of device configuration described above could not be placed in an aircraft, if silver mercury iodide or copper mercury iodide were used as the thermochromic materials, since the present military specifications for materials used in aircraft include a "useful life" over a temperature range of approximately $-55^{\circ}C$ to $+110^{\circ}C$. Silver mercury iodide changes color at $50.5^{\circ}C$ and copper mercury iodide changes color at $69^{\circ}C$. Both of these materials decompose at an appreciable rate at a temperature of $10^{\circ}C$ above their respective transition temperatures. Thus, if the above device configuration were to be utilized, the thermochromic material should be stable and unaltered over the temperature range required by the military specifications and have its color transition temperature around $125 \pm 10^{\circ}C$.

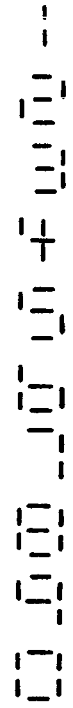
Besides the device configuration previously described, it may also be possible to design a device for situations in which the ambient temperature exceeds the transition temperature of the thermochromic material. In order to display information the temperature of the material could be decreased by thermoelectric cooling of the wires. This would result in "cold" writing on a "hot" background. This device would be limited also by the thermal stability of the material at temperatures above its transition temperature. A device which incorporates both the heating as well as the thermoelectric cooling characteristics could possibly be operated over almost the entire temperature range required by the military specifications. The apparent disadvantages of thermoelectric cooling are the additional power requirement for the device and the more complex configurations required.

3.2 Prototype Display Fabrication and Evaluation

Three simple devices have been built to demonstrate the application of thermochromics to display units. The schematics for these single manually-switched display devices are shown in Figure 6. A photograph of each of the devices is shown in Figure 7. The numeric figure was built from 9 segments of 50 mil nichrome wire woven on a laminated insulated board. Each of the segments had a resistance of about 1/4 ohms. The power to each segment, as supplied by a step down transformer, is 0.5 V, 1 watt at 60 cycles. The segments on the board were sprayed with a suspension of barium titanate in a thinned clear plastic matrix (Rohm and Haas A29+U233). After curing this was sprayed with a suspension of the thermochromic in the same thinned plastic and again allowed to cure. The panel was then covered with a pyrex disc used as a protective cover. In order to prevent accidental overheating of the thermochromic and its subsequent decomposition, a time delay tube was placed into the circuit. In addition to switching off the power to the heater after a set time it will not allow the unit to be turned on again until the thermochromic has had time to cool sufficiently.



NUMBER SHOWN ON PANEL	SEGMENTS "ON"
1	3,7
2	1,4,5,6,9
3	1,4,5,8,9
4	2,3,5,7
5	1,2,5,8,9
6	2,6,9,8,5
7	1,4,8
8	2,1,4,5,8,9,6
9	2,1,4,5,8
0	2,1,4,8,9,6



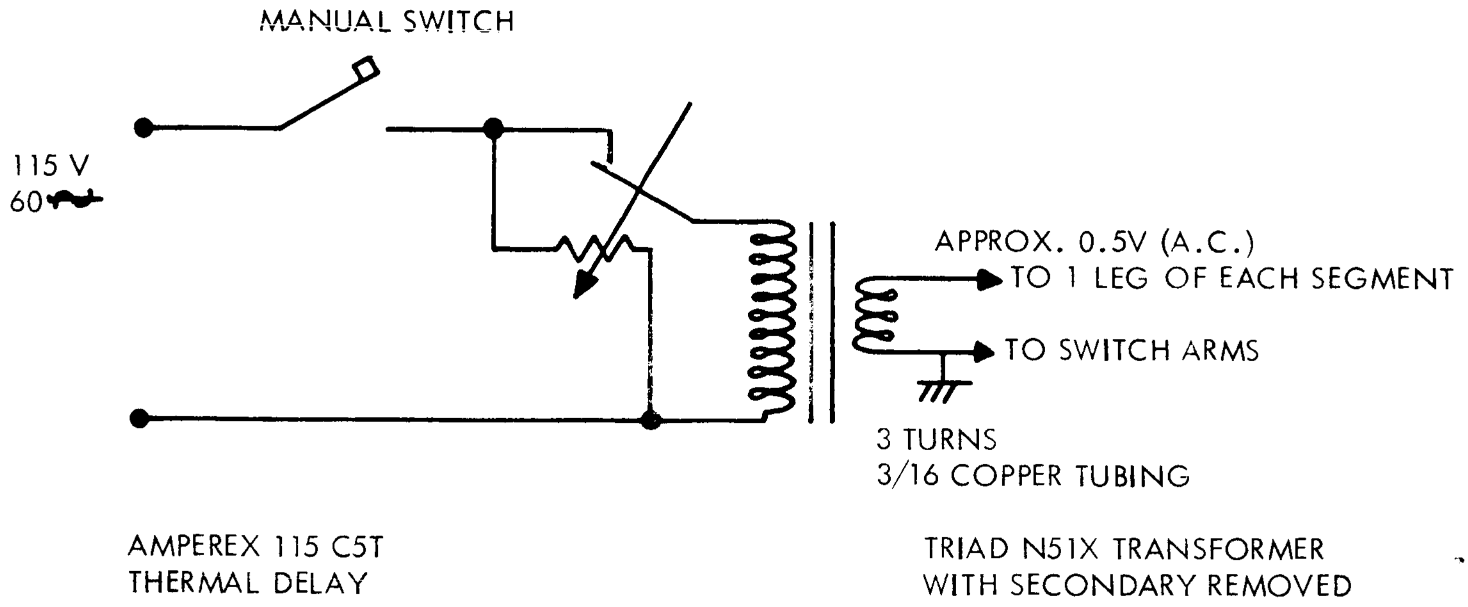


DIAGRAM OF THE PRELIMINARY DISPLAY DEVICE

FIGURE 6

FIGURE 7

PROTOTYPE DISPLAY UNIT


INCHES
1
2
GENERAL PRECISION INC
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In the devices, as constructed, both the write and erasure times are approximately one second in duration. It would appear that this could be improved by the use of more rapid heaters in the writing mode and by the use of a heat sink of some type to absorb heat in the erasing mode. Since optimization of the device was not an objective of this program, no work along these lines was attempted.

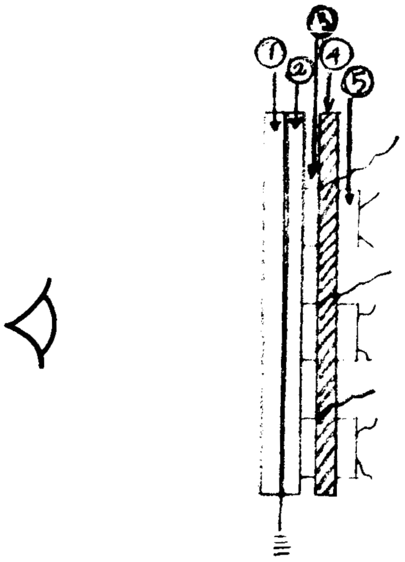
A demonstration device was delivered to the contract administrator, Mr. E. Hilborn, NASA/ERC. The other two devices have been used to demonstrate the use of the known thermochromics Ag_2HgI_4 and Cu_2HgI_4.

3.3 Thermochromic-Electroluminescent Device

Although a display device using a thermochromic alone works very well under high ambient illumination, its utility vanishes at "zero" ambient because observation of the display depends on reflected light. In order to operate such a device under very low or "zero" ambient illumination, one possible solution is to combine the thermochromic material with an electroluminescent (el) material in a single unit. Two possible configurations for such a device are illustrated in Figures 8 and 9.

In Figure 8 a transparent thin film of el material is deposited on conducting glass. The transparent thin film electrodes are deposited on the el material in the configuration of the display arrangement (numeric and/or alpha-numeric). Painted over these layers is a complete coat of thermochromic material after which resistance heating elements are attached in the <u>same</u> configuration as the electrodes. At high ambient illumination the heaters are activated and the thermochromic material is transformed into its high-temperature color; at low ambient illumination the circuit to the el panel is used.

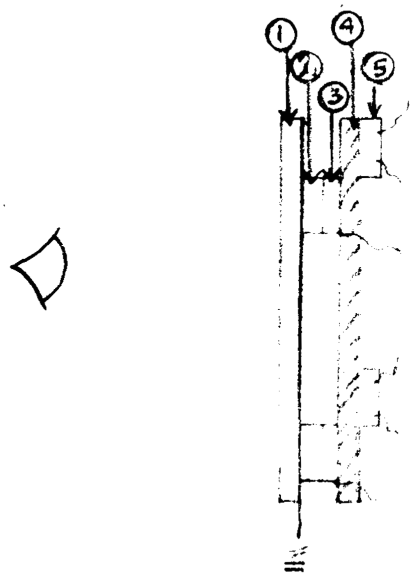
HYBRID THERMOCHROMIC ELECTROLUMINESCENT DISPLAY DEVICE (# 1)



1. - transparent conducting glass
2. - transparent el phosphor film
3. - transparent electrodes
4. - opaque thermochromic
5. - resistance heating elements

FIGURE 8

HYBRID THERMOCHROMIC ELECTROLUMINESCENT DISPLAY DEVICE (#2)



1. - transparent conducting glass
2. - el powder strips
3. - electrode strips
4. - thermochromic
5. - resistance heating elements

FIGURE 9

Figure 9 illustrates a second method of effecting a combined el and thermochromic display. A configuration (numeric or alpha-numeric) of el phosphor powder is deposited on conducting glass and electrodes are applied only covering the phosphor strips. A complete coat of thermochromic material is painted over the entire panel. Heater strips, in the same configuration as the el display, are mounted on top of the thermochromic but <u>offset</u> from the phosphor strips. In order to be useful, the body color of the phosphor strips must match the low-temperature color of the thermochromic material.

In both of the above configurations two circuits are needed, one to activate the el layer and the second to heat the thermochromic layer. In order to reduce the large power requirements necessary to activate high field el materials, materials which can electroluminesce by a mechanism of carrier injection would be used. Carrier injection luminescence has been demonstrated in thin films of GaAs and GaP at room temperature using a d.c. bias voltage of only a few volts.(10)

It is known that there is a large increase in the electrical conductivity of a thermochromic at its transition temperature. In the case of Ag_2HgI_4, for example, the electrical conductivity has been reported (4, 11) to increase by a factor of about 100. In addition, the electrical conductivity of the high temperature form is a thousand times larger than that of other solids which conduct by ion mobility over the temperature range 51 - 145°C. It therefore may be possible to simplify the circuitry further by using the thermochromic material as an electrical switch.

3.4 Thermochromics In A Cathode Ray Tube (CRT)

The feasibility of substituting a thermochromic material for the phosphor in a cathode ray tube has been considered also. In this regard a simple calculation was made of the temperature change expected when a thermochromic material is bombarded with electrons produced by the electron gun. In order to make this calculation, certain assumptions had to be made and certain values of the electron beam current, the accelerating voltage, the beam diameter and the surface density of the thermochromic had to be chosen. It was assumed that all of the kinetic energy of the electrons was converted into heat and all of this heat went into raising the temperature of the material.

The following values of the parameters mentioned before were chosen:

beam current	= 1×10^{-4} ampere
beam diameter	= 0.1 cm
accelerating voltage	= 10,000 volt
surface density	= 10 mg/cm^2

These represent the usual values encountered in an ordinary CRT, although large variations in the beam current and accelerating voltage are possible. The area of the electron beam (A), assuming a circular cross section, is $7.85 \times 10^{-3} \text{cm}^2$. This is also equivalent to the area of the thermochromic irradiated. The energy incident on this area per second (Q/t) is given by Q/t = I V, where I, the beam current is 10^{-4} ampere, and V, the accelerating voltage is 10^4 volts. Therefore:

$\frac{Q}{t} = \frac{1 \text{ volt-coulomb}}{\text{sec}} = 24.2 \times 10^{-2} \frac{\text{cal}}{\text{sec}}$. The increase in temperature is given by the following expression: $\Delta T = \frac{Q}{C_p}$

where m - mass of material irradiated (grams) = SxA,

C_p = specific heat = 0.05 $\frac{\text{cal}}{\text{g-deg}}$ for Ag_2HgI_4, and

S = surface density = 10^{-2} g/cm^2.

Therefore the amount of material irradiated is 7.85×10^{-5} g. For 1 second irradiation Q is 24.4×10^{-2} calories.

The temperature increase is then $\Delta T = \dfrac{24.4 \times 10^{-2}\ \text{cal}}{0.05\ \text{cal/g - deg} \times 7.85 \times 10^{-5}\ \text{g}} =$

$\dfrac{24.4 \times 10^{5}}{39.2} \approx$ 62,000 degrees. Decomposition and ablation of the material would be expected at these temperatures. In order to reduce the temperature increase, a faster sweep rate of the electron beam would have to be used. Theoretically for a millisecond duration of incidence the temperature of the material would rise 62°C. It would appear that this would limit the sweep rates available. However, it is possible to vary the beam current, accelerating voltage and the beam area sufficiently so that a wider range of sweep rates may be available. On the basis of the above calculation "writing" on a thermochromic material with electrons generated in a cathode ray tube appears to be feasible.

In order to design an experiment which will provide a definitive answer to the feasibility of using thermochromics in a CRT the following approach is suggested. A tungsten filament CRT electron gun, which can be repeatedly exposed to air without deterioration, is installed in a bell jar. The associated electronics are connected to the gun through an electrical feedthrough. The thermochromics are placed on a moving target in front of the electron gun to simulate various scan rates. In this way it is expected that definitive experimental evidence on the feasibility of using thermochromics in a CRT can be obtained.

4.0 EXPERIMENTAL RESULTS

A summary of the materials studied and their thermochromic properties are now presented . (a)

(a) A detailed description of the methods used to synthesize these materials and the techniques used to measure their transition temperatures, reflectance spectra, thermal stability, electrical conductivity and other miscellaneous observations are given in the Appendix.

4.1 Partial Ionic Substitution Compositions

An analysis of the mechanism for thermochromism in silver and copper mercuric iodides, that is the disordering of the cations in an unchanged iodide anion lattice, gave rise to the idea that substitution of small amounts of some other elements 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. This change in transition temperature would result from a different mobility in cases where a different cation was substituted. In the case of anion replacement, it would be expected that substitution by a smaller anion would lower the transition temperature because larger holes in the anion lattice would result.

4.1.1 Partial Anionic Substitution

To test the idea of partial anion substitution, the systems, $Ag_2HgI_{4-x}Br_x$, where x varied from 0.17 to 1.40, $Ag_2HgI_{3.75}Cl_{0.25}$, $Cu_2HgI_{3.75}Br_{0.25}$ and $Cu_2HgI_{3.75}Br_{0.25}$ were prepared. All of the silver containing formulations underwent a thermochromic change from yellow to orange and the copper containing formulations changed color from red to black. The transition temperatures for each of these systems are shown in Table 1 in column 2, and compared with those of Ag_2HgI_4 and Cu_2HgI_4. The transition temperatures of these systems were measured by the melting point capillary method. Partial anionic substitution by either Br or Cl caused a lowering in the transition temperature from 50.5°C to 42 ± 2°C for the Ag_2HgI_4 and from 69°C to 50°C for Cu_2HgI_4. There was no linear relation between the amount of bromide ion substituted and the transition temperature. Optimum thermochromic properties for the bromine substituted formulations occurred at four percent Br ion. As the bromide content was increased above four percent the thermochromic color change became more gradual with temperature. Possibly the cations can begin wandering at a lower temperature because of the irregularities in the iodide lattice. This may be due to the disruption of the lattice by the smaller bromide ion, and no exact amount of energy is required to start them all to move, as is the case in Ag_2HgI_4.

In order to obtain some measure of the color change produced when the materials were heated, the reflectance spectra of many of them were determined. The reflectance spectra were measured at room temperature and at 90 ± 10°C. The reflectance curves had a characteristic shape (see Figure 1). At short wavelengths the reflectance was small and relatively independent of wavelength. At intermediate wavelengths the reflectance increased with increasing wavelength. At long wavelengths reflectance was large and also relatively independent of wavelength. In the intermediate wavelength region a shift occurred between the low and high temperature forms toward longer wavelengths. The pertinent data from the reflectance spectra for the ternary mercuric iodides are given in Table I. The maximum shifts between the reflectance

TABLE 1

Reflectance Spectral Data of Substituted Ternary Iodides

Thermochromic	T_{trans} °C	Largest Shift (Hot - Cold)	λ of abs. edge where $I = \frac{I_{red} - I_{blue}}{2}$ cold form (λ_c) angstroms	hot form (λ_h) angstroms	I_{cold} / I_{hot} at $\lambda = \frac{\lambda c + \lambda h}{2}$	I_{cold} / I_{hot} at λ = 5500Å
Ag_2HgI_4	50.5	830Å	5250	5930	4.0	4.9
$Ag_2HgI_{15/4}Br_{1/4}$	43 ± 1	820Å	5270	5930	5.3	6.4
$Ag_2HgI_{15/4}Cl_{1/4}$	43 ± 1	720Å	5320	5950	3.5	4.3
Cu_2HgI_4	69.5	1080Å	6130	7020	3.0	1.0
$Cu_2HgI_{15/4}Br_{1/4}$	50 ± 1	1050Å	6180	7020	4.0	1.0
$Cu_2HgI_{15/4}Cl_{1/4}$	50 ± 1	875Å	6250	6950	3.3	1.0

curves for the high and low temperature forms are given in column 3. The magnitude of these reflectivity shifts was in the 820 - 1080Å range. In the fourth and fifth columns the wavelengths at which the reflected intensity lies halfway between its long wavelength maximum value (I_{red}) and its short wavelength minimum value (I_{blue}) are given for the "cold" (λc) and "hot" (λh) forms respectively. The largest change in reflectivity occurred at the wavelength (λ) which was located at the midpoint between λc and λh. The ratio of the reflected intensities for the "cold" and "hot" forms at λ was then calculated. These values are given in column 6. In the last column the ratio of the reflected intensities for the "cold" and "hot" forms were calculated at 5500Å. Note that for the copper mercuric iodides this ratio at 5500Å is unity indicating that the reflected intensities for both forms are equal at this wavelength. The ratios of the reflected intensities at $\frac{\lambda_c + \lambda_h}{2}$ or at 5500Å have been used as a measure of the contrast between the low and high temperature colors of these materials. These ratios are in no way to be interpreted as a measure of true contrast. The concept of contrast involves, aside from the psychological factors, the differential sensitivity of the eye to increments of wavelength. Changes in hue discrimination are not equal for equal increments of wavelength. Thus, the ability of the eye to distinguish between two colors would not only depend on the magnitude of the shift between the respective reflectance spectra but also on the region of the spectrum in which the shift takes place. This would necessarily include also the slopes of the reflectance spectra for each form. Materials which have steep cut slopes would be amenable to improvement in contrast by overlap of a sharp cut filter. In order to determine an absolute value for contrast an expression, which would include all of the factors mentioned above, would have to be determined. At present no appropriate measure for contrast exists and no attempt, other than the use of the ratio of reflected intensities at a particular wavelength, was made to show the extent of the color change.

4.1.2 Partial Cationic Substitution

In order to test the influence of cation substitution a series of compounds in which the mercuric cation was partially replaced by cadmium were prepared. This series included $Ag_2Hg_{1-x}Cd_xI_4$, $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$, and $Cu_2Hg_{1-x}Cd_xI_4$, where x varied from 0.0 to 0.25. Their transition temperatures were measured by the melting point capillary method and the Dennis melting point method. Cadmium was selected to replace Hg because the compound Cu_2CdI_4 prepared by us earlier was thermochromic. All of the silver-containing formulations undergo a thermochromic change from yellow to orange, which is similar to the change observed in Ag_2HgI_4. The copper containing formulations all went from red to black as is the case with Cu_2HgI_4. Figure 10 shows the effect on the transition temperature of Cd substitution for Hg determined by the melting point capillary methods. In general, there is a rise in transition temperature with increasing Cd content. The vertical lines indicate the range over which the transition occurred in a melting point capillary which was immersed in a stirred oil bath heated at a rate of about 3°C/minute. Figure 11 shows the same parameters plotted for the double substitution formulation $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$. Again the oil bath was heated at a rate of about 3°/minute. The effect is similar to that in $Ag_2Hg_{1-x}Cd_xI_4$ in that there is a general increase in the transition temperature with increasing Cd content. However, since the transition temperature of the Br substituted material is originally lower than the one without Br, and the transition temperatures of the materials having $x = 0.25$ are about the same, the slope of the curve for $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$ is generally greater. Figure 12 shows the same data for $Cu_2Hg_{1-x}Cd_xI_4$ at a heating rate of 1°C/minute. The broadening of the temperature interval over which the transitions occur is greater in this case than in the previous two cases.

The transition temperatures of commercially purchased Ag_2HgI_4 and of the substitutional formulations $Ag_2Hg_{1-x}Cd_xI_4$, $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$, and $Cu_2Hg_{1-x}Cd_xI_4$ were also measured on the temperature gradient stage. These data are shown in Table 2. The

Figure 10

Transition Temperatures of $Ag_2Hg_{1-x}Cd_xI_4$
Determined in Melting Point Capillaries
As a Function of x

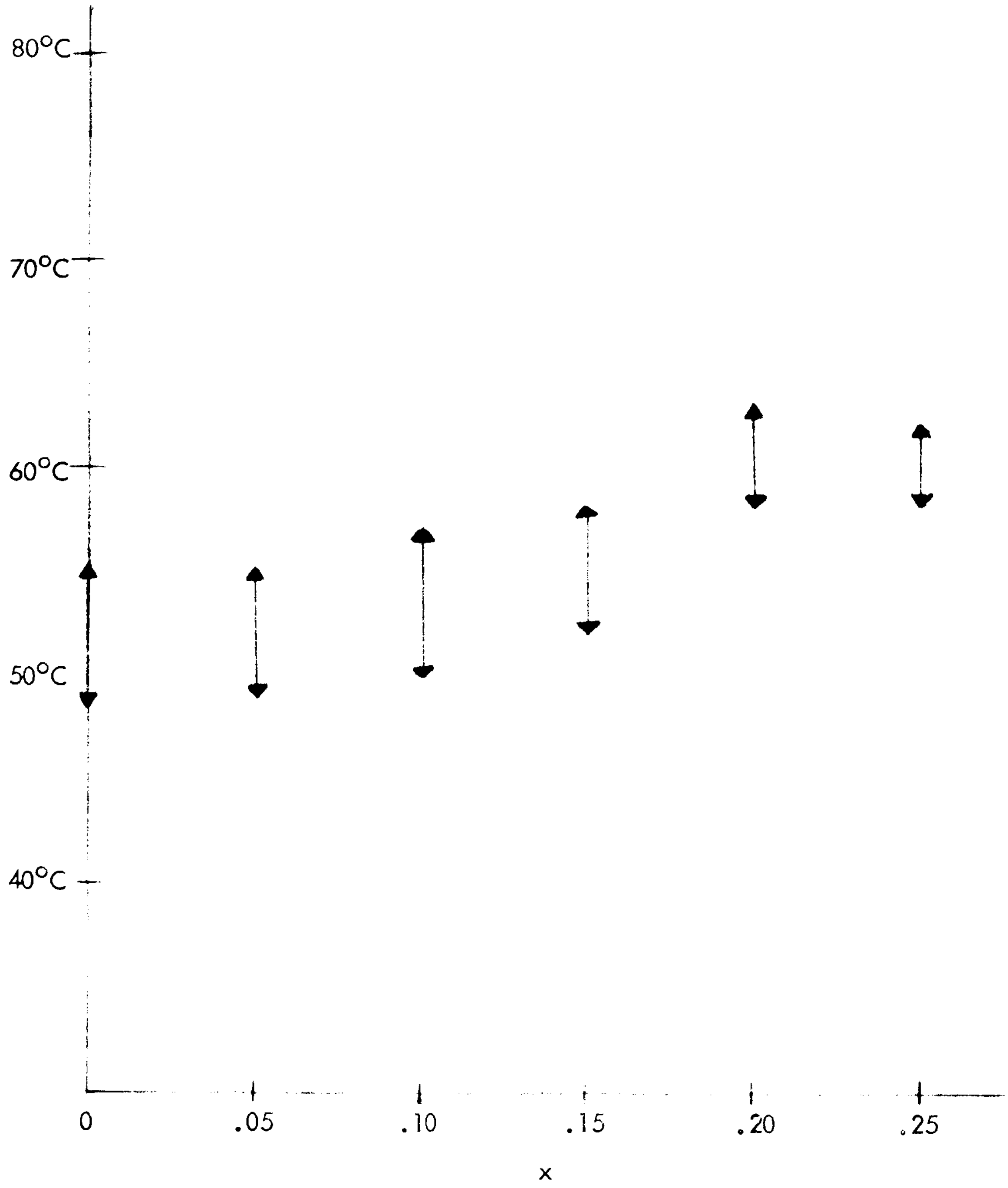


Figure 11

Transition Temperatures of $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$
Determined in Melting Point Capillaries
As a Function of x

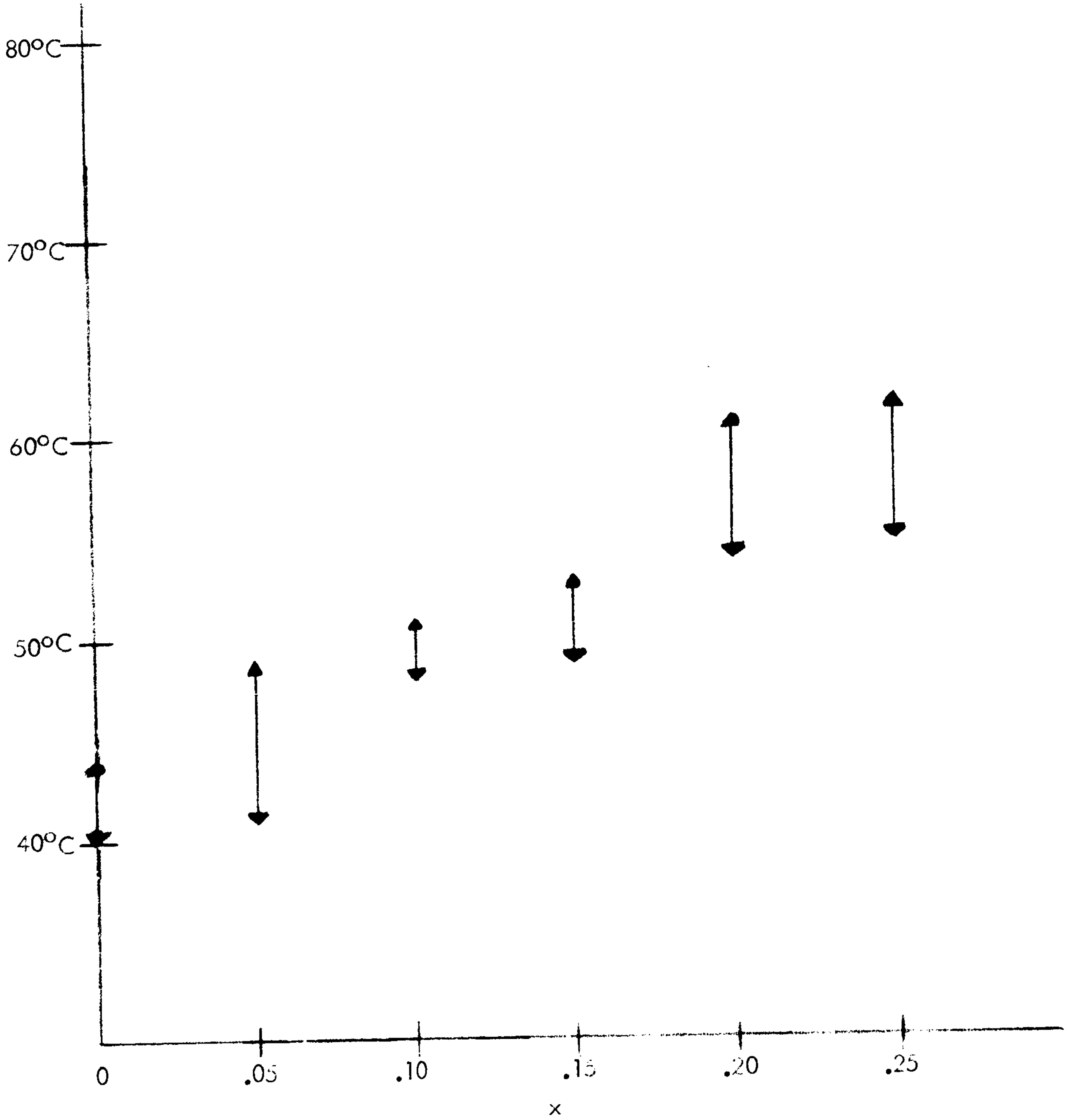


Figure 12

Transition Temperatures of $Cu_2Hg_{1-x}Cd_xI_4$ Determined in Melting Point Capillaries As a Function of x

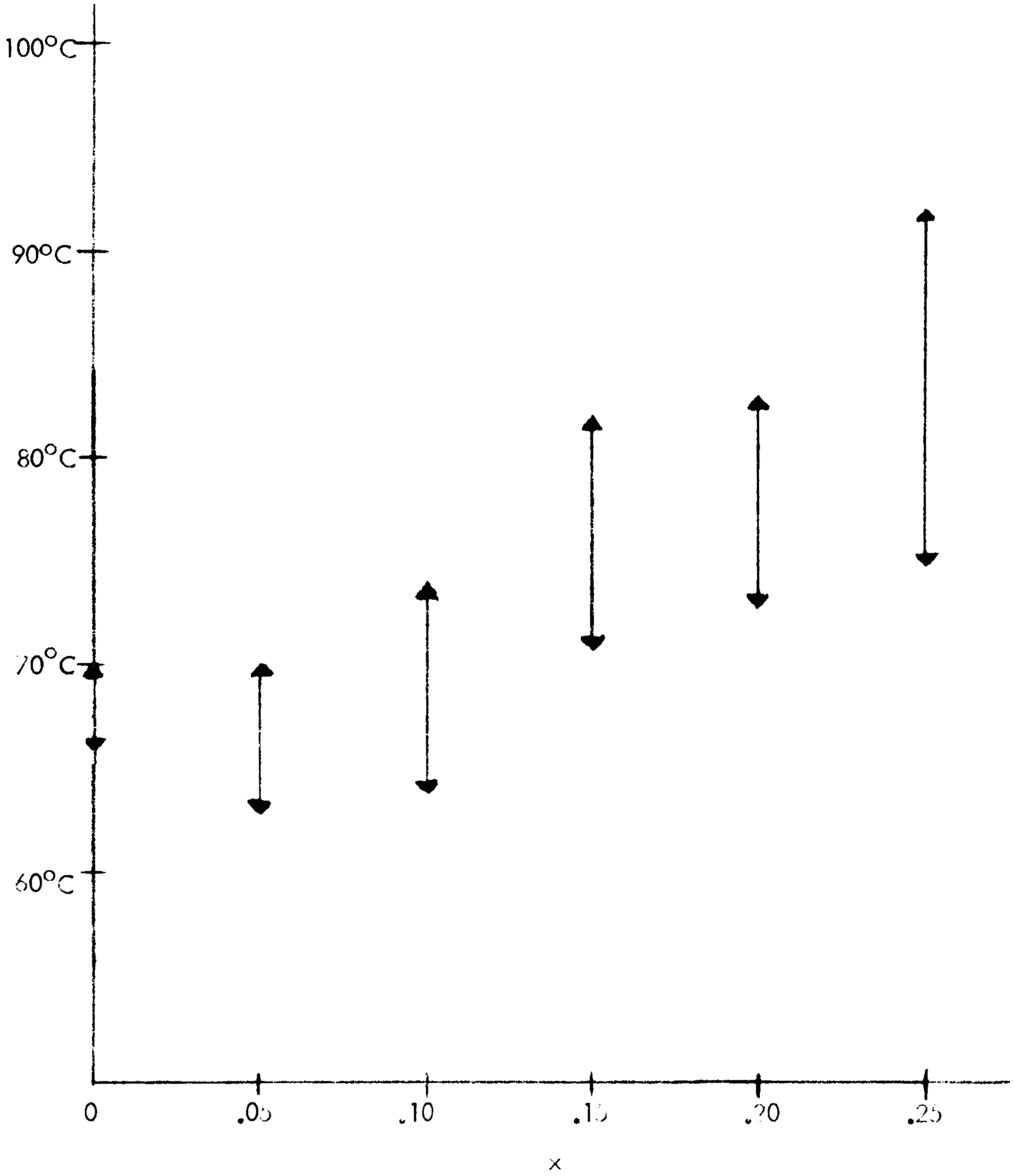


TABLE 2

Transition Temperature of $Ag_2Hg_{1-x}Cd_xI_4$

x	Variable Temperature Stage	Melting Point Capillary
0	47 - 51°C	49 - 55°C
0.05	47 - 55°C	50 - 56°C
0.10	48 - 58°C	51 - 57°C
0.15	52 - 63°C	58 - 62°C
0.20	51 - 65°C	58 - 62°C
0.25	56 - 67°C	58 - 61°C

Transition Temperature of $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$

0	41 - 48°C	41 -44°C
0.05	41 - 51°C	41 - 49°C
0.10	40 - 48°C	48 - 50°C
0.15	43 - 56°C	48 - 52°C
0.20	48 - 59°C	52 - 60°C
0.25	53 - 61°C	53 - 61°C

Transition Temperatures of $Cu_2Hg_{1-x}Cd_xI_4$

0	69 - 71°C	66 - 70°C
0.05	55 - 69°C	67 - 70°C
0.10	66 - 72°C	64 -74°C
0.15	72 - 80°C	71 - 82°C
0.20	76 - 87°C	73 - 83°C
0.25	80 - 90°C	75 - 92°C

data as determined by the melting point capillary method are shown for comparison.

The value for the transition temperature of Ag_2HgI_4 is generally given as 50.5°C but on the stage a definite color gradation was observed in the temperature range of 47°C to 51°C. There was indication of some color change below 47°C but it was difficult to measure. The largest change seems to occur at 49.5°C.

The agreement in the data as determined by the two methods is not too bad, especially if the highest points of the range are compared. The greatest difference evidently lies in distinguishing the various shades of yellow or yellow-orange that are found in the silver containing preparation. The agreement is generally better with the copper materials which undergo a red to black transition.

Analysis of the reasons underlying the broadening of the transition regions will have to wait until the results of an x-ray diffraction analysis of the ratio of the materials formed are available. It is possible that new compounds or mixtures of compounds could be present.

Thus, partial cationic substitution by Cd^{2+} for Hg^{2+} generally caused an increase in the transition temperature with increasing Cd^{2+} content. The color change on heating was more gradual for the cadmium substituted iodides than for the bromine substituted iodides.

The reflectance spectra of these Cd^{2+} substituted iodides were not determined during this study.

4.2 Ternary Chalcogenides

There are twenty-seven possible ternary chalcogenides of the formula MM'_2X_4 where M = Zn, Cd, or Hg, M'=Al, Ga or In and X = S, Se or Te as shown in Table 3. An attempt was made to prepare each of the compounds listed in Table 3. A tabulation of their room temperature color, x-ray data and reflectivity shift are also given. Twenty-two of the twenty-seven ternary chalcogenides were successfully prepared. The five compounds which were not successfully synthesized are designated with a dashed line in the x-ray column of Table 3. These particular five compounds were all reported in the literature to be dark-colored, and no further attempts to synthesize them were made. Any thermochromic change they might undergo would not occur in the visible region of the spectrum. Compound verification in the other twenty-two was obtained by x-ray analysis. This was accomplished by analysis of the Debye-Scherrer powder diffraction patterns and comparison with the published data. The crystal structure for each compound is indicated in the x-ray column. For those compounds which have crystal structures similar to the ternary mercuric iodides discussed earlier, those that are tetragonal represent the β or low temperature form and those that are cubic represent the α- or high temperature form. It should also be noted that some of these compounds have the spinel structure and as such have different crystal structures than the iodides.

The reflectivity shift indicated in Table 3 refers to the change in the position of the absorption edge of the reflectance curve when the sample was heated to about 90°C.

This absorption edge shifted to longer wavelengths on heating for almost all of the materials examined on this program. A few compounds showed no reflectivity shift on heating. This is indicated by "none" in the last column of Table 3.

The only reliable transition temperature determined for the colored ternary chalcogenides listed in Table 3 was for $CdIn_2S_4$ which was in the 95 - 100° range. The color changes

TABLE 3

DESCRIPTION OF TERNARY CHALCOGENIDES

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

n.d. -- not determined

(a) -- color obtained from literature

--- Attempts to prepare these compounds were unsuccessful for the other colored compounds in this family occurred over too broad a temperature range. Thus, it was not possible to specify a definite transition temperature region for them.

The reflectance spectra of the most promising ternary chalcogenide, $CdIn_2S_4$, which turned from a dull orange to a reddish-orange at 95 - 105°C is shown in Figure 13. The color change in white light is not spectacular and occurs over a fairly broad temperature range. The reflectivity shift , however, was quite substantial and suggests that this material might prove of practical use, particularly in conjunction with an appropriate set of filters. It also would appear worthwhile to investigate other materials similar to $CdIn_2S_4$ but containing varying ratios of CdS to In_2S_3.

Other colored ternary chalcogenides such as $ZnGa_2S_4$, $ZnGa_2Se_4$, $CdGa_2S_4$, $CdGa_2Se_4$ and $ZnIn_2S_4$ listed in Table 3 also showed changes in hue on heating. However, the color changes under normal illumination were slight. In addition, a substitution formulation, $ZnGa_2S_3Se$, was prepared. It was no better, and perhaps a little worse, than the others.

The reflection spectra in the visible region of these colored ternary gallium chalcogenides and $ZnIn_2S_4$ showed very small shifts at high temperatures with respect to the low temperature forms. The curves were of the same general shape as those of the silver and copper mercury iodides but the shift was usually of the order of only 100Å . It is not at all certain that the two forms are different in structure. The slight shift could develop gradually upon heating because of lattice expansion, rather than by a disordering of cations. Only high-temperature x-ray data could ascertain whether or not the compounds were in a "high-temperature" cubic form at 90 ± 10°C. To the eye there was no striking contrast between low-and high-temperature forms. The reflectivity shifts and the contrast number for the colored ternary chalcogenides are given in Table 4.

REFLECTANCE CURVES FOR $\beta\text{-Cd In}_2\text{S}_4$

AND $\alpha\text{-Cd In}_2\text{S}_4$

$$\beta\text{-Cd In}_2\text{S}_4 \overset{95-100^\circ\text{C}}{\rightleftharpoons} \alpha\text{-Cd In}_2\text{S}_4$$

DULLISH ORANGE REDDISH-ORANGE

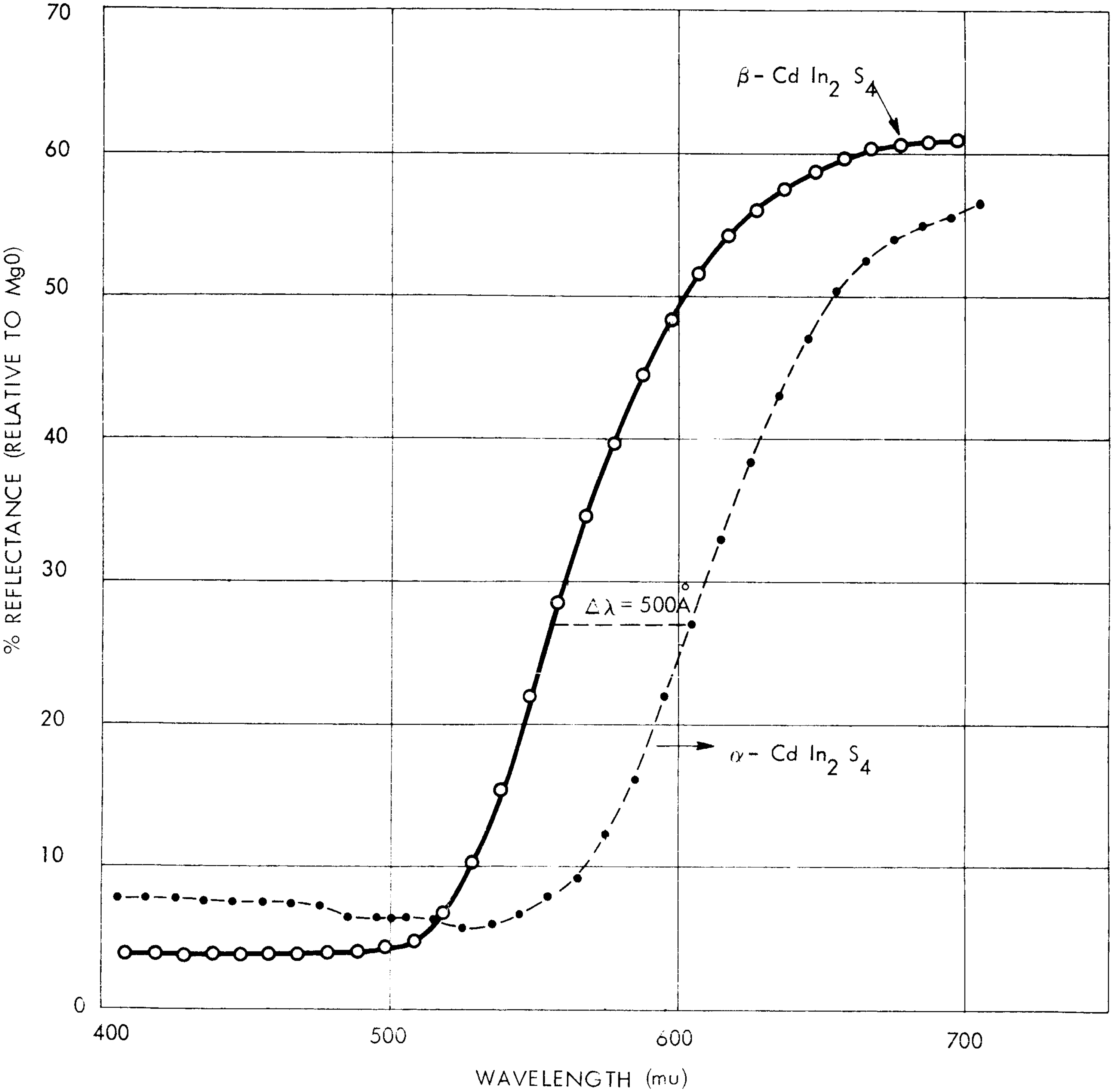


FIGURE 13

TABLE 4

Reflectance Spectral Data For The Colored Ternary Chalcogenides

Colored Ternary Chalcogenide	Largest Shift (Hot-Cold)	λ of abs. edge where $I = \frac{I_{red} - I_{blue}}{2}$		I_{cold} / I_{hot} at $\lambda = \frac{\lambda_c + \lambda_h}{2}$
		cold form λ_c	hot form λ_h	
$CdInS_4$	500Å	5700	6050	3.1
$ZnGa_2S_4$ (I) (pale green)	100Å	4740	4840	1.1
$ZnGa_2Se_4$ (II) (olive green)	100Å	5250	5350	1.1
$ZnGa_2S_3Se$ (II′) (yellow-green)	75Å	5020	5070	1.1
$CdGa_2S_4$ (IV) (tan)	40Å	5220	5260	1.0
$CdGa_2Se_4$ (V) (rust)	80Å	5950	6010	1.1

Reflection spectra in the visible region for the three zinc and aluminum-containing ternary chalcogenides $ZnAl_2S_4$, $ZnAl_2Se_4$, and $ZnAl_2Te_4$ were measured at room temperature and at 90° ± 10°C. The spectrum of the heated grey $ZnAl_2S_4$ was slightly brighter than that of cold material at all wavelengths. However, there is no evidence of a transition in this material between 20° and 100°C. The spectra of cold and hot $ZnAl_2Te_4$ were identical. Possibly a shift occurs in the near infrared. This possibility was not examined because it was concluded that such a shift was due to a lattice expansion and we were interested only in color changes that occurred in the visible region of the spectrum.

The near infrared reflectance spectrum of several black ternary chalcogenides $ZnGa_2Te_4$, $CdGa_2Te_4$, $HgGa_2Se_4$, and $HgGa_2Te_4$ were measured at room temperature and at 90°C.

The results are shown in Table 5. The slopes of the intensity versus wavelength curves were gradual and cannot be called absorption "edges". However, the basic shape of these curves is indeed the same as the curves of the colored compounds in the visible region. Their reflection intensities gradually increase with increasing wavelengths. Both $ZnGa_2Te_4$ and $HgGa_2Te_4$ were found to be in their cubic or high-temperature form at room temperature, yet the absorption edges for the $HgGa_2Te_4$ shifted to longer wavelengths when it was heated. Thus, this shift in absorption edge must be due to a lattice expansion rather than a disordering of cations.

Two black cubic ternary chalcogenides, $HgGa_2Te_4$ and $ZnGa_2Te_4$, were tested for thermochromic activity at lower temperatures. Since these materials were in their high temperature forms at room temperature it was thought they might revert to a colored form at some lower temperature. Samples of each were placed in a sealed glass melting point capillary and placed in an ice bath for 2 hours. No change in color was observed. The capillary was then lowered to "dry ice" temperature (-78°C)

TABLE 5

Near-Infrared Reflectance Spectral Data of Some Black Ternary Chalcogenides

Black Ternary Chalcogenide	Largest Shift (Hot-Cold)	λ of absorption edge (where $I = \frac{I_{14,000} - I_{7000}}{2}$		I_{cold}/I_{hot}
		cold form, λ_c	hot form, λ_h	at $\lambda = \frac{\lambda_c - \lambda_h}{2}$
$ZnGa_2Te_4$ (III)	None	9900	9900	1.0
$CdGa_2Te_4$ (VI)	250Å	8600	8750	1.0
$HgGa_2Se_4$ (VIII)	200Å	6380	6520	1.1
$HgGa_2Te_4$ (IX)	1 0Å	9850	10,000	1.0

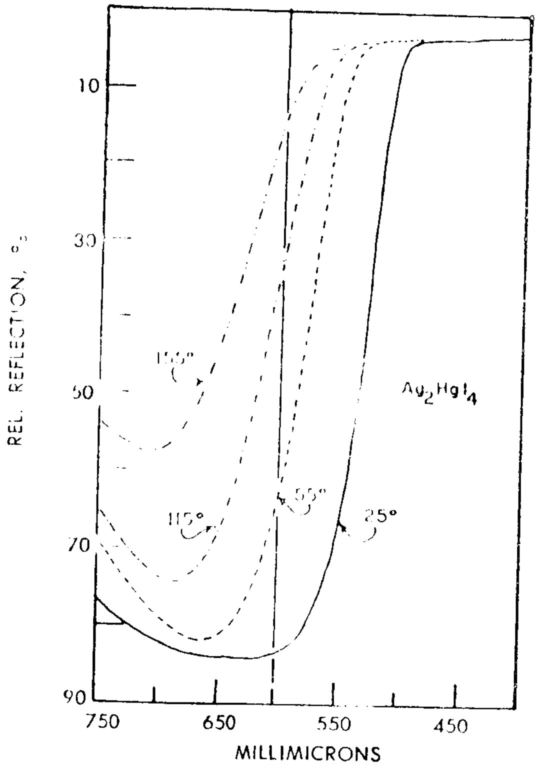
for about one hour. Again no change in color was observed. It is still possible that a low temperature colored form could exist but the rate of its formation is probably very slow.

At the time that the reflection spectra of the various materials were taken we were not aware of some earlier work on the reflectance spectra of thermochromic compounds. It was pointed out that the reflectance spectrum of these materials are a function of the temperature.(12) This effect is shown in Figure 14. Further shifts in the absorption edge occur above the transition temperature. This effect has been confirmed in this laboratory on both Ag_2HgI_4 and $Ag_2HgI_{3.84}Br_{0.16}$. As a result, some of the conclusions drawn from these spectra concerning contrast are only partially correct as the exact form of the reflectance curve should have been determined at carefully controlled temperatures above the transition temperature. It is expected that a thermostatic attachment to the reflectance unit will be built and used in any future work in this area.

4.3 Thermal Stability Studies

Thermal stability studies were conducted on silver mercuric iodide, copper mercuric iodide and two of the most promising thermochromics prepared on this program namely $Ag_2HgI_{3.84}Br_{0.16}$ and $CdIn_2S_4$. These studies were performed in order to determine how well these materials could stand up under actual device operation. Two types of tests were conducted: a static test and a cycling test. In the static test the materials were maintained approximately 10°C above their respective transition temperatures. In the cycling tests the materials were alternately heated above and cooled below their transition temperatures.

The results for the powdered Ag_2HgI_4 and Cu_2HgI_4 are given in Figure 15. Silver mercuric iodide decomposes at a linear rate. A total weight loss of ten

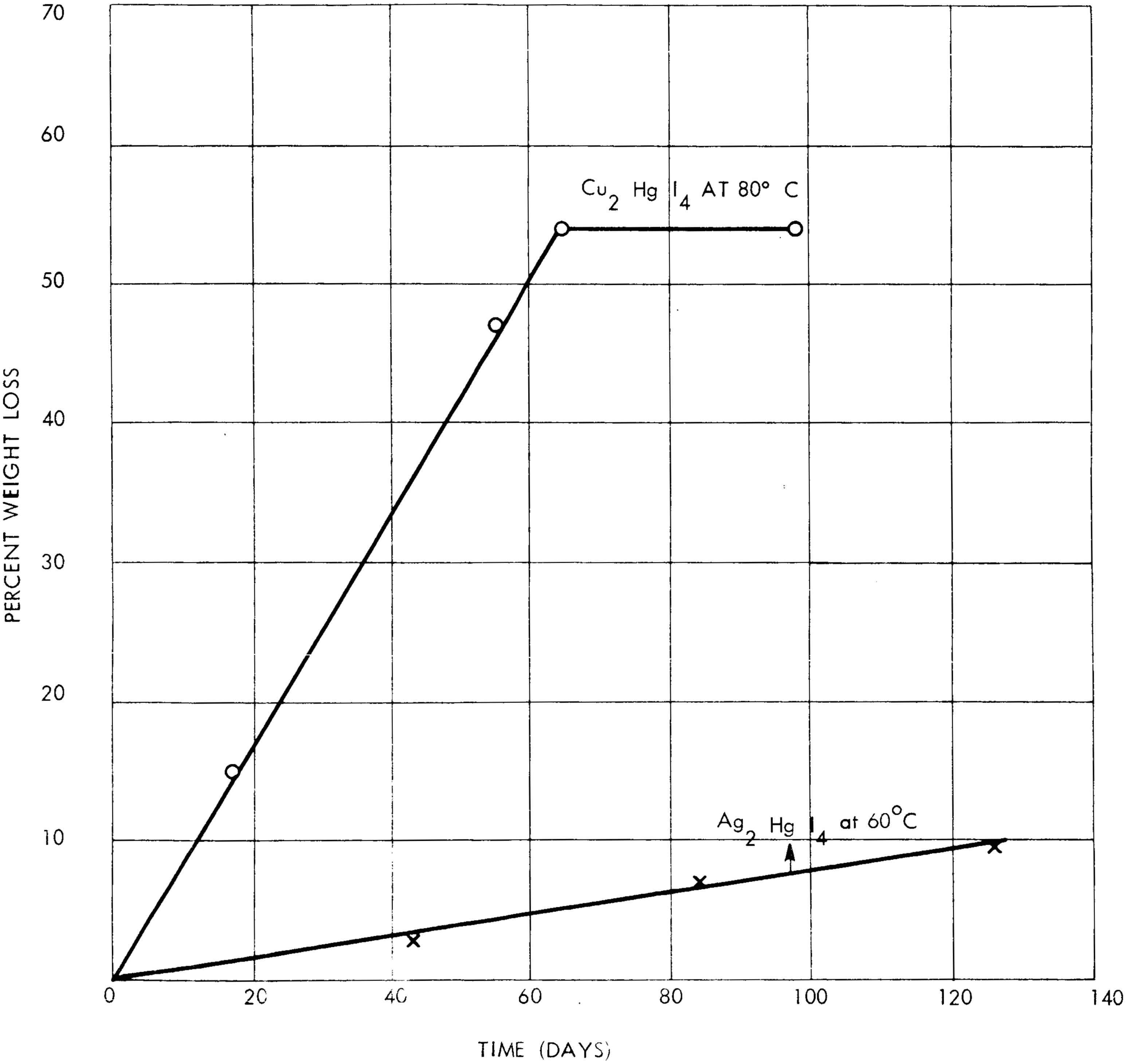


Reflectance Spectra Of Ag_2HgI_4 At Various Temperatures

FIGURE 14

Figure 15

Percent Weight Loss of Powdered Ag_2HgI_4 and Cu_2HgI_4 at Constant Temperature



percent over a 130 day period was measured. The observation of a red deposit, presumably HgI_2, in the cooler parts of the apparatus indicated that the decomposition apparently follows the reaction: Ag_2HgI_4 (orange) = $2AgI + HgI_2$. In the case of Cu_2HgI_4 total decomposition was observed after 65 days at 80°C. The 54 percent weight loss accounts for all of the HgI_2 in Cu_2HgI_4. The decomposition reaction is probably Cu_2HgI_4 (black) = 2CuI (brown) + HgI_2 (red) with volatilization of HgI_2.

A few encapsulation studies were conducted on Ag_2HgI_4 and Cu_2HgI_4 respectively in order to determine whether encapsulation would impede the loss of the volatile HgI_2 thereby improving the lifetime of these materials. The results are shown in Figure 16. The Ag_2HgI_4 showed a loss in "active area" of about four percent in the first week of the test. For the remaining four weeks no significant additional change occurred. The area showing decomposition was at both of the short ends of the slide. No changes were observed in the blank plastic coated slides.

More severe decomposition was noted in the case of the plastic encapsulated Cu_2HgI_4 (prepared in the same way as the Ag_2HgI_4 sample). At the end of five weeks at 80°C eighty percent of the "active area" was lost. The loss was most evident along the edges of the microscope slide. In addition, a coating of a red powder, presumably HgI_2, was noted in the cooler parts of the Abderhalden apparatus. A slight leveling off of the decomposition rate is indicated by the data shown in Figure 16. No change was observed in the blank slide coated with the plastic binder alone.

These differences can be explained in several ways. The Cu_2HgI_4 is inherently less stable at its test temperature of 80°C than the Ag_2HgI_4 at its test temperature of 60°C. This is indicated by the data presented above for the tests on the unencapsulated powders. Diffusion constants usually are strongly increasing functions

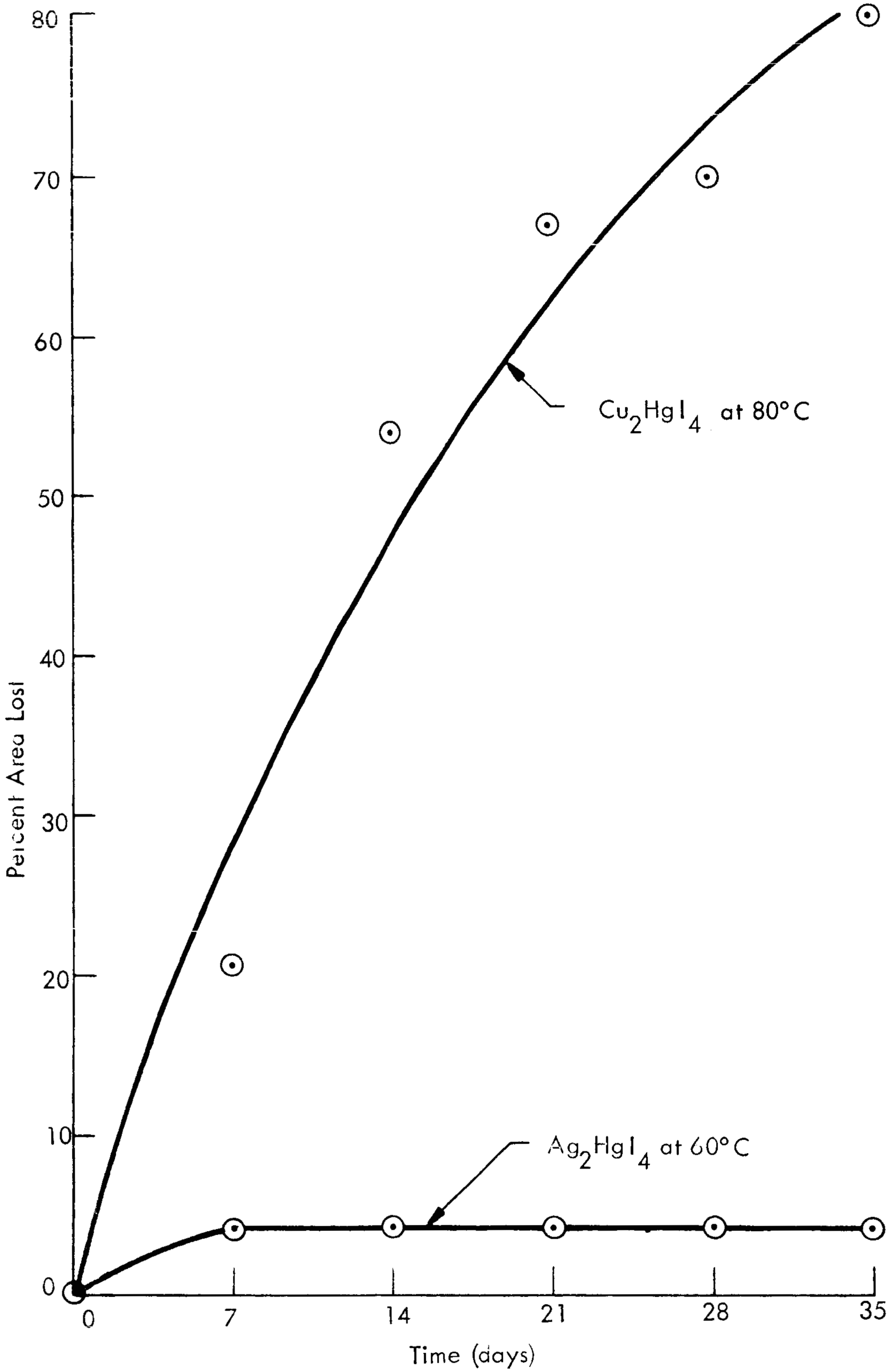


FIGURE 16 - PERCENT AREA LOSS OF PLASTIC ENCAPSULATED Ag_2HgI_4 and Cu_2HgI_4 AS A FUNCTION OF TIME AT A CONSTANT TEMPERATURE

of temperature. Thus, the rate of diffusion of the volatile decomposition product (HgI_2) through the encapsulant would be considerably higher at the higher test temperature of the encapsulated Cu_2HgI_4. Another possible contributing factor is that the particle size of the Cu_2HgI_4 is smaller than that of Ag_2HgI_4. If it is of smaller particle size, the resulting increased specific surface area could also contribute to the higher decomposition rate. Due to the large amount of decomposition of the Cu_2HgI_4 in the encapsulated sample, an attempt was made to change the nature of the encapsulation used. The particular plastic used contains a solvent (xylene) that must evaporate during the curing process. It is possible that porosity is introduced into the plastic as a result of this evaporation. This, of course, would be added to the innate permeability of the plastics. It would be better to use a system that does not involve solvent evaporation during the curing process. It would be best to choose a plastic that has a low permeability value in order to minimize the diffusion of thermochromic decomposition products out of the plastic. Saran and Mylar have been reported (13) to have very low permeability values. Initially it was expected to form a laminate of these plastic films with the thermochromics placed between layers. A few attempts to encapsulate the thermochromics were made using Saran and Mylar but these were unsuccessful. Likewise, a few attempts using water glass as the encapsulant were made. These attempts also failed.

A powdered sample of $Ag_2HgI_{3.84}Br_{0.16}$ was also subjected to a static life test. The test temperature was 50°C maintained by using t-butyl chloride as the boiling liquid. The weight loss after 60 days was determined to be six percent. An earlier experiment on pure Ag_2HgI_4 at 60°C showed a weight loss of five percent after the same length of time.

If the data are correct, there is an indication that the argument employed initially, that lowering the transition temperature and the subsequent lowering of the test temperature would cause a decrease in the decomposition rate, is incorrect. This could be explained in at least two ways. First, the vapor pressure of $HgBr_2$ is higher than that of HgI_2. If a high percentage of $HgBr_2$ is observed in the initial decomposition products this explanation would be valid. Second, the bromide ions may occupy the same positions as the iodide ions in the lattice. Since the bromide ion is smaller than the iodide ion there is more room available for the metal ions to diffuse through the lattice. This increase in the ease of diffusion might more than compensate for the lowered temperature. If this argument is correct the initial decomposition products should contain a relatively small amount of $HgBr_2$.

A similar experiment was performed on $CdIn_2S_4$. The test temperature was 110°C, maintained by using toluene as the boiling liquid. At the end of 60 days the weight loss is 0.11 percent. This value corresponds within experimental error to approximately no decomposition. It would appear that $CdIn_2S_4$, as expected from its composition as a heavy metal sulfide, does not exhibit the thermal instability problems associated with the iodides.

In the cycling tests conducted on Ag_2HgI_4 and Cu_2HgI_4, the Ag_2HgI_4 still showed some thermochromic activity after 475,000 cycles (11 months) while the Cu_2HgI_4 was almost totally decomposed after 153,000 cycles (3 1/2 months). In the samples of Ag_2HgI_4 generally a yellowish residue, probably AgI, was present in that portion of the slide that no longer showed thermochromic activity. In the samples of Cu_2HgI_4 a black-brown residue, probably CuI, remained on the slide. The results of the cycling tests indicate strongly that the decrease in the thermochromic activity is due to thermal decomposition rather than fatigue of the material.

Miscellaneous

In addition to the properties that have been discussed, some miscellaneous behavior was observed particularly with the iodides. These observations included encapsulation studies, the light sensitivity of some silver-containing thermochromics, and some compatability studies. These observations are summarized in the Appendix section 7.4.1 and 7.4.2.

4.4 Electrical Conductivity

It has been reported (11) that the electrical conductivities of Ag_2HgI_4 and Cu_2HgI_4 undergo very large increases at their respective thermochromic transition temperatures. We have measured the electrical conductivity of $Ag_2HgI_{3.84}Br_{0.16}$ above and below its transition temperature in order to determine the magnitude of its increase and compare it with the increase observed with Ag_2HgI_4. A summary of the data is presented in Table 6. Measurements were performed also on Ag_2HgI_4 in order to compare with the literature values.

TABLE 6

Electrical Conductivities As A Function Of Temperature

Temperature	$Ag_2HgI_{3.84}Br_{0.16}$	Ag_2HgI_4	Ag_2HgI_4 (literature value)
23°C	3.5×10^5 ohm-cm	5.0×10^5 ohm-cm	8.5×10^5 ohm-cm
54°C	2.3×10^4 ohm-cm	2.5×10^4 ohm-cm	7.2×10^2 ohm-cm

At 23°C, the agreement between the value of the specific resistance of Ag_2HgI_4 as determined in this laboratory and that reported in the literature is reasonable. This especially is true when it is realized that the actual values obtained depend upon the manner of preparation of the sample. Perfect agreement is not expected. The value for the bromine substituted material is a little lower but still of the same order of magnitude.

At 54°C the value of 2.5 x 10^4 ohm-cm obtained in this laboratory for Ag_2HgI_4 is considerably higher than the value reported in the literature. The value for the bromine substituted material is about the same as for Ag_2HgI_4. A possible explanation for this discrepancy may be in the manner in which the resistivity measurements were made. The literature values were obtained with a clamping arrangement on the pellet and the force exerted would not be expected to be easily reproducible under those circumstances. In the method employed by us the force exerted on the pellet is reproducible. Another possibility is that the pellets tend to discolor during pressing. Suchow and Pond were able to eliminate this by working at very low pressures.

4.5 Other Thermochromics

In addition to the compounds described above a continual search of the scientific literature for other thermochromic materials was maintained. Two other materials which change color via a phase transition were noted, namely thallous iodide ($T\ell I$) and mercuric iodide (HgI_2). Nothing was reported concerning their thermochromic activity. Both of these materials looked attractive from the standpoint of thermal stability. Any loss of thermochromic activity should result from loss of material by volatilazation rather than thermal decomposition. $T\ell I$ is extremely involatile. Its boiling point is 824°C. Mercuric iodide is much more volatile. Its boiling point is 354°C. Some experimental work was performed on $T\ell I$ and it is described below.

4.5.1 Thallous Iodide

It was noted (14) that thallous iodide (Tℓ I) undergoes a thermochromic phase transition at 170°C from an orthorhombic yellow form to a cubic red form. The structure of these materials are not of the same symmetry classes as the copper and silver mercuric iodides and it was expected that the thermochromic phase transition would be sluggish.

Experiments to reproduce the transition temperature of thallous iodide were performed. Using the melting point apparatus a color change was noted at about 191°C. Initially, this change was slow and not easily reversible; it was possible to cool the virgin material to about 140°C before noting a change from the red high temperature phase to the pale-yellow low temperature phase. The rate of a solid state phase transition often can be increased if the material is cycled several times through the transition temperature region. This is probably due to the formation of nucleation centers for the two phases. The thallous iodide was cycled about a half dozen times and, as expected, the thermochromic change began to take place sharply and reversibly at a lower temperature (178°C). The contrast of this system appears to be good at least insofar as it can be estimated visually. Its high melting and boiling points (440°C and 823°C respectively) suggest that this material could be useful in some applications where its high transition temperature and toxicity would not be deleterious.

4.5.2 Mercuric Iodide

Mercuric iodide has been reported to undergo a phase transition at 126°C (15) with an accompanying change in color from red to yellow. It was not studied because its high volatility in the region of the color transition would require that it be encapsulated in some medium in order for it to be applicable in a device.

5.0 ANALYSIS

A few simple numeric display devices in which the known thermochromics Ag_2HgI_4 and Cu_2HgI_4 were used to display the numerals were fabricated on this program.

These devices performed very satisfactorily although no attempt was made to optimize their operating characteristics. The numerals displayed on the panel could be observed very readily under bright room illumination. Certainly these devices demonstrated that thermochromics could be satisfactorily utilized in such devices. Although it has been demonstrated that thermochromics have potential applicability in display devices which can be used under conditions of high ambient illumination, thermal studies on Ag_2HgI_4 and Cu_2HgI_4 showed that these devices would have a limited life.

Both of these compounds were found to decompose at a temperature of only 10°C above their respective transition temperatures. Since the decomposition presumably involves the formation of the relatively volatile mercuric iodide, some preliminary encapsulation techniques were attempted to impede the loss of thermochromic activity. Although these preliminary efforts were not overly successful, they did indicate that encapsulants should have very low permeability if they are to impede the loss of mercuric iodide. The plastic medium which was used throughout most of this work, namely Rohm & Haas (A29 + F233) uses xylene as a solvent. Xylene is volatile and on evaporation creates "holes" in the plastic when it hardens. It should be emphasized again, however, that proper encapsulation could prevent the loss of HgI_2 and probably maintain the thermochromic activity of these ternary iodides. The search for other thermochromics was made since only four thermochromics were known at the start of this program namely Ag_2HgI_4, Cu_2HgI_4, $Ag_{1.14}Cu_{0.86}HgI_4$ and $T\ell_2HgI_4$.

The preparation of the thermochromic, Cu_2CdI_4 in this laboratory led to the idea that anionic or cationic substitution in Ag_2HgI_4 or Cu_2HgI_4 could lead to a change in the thermochromic properties of these materials. This idea was substantiated by the preparation of formulations such as: $Ag_2HgI_{4-x}Br_x$, $Cu_2HgI_{3.75}Br_{0.25}$, $Ag_2HgI_{3.75}C\ell_{0.25}$, $Cu_2HgI_{3.75}C\ell_{0.25}$, $Ag_2Hg_{1-x}Cd_xI_4$, $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$ and $Cu_2Hg_{1-x}Cd_xI_4$. In the case of partial anionic substitution by Br or $C\ell$ the transition temperature was lowered to a fixed value. For all the values of x that were used in this study the transition temperature was lowered from 50.5°C to 42 ± 2°C for Ag_2HgI_4 and was lowered from 69°C to 50°C for Cu_2HgI_4. The contrast number between the high and low temperature forms for the formulation $Ag_2HgI_{3.84}Br_{0.16}$ was higher than for Ag_2HgI_4. Addition of more than four percent Br ($x = 0.16$), however, made the color change become more gradual with temperature. The thermal stability of $Ag_2HgI_{3.84}Br_{0.16}$ at 50°C was found to be somewhat poorer than Ag_2HgI_4 at 60°C, which was contrary to our earlier expectation. Thus, if these bromide substitutional formulations are to be used, encapsulation will be required also.

Partial substitution of Cd^{+2} for Hg^{+2} led to an increase in the transition temperature with increasing cadmium content. This was unlike the result obtained with partial anionic substitution where transition temperature was constant with varying bromide ion content. In order to better explain these results a comprehensive study of the phase diagram for each of these systems would be necessary. Thermal stability studies were not performed on any of the cadmium substituted formulations, because the color change occurred over a wider temperature range than in the case of the parent compounds or the bromide substituted ternary iodides. In earlier work by Suchow and Pond the eutectoid $Ag_{1.14}Cu_{0.86}HgI_4$ was prepared and its transition temperature was 34°C. Thus, substitution of the monovalent and divalent cation as well as anion substitution in the ternary iodides are possible, thereby expanding greatly the number of thermochromic formulations available. The substitution concept also increases the number of transition temperatures possible. In addition the thermochromic activity of ternary chalcogenides was examined. Originally 27 of these compounds were to be prepared. An attempt was made to prepare all 27 but only 22 were successfully synthesized. The remaining 5 compounds were reported to be black.

The most promising ternary chalcogenide with regard to thermochromic activity was $CdIn_2S_4$. It changed color from dull orange to orange-red at 95 - 100°C but the change in color was gradual. The $CdIn_2S_4$ was found to be very stable thermally at 100°C. The material has been reported in the literature as being a cubic crystal with the spinel structure which is a different structure than the ternary iodides. While the thermochromic color change is not very dramatic its existence suggests that thermochromic might occur in other spinel materials. The compound $CaIn_2S_4$ has been reported to be a colored cubic spinel and would be a good system for future study. If any thermochromic activity is observed it may be possible to optimize its properties by variation in stoichiometry or by partial substitution of some other ions in the crystal lattice. All of the other colored ternary chalcogenides studied on this program showed very small reflectivity shifts on heating and these shifts may be due simply to lattice expansion rather than a disordering of the cations in the anionic crystalline lattice.

Experience with the simple display device described above has indicated the feasibility of thermochromics in a display medium. This concept, however, is fairly simple and it is difficult to see too many applications of it in its present configuration. There are, however, two other applications that are worthy of further consideration.

The first of these involves the use of thermochromics as the imaging material in a cathode ray tube. Preliminary calculations indicate that there is sufficient energy available in the electron beam of available CRT's to bring about the thermochromic color change. This type of system would have the significant advantage of being visible under conditions of high ambient illumination. Present light emitting systems tend to wash out under these conditions. A potentially serious difficulty that may arise is the decomposition of the thermochromic (especially the iodides) under electron impact. This subject should be investigated at any early stage in future studies. In addition, there are other problems with regard to the feasibility of forming thin films of thermochromics and their stability under vacuum conditions that exist in a CRT.

The second application that appears most worthy of further study is the use of a thermochromic-electroluminescent display. This would have the significant advantage of high visibility over a large range of ambient illumination levels. Possible configurations for these devices are discussed in the report. Difficulties that may arise are related to the sensitivity of many phosphors to contaminants. As a result compatibility studies with standard EL materials should be initiated. Both time and temperature studies should also be done.

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7.0 APPENDIX

7.1 Preparation of Substitutional Iodides

The System $Ag_2HgI_{4-x}Br_x$

The reactants used for these preparations were HgI_2, AgI, and AgBr. In the case of the compositions containing chlorine calculated amounts of AgCl were used in place of the AgBr. They were sealed in evacuated pyrex test tubes and fired at 300 - 400 °C. The samples formed orange melts of very uniform appearance.

Two sets of $Ag_2HgI_{4-x}Br_x$ samples were prepared. Series I where x = 0.16, 0.40, 0.60, 0.80, 1.00 and Series II where x = 0.16, 0.60, 1.00, 1.40. Series I was fired 64 hours at 350°C and slowly cooled. Series II was fired 2 days at 220°C, then 24 hours at 400°C and rapidly quenched to room temperature. The quenched melts were uniform and orange in color. The formulations in Series I were less uniform in appearance. After grinding, all samples were yellow. The compound $Ag_2HgI_{3.84}Br_{0.16}$ was the most greenish yellow, the others were more orange-yellow.

The systems $Ag_2Hg_{1-x}Cd_xI_4$, $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$ and $Cu_2Hg_{1-x}Cd_xI_4$. Fifteen substitution formulations were prepared: five were of composition $Ag_2Hg_{1-x}Cd_xI_4$, five of composition $Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$ and five of composition $Cu_2Hg_{1-x}Cd_xI_4$. In all cases x was given the values 0.05, 0.10, 0.15, 0.20, and 0.25. These materials were also prepared by sealing carefully weighed amounts of the appropriate binary iodides in evacuated quartz ampoules. In the case of the compositions containing bromine, calculated amounts of AgBr were used in place of some of the AgI. The materials were all fired at 400°C. After grinding each powder to a homogeneous mass, the transition temperature of each was determined.

7.2 Preparation of Ternary Chalcogenides

The simplest and most appropriate technique for the preparation of these ternary compounds consisted in heating a mixture of starting materials in an evacuated sealed quartz ampoule. The starting materials were mixed intimately before being placed in the quartz ampoules. The ampoules were evacuated with a mechanical pump which reduced the pressure to about 0.1 mm of Hg. An acetylene-oxygen flame was used to seal off the ampoules. The starting materials usually consisted of the appropriate binary compounds, that is MX + M'_2X_3. Sometimes, however, the elements were used. The reaction mixture was then subjected to a firing schedule which usually consisted of a preheat period of about 24 hours at 400 - 600°C, followed by a firing period of a few days at 900°C. An annealing period at 600°C from 2 - 3 days followed the firing period.

In the course of preparing $HgAl_2Se_4$, $HgAl_2Te_4$, $CdAl_2S_4$, $HgAl_2S_4$, $CdIn_2S_3Se$, $CdIn_2SSe_3$, $CdInGaS_4$, and $CdIn_2S_4$, an explosion occurred in the furnace containing ampoules of mixtures of chemicals leading to the above compositions after the temperature was raised to 900°C. The quartz ampoules were broken and their contents scattered. It was difficult to ascertain the exact cause of the explosion.

On another occasion an explosion occurred when mixtures of materials leading to the following ternary chalcogenides were fired: $CdAl_2S_4$, $HgAl_2S_4$, $HgAl_2Te_4$, $HgIn_2Te_4$, and $HgAl_2Se_4$. This time the explosion occurred when the temperature was lowered from 900°C to 600°C. The ampoules containing $HgAl_2Te_4$ and $HgIn_2Te_4$ were intact indicating neither of these two mixtures were explosive under the experimental conditions. The cause of this explosion was not understood. Later efforts resulted in the successful synthesis of $HgAl_2S_4$, $CdAl_2S_4$, and $CdIn_2S_4$ according to the experimental procedure outlined earlier. Thus, mixtures of materials leading to these compositions are not explosive under these experimental conditions. No further attempts were made to synthesize $HgAl_2Se_4$ or any of the substitutional cadmium indium sulfides. Since we were not able to ascertain the cause of these explosions any future attempt to synthesize $HgAl_2Se_4$, $CdIn_2S_3Se$, $CdIn_2S_2Se_2$, $CdIn_2SSe_3$, or $CdInGaS_4$ should be undertaken with extreme precaution.

7.3 Thermochromic Property Measurements

For the purpose of evaluating the thermochromic properties of the materials prepared on this program, the following physical measurements were conducted.

7.3.1 Transition Temperature

The transition temperatures of the materials studied on this program were determined by the melting point capillary method and the Dennis Melting Point Method.

In the melting point capillary method the thermochromic is placed in a glass capillary tube which is then immersed in a transparent oil bath. The oil bath is heated and stirred to maintain a constant temperature around the capillary. The temperature at which the color of the thermochromic material changes. is recorded as the transition temperature.

The melting point capillary method of determining transition temperatures is not reproducible because a continuous comparison of the color as the sample temperature is raised or lowered is necessary. This comparison method requires that one sample be heated (or cooled) and the temperature (therefore the color) of the other be maintained constant. Such a requirement cannot be conveniently achieved by the melting point capillary method. This requires that the two samples at different temperatures be viewed simultaneously. In order to eliminate this non-reproducibility a Dennis Melting Point apparatus was obtained. The heated stage of the device consists of a long silver plated copper bar with an electric heater at one end which produces a temperature gradient along the length of the bar. The color can be observed at each point. In this way it is easier to compare color at various temperatures as they are all visible at the same time. The temperature at any point is determined by touching the bar at that point with a constantan wire pointer, thereby forming a copper-constantan thermocouple. Temperature calibration was checked with USP melting point standards and agreement was within the range given with the samples.

7.3.2 Reflectance Spectra Measurements

The technique of measuring the reflectance curves of low and high temperature forms of the thermochromic materials synthesized on this program is described. A typical sketch of a reflectance spectra is given in Figures4 and 7. The Beckman DK-2A spectrophotometer was adopted for the measurement of reflection spectra by installing and aligning the reflection attachment to this instrument. Reflection spectra were taken in the visible range, 4000 - 7000 Å, at room temperature and at 90 ± 10°C. The samples were mounted on pyrex microscope slides by mixing the powders with a thinned clear plastic (Rohm and Haas A 29 + F 233) and curing them in a 60°C oven for 65 hours in the form of 1" diameter painted spots on the slides. The light source in the spectrometer was a glowing tungsten filament and the detector was a phototube. The "total reflection" was recorded by tilting the samples 5 degrees away from the vertical. This tilt avoids any effect of surface roughness of the samples on the intensity of the reflected light. Heating of the samples was accomplished with a heating element. The heater was clamped against the glass side of the sample slide. It was difficult to insert a thermocouple in the sample without disturbing its reflection spectra, so the temperature is known only to approximately ± 10°C.

The reflectance spectra of some of the black compounds synthesized on this program were obtained in the 6000 to 14,000Å spectral region by using the same spectrophotometer described above, except a lead sulfide detector, which is sensitive between 5500 and 27,000Å, replaced the 1P-28 phototube.

7.3.3 Thermal Stability Tests

7.3.3.1 Static Life Tests

These tests were conducted in an "Abderhalden" drying apparatus shown in Figure 17. A liquid of suitable boiling point is placed in the flask and maintained at its boiling point. The condensing vapors surround the sample chamber and keep it at a constant temperature equal to the boiling point of the liquid. For each material a stable organic liquid with a boiling point as close as possible to 10°C above the transition temperature of the material was chosen as the constant boiling liquid. The weight loss of each material was followed as a function of time.

The continuous life test of the high temperature form Ag_2HgI_4, the transition temperature of which lies at 50.5°C, was run in one "Abderhalden" apparatus, for almost five months. Boiling 1,2-dichloroethylene kept a powdered sample of Ag_2HgI_4 at a constant 60°C.

A continuous high temperature life test on Cu_2HgI_4 was performed in another "Abderhalden" apparatus. Cu_2HgI_4 has its

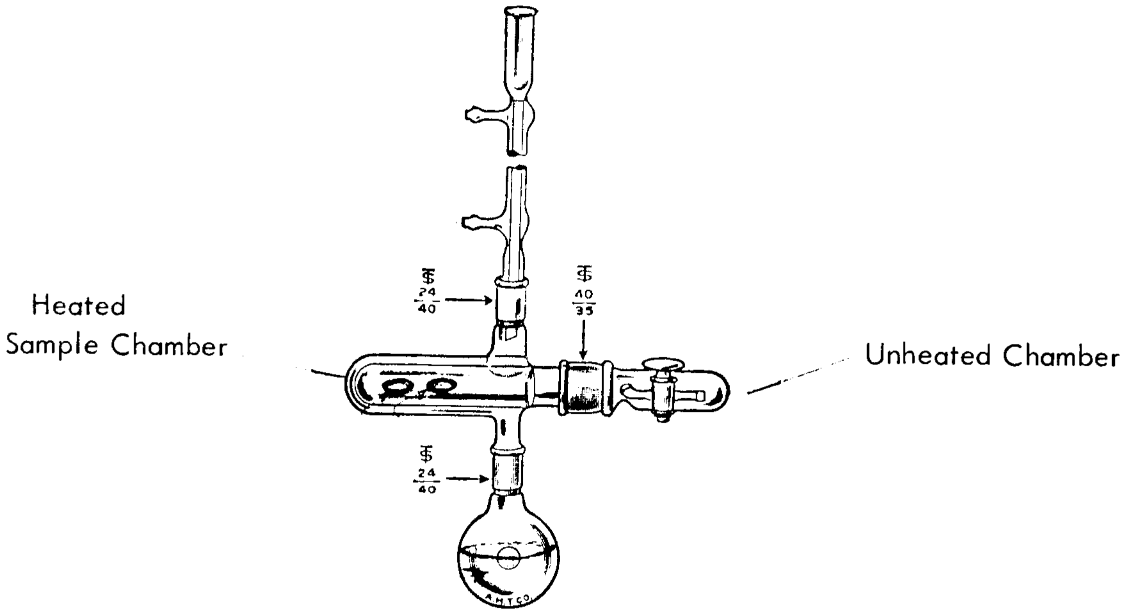


FIGURE 17

ABDERHALDEN CONSTANT-TEMPERATURE APPARATUS transition point (red to black) at 69.5°C. Boiling benzene holds the sample at a constant 80°C.

The same procedure was used for Ag_2HgI_4 and Cu_2HgI_4 when they were encapsulated in a plastic binder. Boiling t-butyl chloride (52°C) and boiling toluene (110°C) maintained $Ag_2HgI_{3.84}Br_{0.16}$ and $CdIn_2S_4$ 10°C above their respective transition temperatures.

7.3.3.2 Cycling Life Tests

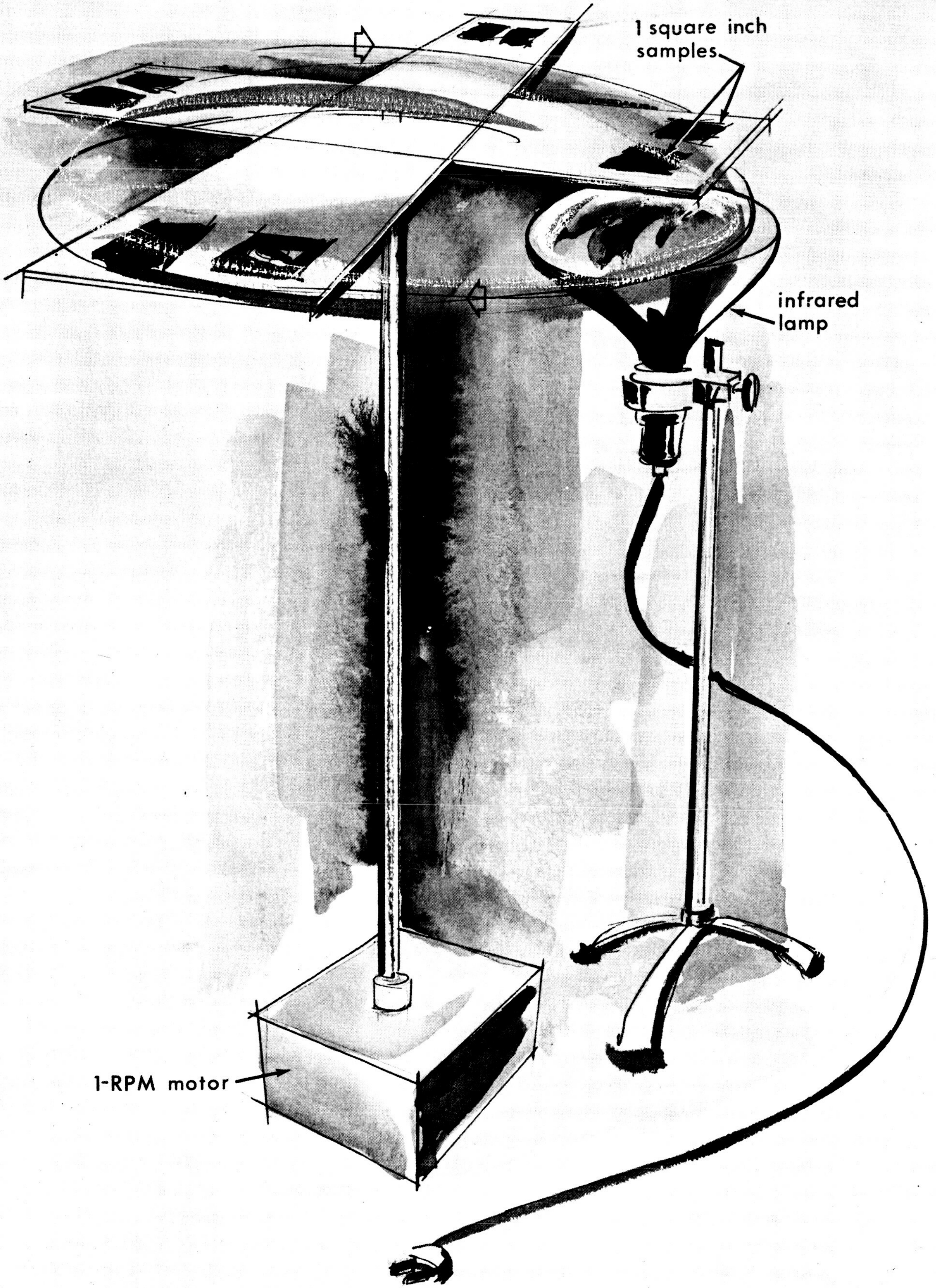
Figure 18 illustrates the device used in all cycling life experiments. The sample is placed on a cardboard sheet which is rotated at one cycle per minute over an infrared lamp. The heat from the lamp was adjusted so as to be just sufficient to cause the thermochromic change to occur. The sample is able to in the course of a single revolution to cool below the thermochromic transition temperature before it again is heated by the lamp.

Tests of powdered Ag_2HgI_4 on both brass and aluminum foil indicated that chemical reaction could occur with these metals.

Because of this chemical reactivity, aluminum substrates were replaced by glass. For best heat conductivity, the thinnest available glass, microscope slide cover glasses, was obtained for this purpose. The thermochromic powder was mixed in

FIGURE 18

SET-UP FOR CYCLING TESTS


1 square inch samples
infrared lamp
1-RPM motor

benzene so that one drop of this suspension on a 1 inch square cover glass would leave a very thin layer of the thermochromic powder after the solvent had evaporated. A second cover glass was used to protect the sample from dust or air currents. Four samples of Cu_2HgI_4 prepared this way were allowed to cycle for a total of 153,000 cycles (3 1/2 months).

7.4 Encapsulation Studies

Two life tests were completed on samples of Cu_2HgI_4 and Ag_2HgI_4 dispersed in a plastic binder. The object of these tests was to determine whether encapsulation of the thermochromic would improve its thermal stability. Two 1" x 3" microscope slides were placed in the 60°C "Abderhalden" apparatus. One slide was sprayed with Ag_2HgI_4 in plastic, the other just with the plastic, Rohm and Haas (A29 + F233). The quantity of Ag_2HgI_4 is estimated as 0.04 grams. The extent of decomposition can be estimated by periodically observing the area which ceases to be thermochromic.

A few preliminary experiments on the use of Saran film and Mylar film as encapsulating media were performed. Using a Teflon coated iron the Saran and Mylar were each heated to fusion. When this was done the material shrunk drastically. At lower temperatures they would not adhere to themselves. This indicates that if Saran or Mylar is to be used the method of preparation will have to be more elaborate and probably cannot start with the prepared film.

Samples of Ag_2HgI_4 and Cu_2HgI_4 were each mixed with equal weights of water glass (40°Be, $SiO_2/Na_2O = 3.25$). The viscous mixtures were spread on microscope slides and allowed to air dry. The Cu_2HgI_4 material discolored to a greenish color, but the Ag_2HgI_4 did not. Both samples showed thermochromic activity. The surface of the dried mixture looked much too porous for any practical use as an encapsulating material. It may be possible to get around this difficulty by allowing the mixture to dry in a more humid atmosphere, thereby slowing down the rate of moisture loss and decreasing the resulting porosity.

7.4.1 Light Sensitivity of Some Ag Containing Thermochromics

A sample of powdered Ag_2HgI_4 was partially covered by a thin microscope cover glass and was allowed to lay on a lab bench for a few hours. The portion that was not covered by glass had darkened in that time. This is probably due to the ultraviolet radiation coming from the fluorescent lights in the room. In the case of Br and Cl substituted Ag_2HgI_4 the effect was noted in a soft-glass vial. These materials turned orange on exposure to fluorescent light. It should be noted that many compounds of silver (and also many of mercury) are sensitive to light and that this effect is in no way unusual. It would probably be necessary in any device application to be sure that these thermochromics are shielded from ultraviolet light. A suitable U.V. absorbing cover glass would probably be sufficient for this purpose.

7.4.2 Compatibility Tests

X-ray analysis of mixtures of Ag_2HgI_4 and SnO_2 which were allowed to stand at room temperature and at $62^\circ C$ for 192 hours showed no evidence for chemical reaction. This test was performed in order to determine if Ag_2HgI_4 would react with the tin oxide coatings which is used on conducting glass.

A visual examination revealed that Ag_2HgI_4 and its substitutional formulations can react with brass, aluminum and silver. Cu_2HgI_4 and its substitutional formulations also reacted with silver.

Another undesirable effect was noted with the bromine substituted formulations. The plastic (Rohm and Haas, A 29 + F233) and its solvent (xylene), which was used successfully to encapsulate the parent compound Ag_2HgI_4, discolored the yellow samples to orange at room temperature. This chemical color change cannot be reversed by heating and subsequent cooling and was increasingly more pronounced with increasing Br content.

It was also observed that Cu_2HgI_4 in the same plastic matrix described above discolors upon exposure to air for long periods of time. The "red" form looks dull with a brownish cast presumably due to CuI. The reflectance spectra show this discoloration in the form of a low-intensity reflection over a very wide band (4200 - 5700Å) thus, diminishing the contrast upon transition. When viewed through the glass slide, this low intensity reflection does not occur and intensities of both hot and cold forms stay low until they approach their respective absorption edges.

7.5 Electrical Conductivity

One gram samples of $Ag_2HgI_{3.84}Br_{0.16}$ and Ag_2HgI_4 were compressed in a pellet press having a cross sectional area of 1.47 cm^2 at a total load of 310 pounds per square centimeter. Each face of the pellet was painted with an alcohol suspension of graphite. For good electrical contact it was necessary to paint the surfaces three or four times in order to build up a layer of graphite that was sufficiently thick. In all measurements the pellet was placed on a flat massive stainless steel surface and a flat stainless steel cylinder weighing 1.5 pounds was placed on top of the pellet. Leads were attached to the steel pieces with alligator clamps and the resistance values were measured with an Industrial Instrument Conductivity Bridge, Model RC 16B2.