
NCEL

Technical Note

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By Thomas Novinson, Ph.D.

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ENERGY CONSERVING COATINGS - PIGMENT RESEARCH

ABSTRACT This report documents research into novel experimental paints made from color-reversible pigments. These pigments are of two types: photochromic and thermochromic. The first group changes color on exposure to light, and the second changes color when subjected to a change in temperature. If successfully incorporated into a coating and applied to walls and roofs, these pigments could reduce heating and cooling costs by presenting a more absorbent color in the winter and a more reflective color in the summer.

NAVAL CIVIL ENGINEERING LABORATORY PORT HUENEME CALIFORNIA 93043-5003

APPROXIMATE CONVERSION FACILITIES

Approximate Conversions to Metric Measures				Approximate Conversions from Metric Measures			
Symbol	When You Know	Multiply by	To Find	Symbol	When You Know	Multiply by	To Find
in	inches	2.54	centimeters	mm	millimeters	0.04	inches
ft	feet	30	centimeters	cm	centimeters	0.4	inches
yd	yards	0.9	meters	m	meters	3.3	feet
mi	miles	1.6	kilometers	km	kilometers	1.1	yards
						0.6	miles
in ²	square inches	6.5	square centimeters	cm ²	square centimeters	0.16	square inches
ft ²	square feet	0.09	square meters	m ²	square meters	1.2	square yards
yd ²	square yards	0.8	square meters	m ²	square kilometers	0.4	square miles
mi ²	square miles	2.6	square kilometers	km ²	hectares (10,000 m ²)	2.5	acres
	acres	0.4	hectares	ha			
oz	ounces	28	grams	g	grams	0.036	ounces
lb	pounds	0.46	kilograms	kg	kilograms	2.2	pounds
	short tons (2,000 lb)	0.9	tonnes	t	tonnes (1,000 kg)	1.1	short tons
tsp	teaspoons	5	milliliters	ml	milliliters	0.03	fluid ounces
Tbsp	tablespoons	15	milliliters	ml	liters	2.1	pints
fl oz	fluid ounces	30	milliliters	ml	liters	1.06	quarts
c	cups	0.24	liters	l	liters	0.26	gallons
pt	pints	0.47	liters	l	cubic meters	.36	cubic feet
qt	quarts	0.96	liters	l	cubic meters	1.3	cubic yards
gal	gallons	3.8	liters	l			
ft ³	cubic feet	0.03	cubic meters	m ³			
yd ³	cubic yards	0.76	cubic meters	m ³			
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 288, Units of Weights and Measures, Price \$2.25, SD Catalog No. C13.10-288.



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EXECUTIVE SUMMARY

This report covers the first 2 years of a 6.2 work unit entitled, "Energy Conserving Coatings," listed as task E-1 "Paints and Coatings" in the NCEL block plan for materials. This work unit, funded by ONT, involves research and development of novel experimental paints from color reversible pigments for controlling solar energy absorption and reflection from buildings. The pigments were studied in a 6.1 ONR funded research project on the determination of the molecular mechanisms for the observed photochromic and thermochromic color changes.

The ONT sponsored work unit is the first phase of development of these photochromic and thermochromic pigments into energy conservation paints. Experiments were performed in FY90 to determine the color changes of these pigments when exposed to: (a) sunlight and darkness (shade) conditions, and (b) simulated hot and cold climate conditions.

The pigments that were studied included:

1. Photochromic benzoindolinopyrspirans (BIPS)
2. Thermochromic tetraiodomercurates (TIMs)
3. Thermochromic aryl lactones (CVL series)

The BIPS were dissolved in solvents and the color changes of the solutions were studied spectroscopically. Although the BIPS could be formulated as pigments for a paint, their hiding power as solids was weak. The color changes were more pronounced when the solid compounds were dissolved in solvents. No further work is planned for this class of materials because the color change is generally limited from white in the dark and colored (generally blue or red) in bright sunlight.

The TIMs were prepared from the reactions of metal nitrates or metal iodides with potassium tetraiodomercurate (TIM). The pigments were easily made in high purity and made excellent paints when mixed with unpigmented silicone-alkyd paint bases. However, the color changes were also within a narrow range, generally changing from yellow to orange or orange to red. Another problem was the toxicity issue. The most intense color changes were observed with analogues of silver mercury iodide (silver TIM). Substitution of the mercury with cadmium or zinc generally decreased the hue and intensity of the thermochromic pigments.

The most exciting work in FY90 was the discovery of thermochromism in the CVL pigments. In combination with a proton donator or "activator" and a low melting waxy ester or alcohol, the CVL pigment mixture changes from blue to white. The temperature transition can be controlled by selecting a waxy ester with the desired melting point, such as 35°C (90°F). Work is planned in FY91 for converting this waxy pigment complex into a thermochromic pigment by microencapsulating the mixture in a shell forming plastic. The pigment can then be converted into a paint.

CONTENTS

	Page
INTRODUCTION	1
BACKGROUND	2
Photochromic Pigments and Dyes	3
Thermochromic Inorganic Pigments	3
Thermochromic Organic Pigments	4
EXPERIMENTAL SECTION	4
PREPARATION OF THE PIGMENTS	4
Photochromic Pigments	5
Thermochromic Metal Halide Complexes	5
Thermochromic CVL Mixtures	5
PREPARATION OF THE PAINTS FROM PIGMENTS	6
PREPARATION OF THE WAXY CVL THERMOCHROMIC COATING	6
THERMOELECTRIC HEATER-COOLER	7
SPECTROSCOPY STUDY	7
RESULTS	7
DISCUSSION	9
CONCLUSIONS	10
RECOMMENDATIONS	11
FUTURE PLANS	12
FUTURE TRANSITION	12
ACKNOWLEDGMENTS	13
REFERENCES	13

INTRODUCTION

The Secretary of the Navy (SECNAV) has ordered the Naval Shore Establishment to reduce the \$250 million/year energy costs at naval facilities by 30 percent by 1999. Both heating and air-conditioning now rely on combustion of conventional fuels. In times of emergency, such as the current crisis in the Persian Gulf area, fuel supplies to the fleet will be given priority. Even in peacetime, there will be continued pressure to conserve energy because: (1) the cost of fuel may increase, (2) supplies may dwindle, (3) less funding may be available for heating and cooling naval facilities, and (4) environmental pressures and legislation will reshape our use of petroleum and related fuels.

The Naval Civil Engineering Laboratory (NCEL) and other laboratories have considered many options for heating and cooling buildings. Among these are solar, geothermal, and wind energy; building design and orientation toward the path of the sun; and insulation retrofitting. It is beyond the scope of this research and development report to discuss all the energy conservation alternatives.

Control of solar energy by absorption and reflection from walls or roofs is one possible option for reducing heating and cooling costs. It has long been known that dark coatings absorb solar energy and white coatings reflect it. A study on black, gray, and white built-up roofs was performed by NCEL in 1981 (Ref 1). It was proposed that fuel-based heating and cooling (air conditioning) could be effectively augmented in a four-season climate by having the roofs or walls of buildings changed from dark in winter to light in summer.

In 1981, no chameleon-type coatings were known to be commercially available. NCEL proposed the concept of a reversible coating as a 6.1 research topic. A feasibility report was prepared (Ref 2) describing the state of the art in color changing materials, from liquid crystals to thermochromic metal complexes to photochromic spiran dyes. The research was funded by the Office of Naval Research (ONR). The focus of the work was limited to thermochromic metal halide complexes and photochromic spiran dyes. Several papers were published by NCEL and university co-investigators describing the mechanisms for the color changes in these classes of compounds (Refs 3, 4 and 5). A technical workshop of all research participants was held at NCEL in 1985 and a report was published describing research progress on thermochromic and photochromic pigments (Ref 6).

Although an economic assessment of energy conserving coatings was not incorporated into this NCEL research and development phase, an important economic and engineering feasibility has been performed elsewhere on expected energy savings from buildings painted either with light or dark, nonreversible coatings. Los Alamos National Laboratory (LANL) and the NCEL energy division calculated the potential savings of painting buildings either dark or light colors in 12 U.S. cities in various weather zones (Ref 7).

In the moderate winter climates (Figure 1) of San Francisco, California; Jacksonville, Florida; New Orleans, Louisiana; and Charleston, South Carolina, possible energy savings were calculated to range from 40 billion to 125 billion Btu. In the colder winter climates of Norfolk, Virginia; Los Alamos, New Mexico; Seattle, Washington; Boston, Massachusetts; and Chicago, Illinois, the savings were even greater and ranged from 137 to 165 billion Btu (Figure 2).

LANL provided NCEL with a list (Table 1) of absorbance coefficients measured for various paints and coatings and pigmented materials (Ref 8). The sum of absorbance, reflectance, and emittance of coatings is defined as 1.0. If emittance is very small, the equation can be written as $1 - \text{absorbance} = \text{reflectance}$.

The measured absorbance coefficients for many materials are shown in Table 1. For example, the absorbance coefficient for black paint is approximately 0.95, whereas the coefficient is 0.75 for a light gray paint and 0.25 for a white paint.

This report describes the first 2 years of development of thermochromic and photochromic pigments for a unique chameleon-type energy conserving coating. The work is sponsored by the Office of Naval Technology (6.2 program) and the proponent is the Naval Facilities Engineering Command (NAVFAC).

BACKGROUND

The overall purpose of this research is to develop and study new reversible pigments that can undergo color change and the solar energy control coatings made from them. In the ONR sponsored research phase (6.1), we investigated two types of pigments: (1) photochromic, or light dependent, and (2) thermochromic, or temperature dependent.

It should be noted that the complete 6.2 development phase consists of several steps:

1. Synthesis of promising pigments
2. Preparation of experimental coatings from the experimental pigments
3. Coating of metal coupons
4. Measurement of ultraviolet (UV) and visible (VS) spectra at room temperature (25°C)
5. Measurement of ultraviolet and visible spectra at hot (50°C) and cold (0°C) temperatures
6. Correlation of spectral changes with color changes
7. Preparation of a final report

In the past few years, two Japanese companies have invented unique thermochromic paints that change color over a relatively narrow range of temperatures. These paints are not available in the U.S. and they are

not related to the well-known "liquid crystals." The chemistry of the pigments and the paint base are carefully guarded trade secrets. We attempted to analyze the dry coatings from thermochromic toy cars made in Asia, but were unable to determine the composition. The pigments are well incorporated in highly insoluble epoxy and polyester paint films, which limits the chemical analysis.

Photochromic Pigments and Dyes (Table 2)

The spiropyran (BIPS)-merocyanine dyes have been known as far back as the 1960's (Ref 9). The Air Force studied the color reversible spiropyrans as potential pigments for canopies and shields to protect aircraft pilots from intense ultraviolet radiation (Ref 10). These compounds generally change from a white or ivory color to a purple on exposure to sunlight. More recently, a Soviet chemist has written a book summarizing worldwide research on the BIPS and related photochromic chemicals (Ref 11).

Research performed by NCEL and university co-investigators focused on mechanisms of the reversible photochemical rearrangement in the BIPS molecules. Although this work is important from the standpoint of basic chemical research, a further research and development program is needed to synthesize the desired pigments before the coatings can be made.

The objectives of the research reported herein were to: (1) determine the color changes of the BIPS we synthesized, and (2) determine whether or not the BIPS could be incorporated into a paint base as a pigment.

Thermochromic Inorganic Pigments (Table 3)

Thermochromic compounds, such as silver tetraiodomercurate (TIM) were reported by Ketalaar (Ref 12) as early as 1935. However, Ketalaar thought that the compound existed as a mixed double salt of silver iodide and mercuric iodide. It has since been demonstrated, both by our published work (Ref 3) and by a recent Japanese book (Ref 13), that silver TIM and copper TIM are true metal salts of the tetraiodomercurate anion rather than mixed double salts.

Silver TIM is a yellow solid at room temperature. Heating the yellow powder to 50°C or higher causes a color change to orange and then red. When the heat source is removed and the compound cools back to room temperature, the yellow color returns. The mechanism is due to a type of thermal crystal distortion. The same color changes can be accomplished by high pressure at room temperature.

The copper TIM is a red solid that changes color and becomes maroon above 70°C. As in the case of the silver salt, copper TIM also undergoes thermal crystal distortion.

Since silver and copper TIMs are easily made from the corresponding silver or copper nitrates, NCEL made other metal TIMs from analogous metal nitrates including gold (I), thallium (I), indium (I), and lithium (I), as well as cadmium (II) and lead (II). Other compounds were made for NCEL at the University of Hawaii in which cadmium or zinc replaced mercury in the silver and copper TIMs.

Thermochromic Organic Pigments (Table 4)

As mentioned earlier, the 6.2 development phase was primarily based on the research findings of the 6.1 project, which focused on the photochromic BIPS and the thermochromic metal TIMs. It was recognized that there might be limitations in both these pigment classes, so a third class of color changing compounds was explored. These compounds included the aryl lactones (phthalides), which have been reported to change from a colorless form to a blue color, reversibly, in the presence of acids and bases (Ref 14).

NCEL was interested in learning whether the color of the lactone dye could be changed by mixing it with a weak Lewis acid (proton donor) in a low melting waxy ester or alcohol. At room temperature, the waxy ester would separate the colored dye from the proton donor, but as the ester melted, the dye and activator would react, causing thermal bleaching of the mixture.

EXPERIMENTAL SECTION

The work breakdown structure can be described as:

1. Preparation of pigments
2. Combination of pigments with paint bases -
 - (a) epoxy
 - (b) alkyd-silicone
 - (c) water-based acrylic latex
3. Preparation of painted steel panels
4. Assembly of temperature controlled spectrophotometric measurement system
5. Design and assembly of heating-cooling device
6. Spectrophotometric measurements
7. Data collection (spectra)
8. Data reduction
9. Data interpretation
10. Draft of decision report (TM)

PREPARATION OF THE PIGMENTS

As mentioned in the Introduction and Background sections of this report, we have published the synthesis of several compounds. The synthesis of these compounds can be summarized briefly as follows.

Photochromic Pigments

The photochromic organic compounds were synthesized from an 1-phenylindole derivative made from diphenyl hydrazine. The 1-phenylindole derivative was condensed in ethanol with various substituted salicaldehydes made by NCEL or its research contractors, including Eastman Kodak Corporation, the University of California at Santa Barbara (UCSB), and California Polytechnic State University at San Luis Obispo (CALPOLY). The final products, all derivatives of 1-phenyl-3,3-dimethylindol[2,2'] benzopyran spiran, are abbreviated as BIPS throughout this report. The synthesis and purification are described in Reference 4.

Thermochromic Metal Halide Complexes

The metal halide complexes were made by reacting appropriate metal nitrate with potassium tetraiodomercurate (TIM) in aqueous solution to produce the pigment. For example, silver nitrate was dissolved in hot water and added to a solution of potassium TIM in hot water, with stirring. The two chemicals reacted and formed a precipitate that was yellow when cold and orange when warm. The precipitate was filtered, washed with water, and air dried. Chemical analysis was performed at Galbraith Labs in Knoxville, Tennessee. The details of synthesis, purification, and analysis are described in References 3 and 5.

Other metal TIMs were made from copper nitrate, thallium nitrate, indium nitrate, and lead and cadmium nitrates. In the case of gold, where gold nitrate is not known, gold (I) iodide was used instead.

Considering the general hazards of using mercury compounds in paints and coatings, alternative metals were substituted in an attempt to find more acceptable pigments. Both zinc and cadmium are in the same chemical family as mercury, and analogous compounds with these metals should have similar properties to the mercury pigments.

We attempted to make the corresponding potassium tetraiodozincate (TIZ) and potassium tetraiodocadmiate (TIC) by reacting potassium iodide with cadmium iodide and zinc iodide, respectively. The reactions did not proceed in water. The potassium TIC and TIZ were made by direct fusion under anhydrous conditions. This work was subcontracted to the University of Hawaii because they have the appropriate equipment for high temperature synthesis.

The synthesis is still being performed, but preliminary work indicates that the majority of the zinc and cadmium analogues of the mercury compounds, such as silver and copper TIM, are not as highly colored. For example, silver tetraiodocadmiate (TIC) and silver tetraiodozincate (TIZ) are pale yellow and only become a darker yellow upon heating from 25 to 40°C; whereas the silver TIM, as indicated above, changes from yellow to orange.

Thermochromic CVL Mixtures

Thermochromic dye mixtures were made by reacting specific leuco (colorless form) dyes with various different proton donors in waxy esters and alcohols. The mixtures were prepared in different ratios in test tubes, then heated to 90°C for 10 minutes, cooled, and used as the thermochromic pigment.

PREPARATION OF THE PAINTS FROM PIGMENTS

The paints were prepared in the following manner: 5 ml of unpigmented alkyd-silicone paint (see specifications below) was placed in a 10-ml ceramic container, along with 0.5 gms of pigment and a 2-cm-diameter ceramic (yttria, zirconia, or alumina) ball. The container was secured in a Brinkmann shaker-mixer. The instrument was activated by a switch and the container (actually a miniature ball mill) was shaken horizontally for 15 to 30 minutes at about 100 cycles per second.

The apparatus for making 5 to 10 ml of paint is shown in Figure 3. The pigment and paint base (resin and solvent) were placed in an alumina, yttria, or zirconia container, housed in a steel jacket. A grinding ball was added to the mixture and the paint preparation apparatus was tightly secured in place with screw locks. The Brinkmann mixer-shaker was then operated for 30 to 60 minutes at a preset shaking speed, and the paint was prepared as a homogeneous mix. The paints prepared in this manner were of fine quality, equal to larger batches prepared in commercial ball mills that grind pigment with paint bases.

After mixing the ingredients, the shaker was stopped and the paint was removed from the container. The steel coupons were immediately painted and allowed to dry. Preliminary practice was obtained by making paints using conventional pigments, such as zinc or copper phthalocyanine. The unpigmented paint bases were procured from the Proline Paint Company in San Diego, California, that regularly formulates products meeting the military or federal specifications indicated below:

alkyd-silicone	Federal Specification TT-E-490
urethane	Military Specification Mil-C-83286
epoxy	Military Specification Mil-P-24441
acrylic latex	Federal Specification Mil-P-28578

The alkyd-silicone, Federal Specification TT-E-490, gave the highest gloss and most uniform coloration with the experimental pigments.

The steel coupons, which were 2 by 2 inches, were first sand blasted and then coated with the epoxy MIL-P-24441 as a primer. The experimental and control paints were then applied, either by dip coating or brushing. A doctor blade was used to drawdown a wet film thickness of about 3 mil (0.003 inch) corresponding to a dry film thickness of about 1 mil (0.001 inch).

PREPARATION OF THE WAXY CVL THERMOCHROMIC COATING

The color changing blue CVL mixture has not been formulated into a paint yet. The waxy pigment cannot be directly mixed with the unpigmented paint vehicles because there are no common solvents. This problem will be solved next year by microencapsulation, as noted in the Plans section of this report.

THERMOELECTRIC HEATER-COOLER

The thermoelectric heater-cooler was designed, assembled, and tested by Crilly and Associates of Camarillo, California, and DonJon Associates of Oxnard, California. The heating-cooling device was upgraded by the Electrical and Electronics Division at NCEL by replacing the power supply, thermocouple sensors, and resistors.

The thermoelectric cooler-heater device is based on the Pelletier principle. As current is passed in one direction, a series of conducting plates (brass) heat up, and the temperature rises. As current is passed in the opposite direction, the heat is removed and the device cools down. The excess heat is removed by recirculation of water through hoses driven by a pump and waterbath.

SPECTROSCOPY STUDY

The painted panels were each attached to the Pelletier thermoelectric heater-cooler, which was then adjusted to a temperature of 0, 25, or 50°C. The spectrum of the paint was recorded at each of these temperatures, using a reflection apparatus known as an "integrating sphere," attached to a Perkin Elmer lambda-9 spectrophotometer. Any modern single beam or double beam recording spectrophotometer would be suitable for this purpose. The spectra of both the conventional and experimental paints and coatings were taken at the three temperatures to determine the color changes in the ultraviolet, visible, and near infrared, covering the region from 0.2 microns to 1.5 microns.

Figures 4 through 6 show the apparatus used in recording the spectra of the paints as a function of temperature. Figure 4 is the overall view of the Perkin Elmer UV/VIS/IR spectrophotometer with the water pump, thermoelectric cooler-heater, thermocouple wires and attachment, and temperature controller used as accessories. Figure 5 shows the integrating sphere with the clamp to hold the painted metal plate (section 1) and the thermoelectric cooler-heater device (section 2). Figure 6 illustrates the temperature controller and the thermocouple socket.

RESULTS

It was found that:

1. The BIPS are not useful pigments for paints. They do change color, but only when they are dissolved in organic solvents or are exposed to sunlight or intense ultraviolet light. The color change occurs from light (white) to dark (purple). Additionally, only the 6-nitro BIPS readily darkens in sunlight and returns to the original white or ivory color rapidly. Additionally, it was found that many of the BIPS decomposed when the solids (powder) were exposed to sunlight or intense ultraviolet radiation (UV).

2. The TIMS are useful as paint pigments. They can easily be ground down and mixed with the unpigmented paint vehicle to form a paint. Most of the color changes, however, are limited to yellow to

orange, or orange to red, or red to maroon. None of the compounds made in this study changed from blue or green to yellow. All of the compounds in this study changed color only at temperatures of 50°C or higher, which is much higher than the desired range of 20 to 35°C.

3. The CVL mixture also has promise as a reversible pigment. This remarkable pigment mixture changes color from blue to white at temperatures of 10 to 50°C, depending on the melting point of the ester. It appears that the pigment is blue when the waxy ester is a solid and the activator is prevented from reacting with the dye. However, when the long chain ester melts, the dye and the activator mix and the color bleaches. The process appears to be reversible many times. Future work will determine how many times the color can be cycled through hot and cold conditions.

4. Figures 7 through 9 show the spectra recorded for white (Figure 7), gray (Figure 8), and black (Figure 9) painted metal coupons at temperatures of 0, 25, and 50°C. Note that the spectra for the white and gray paints change only slightly between 0 and 25°C. The change is a decrease in absorbance and may be due to expansion of the paint film. The change in the spectra of the black paint is uniform throughout the UV to NIR region, but is still only due to changes in the volume of the paint film, as no new absorbance peaks either appear or disappear. Similar minor changes are seen in the spectra of the yellow (Figure 10), orange (Figure 11), and red (Figure 12) paints. In the thermochromic metal mercury iodides (TIMs), however, the changes are definitely due to shifts in wavelength as a function of temperature. The shift in wavelength for the silver TIM (Figure 13) over the 0 to 50°C temperature range is 80 nm. For the copper TIM (Figure 14), it is only about 30 nm.

5. For the thallium paint (Figure 15), the shift is only 10 nm but there are two inflections in the curve that might represent multiple transitions. The cadmium TIM paint (Figure 16) also shows transition of only 10 nm. The lead TIM paint (Figure 17), which was similar to the thallium paint, shows two inflections, but the change in wavelength is still only about 15 nm.

6. The spectra of a conventional, nonreversible blue paint (copper phthalocyanine pigment) was taken at the three temperatures (Figure 18). As in the case of other conventional paints, the main change is seen between 0°C and 25°C, where the absorbance maxima changes, probably due to film expansion. However, when the CVL-phenol-ester mixture was coated onto a metal plate and the spectra was taken (Figure 19), there was a significant decrease in absorbance only at one band of 620 nm. This decrease in visible absorbance correlates well with a disappearance of color as the CVL changes from blue to white.

7. Thermal analysis (DSC) was performed on the CVL mixture (Figure 20) and this proves that there is an exothermic change at 35°C, where the color discharges from blue to white. A similar DSC of methyl stearate (Figure 21) shows that the color change takes place close to the melting point of the ester (37 to 39°C). Our theory is that the temperature

change is controlled by the melting point of the ester used in the formulation. Apparently the dye and the proton donor are separated when the waxy ester is a solid, but the chemicals react reversibly with the dye when the ester is liquefied, thus producing the color change.

DISCUSSION

As mentioned in the Introduction section of this report, Los Alamos (LANL) obtained the absorbance coefficients of a number of different colored paints and other materials. These data are reproduced in Table 1. Since emittance is constant and relatively small, the reflectance of the lighter colored materials is approximately unity minus the absorbance coefficient, as shown in the following formula:

$$\rho = 1 - \alpha$$

where ρ = reflectance
 α = absorbance

It can be seen from Table 1 that the most reflective white paint has an absorbance of about 0.25 and hence a reflectance of 0.75. The black paints have an absorbance of about 0.95 and therefore a reflectance of 0.05. The black and white paints would thus define the maximum and minimum values that one would expect if the ideal white to black reversible paint were available.

In the original feasibility report, it was noted that only a few reported compounds underwent thermal or photochemical changes from one distinct color to another. In most cases, the colors were close to each other in the visible region, such as yellow to orange to red. Only the spirans appeared to undergo large changes from white to purple. The reason for these changes is that the spirans exist in equilibrium as two forms, one with an absorbance band in the ultraviolet (which appears white to the eye) and the other in the visible region (the purple merocyanine form).

Although black, gray, and white coatings have very distinct absorbance or reflectance coefficients, it is not necessarily easy to predict the coefficient of materials we call "colored." For example, Table 1 shows that colors from blue and green through yellow, orange, and red all have absorbance values of about 0.50. Actual coefficients may vary slightly due to texture and other factors. Figure 22 shows the actual temperatures recorded under 2- by 2-inch steel plates painted with black, gray, and white coatings. The painted steel panels were placed over an aperture in a small box (dimensions 4 by 4 by 5 inches). The temperatures were recorded in front and back of the panels using conventional thermocouples attached to a multichannel recorder. The black panel ranged in temperature from 100 to 110°F, while the gray panel varied from 90 to 100°F, and the white panel ranged from 75 to 85°F. Although these measurements were made with a small model, the differences in thermal energy retained or reflected can be readily observed.

In this report, we have sketched hypothetical or theoretical spectra, based on known chemical mechanisms, to illustrate possible spectral changes that would accompany a visible change in color of a single thermochromic or photochromic pigment. For example, in Figure 23, an observed change in color could be due to a shift in absorbance band from a short wavelength to a longer wavelength (a red shift) as the temperature increases. The net result is that the shorter wavelengths are filtered out or "cut off," so that only the longer wavelength color is observed. Another possibility is the disappearance of an absorbance band rather than a shift. In Figure 24, a hypothetical spectra is shown where an intense band in the visible region slowly disappears. The net result is that the color appears to discharge. In the case of the BIPS molecules, the color changes are due to appearance and disappearance of bands in the visible and ultraviolet regions due to structural rearrangement of the compound (reversible change in position of the atoms in the molecule).

CONCLUSIONS

It can be concluded that:

1. The usefulness of the photochromic spirans (BIPS) as solar control pigments is limited because:
 - (a) The pigments do not change color in the desired direction.
 - (b) Chemical modification has not enhanced the basic pigment changes, direction, or color development.
 - (c) The pigments lack the opacity needed to be effective paint pigments.
2. The usefulness of the thermochromic metal TIMs complexes is also limited because:
 - (a) The color change is narrow (yellow to orange or orange to red).
 - (b) The color changes occur at higher than desirable (48°C to over 150°C) temperatures for development as a paint pigment.
 - (c) Substitution of mercury by cadmium or zinc does not enhance the color changes or direction of color change.
 - (d) The environmental impact of mercury compounds does not warrant further developmental expense.
3. Preliminary experiments with the CVL complexes indicated an exciting research lead because:
 - (a) The color change was from blue to white.
 - (b) The change in color was in the right direction.

- (c) The change occurred at a desirable temperature (35°C).
- (d) The color change was reversible many times.

RECOMMENDATIONS

It is recommended that all research and development efforts be devoted to the development of pigments related to the CVL mixture. Efforts should focus on these general areas:

1. Polymer chemistry should be continued to microencapsulate the waxy pigment complex into a dry pigment powder. The dry powder is needed for compatibility with several military and federal specification paint bases, as well as elastomeric and plastic materials needed for roofing materials.

2. Microencapsulation experiments should be performed with: (a) epoxies, (b) polyesters, (c) polyamides, (d) acrylics and, perhaps, (d) polyurethanes. All of these plastics can be used in microencapsulation procedures on a small scale in our laboratory. It is not known at this time which plastic or procedure would be most successful or which microencapsulated mixture would produce the most desirable, reversible, thermochromic pigment.

3. Further chemistry research and development work should be performed on related lactone or phthalide pigments to protect the patent potential of the Navy and federal government. More than one example of a color changing thermochromic mixture would be needed to file a patent application.

4. It is recommended that modifications of the CVL pigment be made using logical organic chemistry procedures, such as the substitution of dimethylamino groups with methoxy, ethoxy, propoxy, benzylamino, anilino, diethylamino and other related electron donating groups. Pigment research and development should also be performed on related arylfuranone lactones to determine the scope of this color change. It may be possible to develop pigment complexes that change from black, red, green, orange, or violet to white.

5. It is also recommended that research and development be continued to identify other activators and deactivators for the color change, in case the present chemical modifiers of the pigment are photochemically unstable (in sunlight), oxidizable (in air), or otherwise changed by natural environmental conditions.

6. All of these chemicals can be purchased commercially in small quantities. The chemical research is well planned. Both the safety and environmental risks have been considered and the research can be carried out at NCEL by experienced chemists in a safe manner. Once the patent application has been filed, larger scale chemistry work can be contracted to private industry.

FUTURE PLANS

The CVL mixture will be microencapsulated in one or more of the following plastic microspheres:

1. Epoxy-polyamide, prepared in situ
2. Polyester, catalyzed
3. Acrylic, catalyzed
4. Urethane, prepared in situ
5. Gelatin toughened by paraldehyde
6. Urea-glutaraldehyde condensation product

The procedures for microencapsulation are easy and straightforward and can be performed in the NCEL chemistry laboratory. To describe the procedure in general terms, the pigment mixture is dissolved, or melted, and suspended in one of the two components of a two-component reaction. The first component containing the dye mixture is added, as a liquid, slowly to the second component in a large beaker, with rapid stirring. The plastic forms at the interphase of the two components as a series of hollow microspheres that encapsulate the mixture of interest.

Trial runs will be conducted on other liquids, oils, and melted waxes to find the best conditions for microencapsulation. The microencapsulated dye, which will then appear to be a dry powder, will be mixed with the unpigmented paint bases, as described in the Experimental section of this report, to make the final paints.

FUTURE TRANSITION

It is important that we complete the work to the point of making at least a pint of thermochromic paint, plus draft manufacturing specifications. Considering the utility of a reversible architectural coating, there will probably be many companies eager to acquire the technology from the Navy under the Technology Transfer Act. The principal investigator has already talked with the technical director of the Manville Corporation in Denver, who is interested in testing a thermochromic energy conserving paint developed by NCEL, at corporate expense. Discussions were held with Professor Fred Krieger, AIA, a faculty member in the School of Architecture at the University of Hawaii. He is currently conducting research for both the Army and the State of Hawaii on energy conserving materials, using experimental systems similar to those we had planned to use. He had been in private industry both in the state of Washington and Minnesota and he said that he knew of private companies that would be interested in the Navy technology transfer once we had a paint.

ACKNOWLEDGMENTS

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Table 1. Solar Absorptance of Various Materials*

Optical flat black paint	0.98
Flat black paint	0.95
Black lacquer	0.92
Dark gray paint	0.91
Black concrete	0.91
Dark blue lacquer	0.91
Black oil paint	0.90
Stafford blue bricks	0.89
Dark olive drab paint	0.89
Dark brown paint	0.88
Dark blue-gray paint	0.88
Azure blue or dark green lacquer	0.88
Brown concrete	0.85
Medium brown paint	0.84
Medium light brown paint	0.80
Brown or green lacquer	0.79
Medium rust paint	0.78
Light gray oil paint	0.75
Red oil paint	0.74
Red bricks	0.70
Uncolored concrete	0.65
Moderately light buff bricks	0.60
Medium dull green paint	0.59
Medium orange paint	0.58
Medium yellow paint	0.57
Medium blue paint	0.51
Medium Kelly green paint	0.51
Light green paint	0.47
White semi-gloss paint	0.30
White gloss paint	0.25
Silver paint	0.25
White lacquer	0.21
Polished aluminum reflector sheet	0.12
Aluminized mylar film	0.10
Laboratory vapor deposited coatings	0.02

This table is meant to serve as a guide only. Variations in texture, tone, overcoats, pigments, binders, etc. can vary these values.

*G. G. Gubareff et al, Thermal Radiation Properties Survey, second edition, Honeywell Research Center, Minneapolis-Honeywell Regulator Company, Minneapolis, Minnesota, 1960.
S. Moore, Los Alamos Scientific Laboratory, Solar Energy Group, unpublished data.

Table 2. Color Changes in Photochromic BIPS

Number	Pigment Name	Color Change	
		Darkness	Bright Light
1	6-amino	pale yellow	yellow
2	8-fluoro	light yellow	olive green
3	8-methoxy	colorless	yellow
4	6-phenylazo	yellow-orange	yellow
5	6-benzyl	colorless	
6	6-tert-butyl	colorless	pink
7	6-methyl	colorless	colorless
8	6-phenyl	colorless	pink-purple
9	6-bromo	colorless	pink-orange
10	6-nitro	yellow	blue
11	6-chloro	colorless	pink
12	6-hydroxy	pink	cherry red
13	6-methoxy	colorless	colorless
14	8-nitro	blue	deep blue

Table 3. Color Changes in Thermochromic TIMS (tetraiodomercurates)

Number	Compound Name	Color Change	
		Low Temp	High Temp
1	silver mercury iodide	yellow (25°C)	red-orange (50°C)
2	copper mercury iodide	orange (25°C)	red (70°C)
3	thallium mercury iodide	yellow (25°C)	orange (140°C)
4	cadmium mercury iodide	orange (25°C)	red (120°C)
5	lead mercury iodide	orange (25°C)	red (150°C)

Table 4. Color Changes in Thermochromic Dye Mixtures
with Acid Activator and Ester

Number	Name of Dye	Acid	Ester	Color Change	Temperature
1	CVL	bisphenol A	methyl stearate	blue-> white	35°C
2	CVL	maleic acid	methyl stearate	blue-> pale blue	30°C
3	CVL	bis(hydroxy phenyl) methane	neopentyl stearate	blue-> blue (no change)	30°C
4	CVL	benzyl (2-hydroxy phenyl) methane	neopentyl stearate	blue-> blue (no change)	30°C
5	Green SF Yellowish	phenyl phosphonic	neopentyl stearate	yellow green-> colorless	10°C
6	Brilliant Green	phenyl phosphonic	neopentyl stearate	green-> brown green	40°C
7	Leuco Malachite Green	phenyl phosphonic	neopentyl stearate	green-> green (no change)	35°C
8	Leuco Crystal Violet	phenyl phosphonic	neopentyl stearate	violet-> violet (no change)	35°C

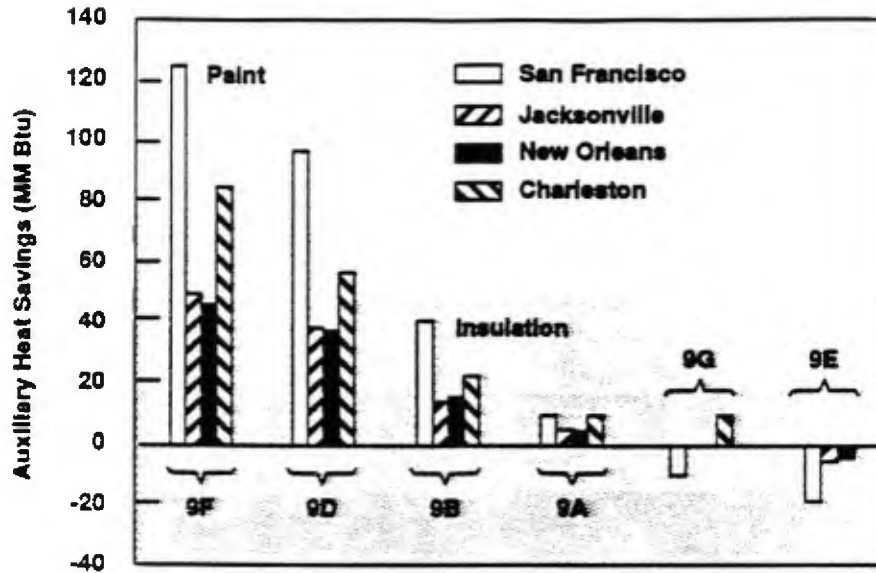


Figure 1 Auxillary heat savings for six retrofit designs in cities with moderate winter climates

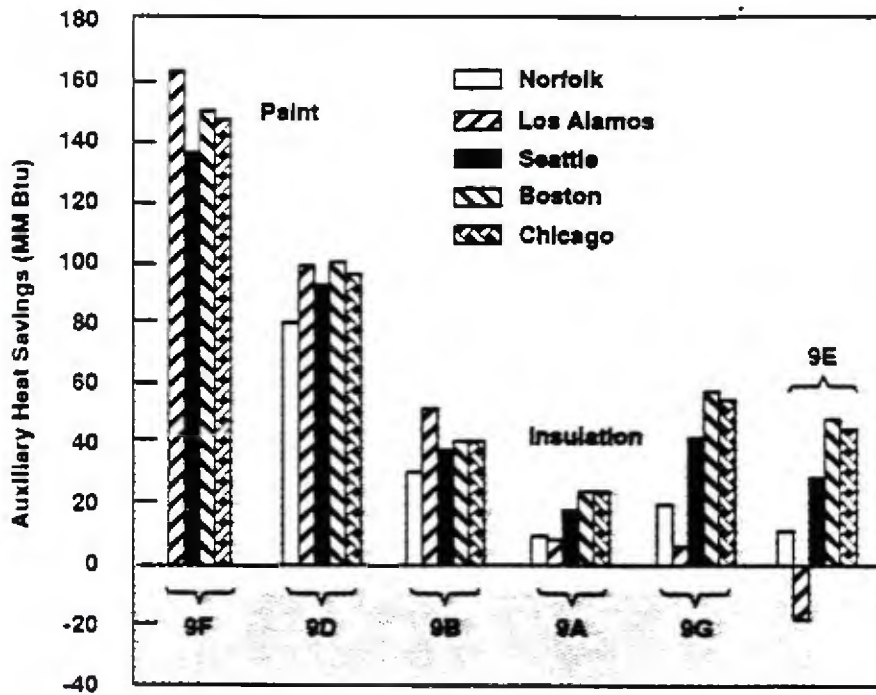


Figure 2 Auxillary heat savings for six retrofit designs in cities with severe winter climates

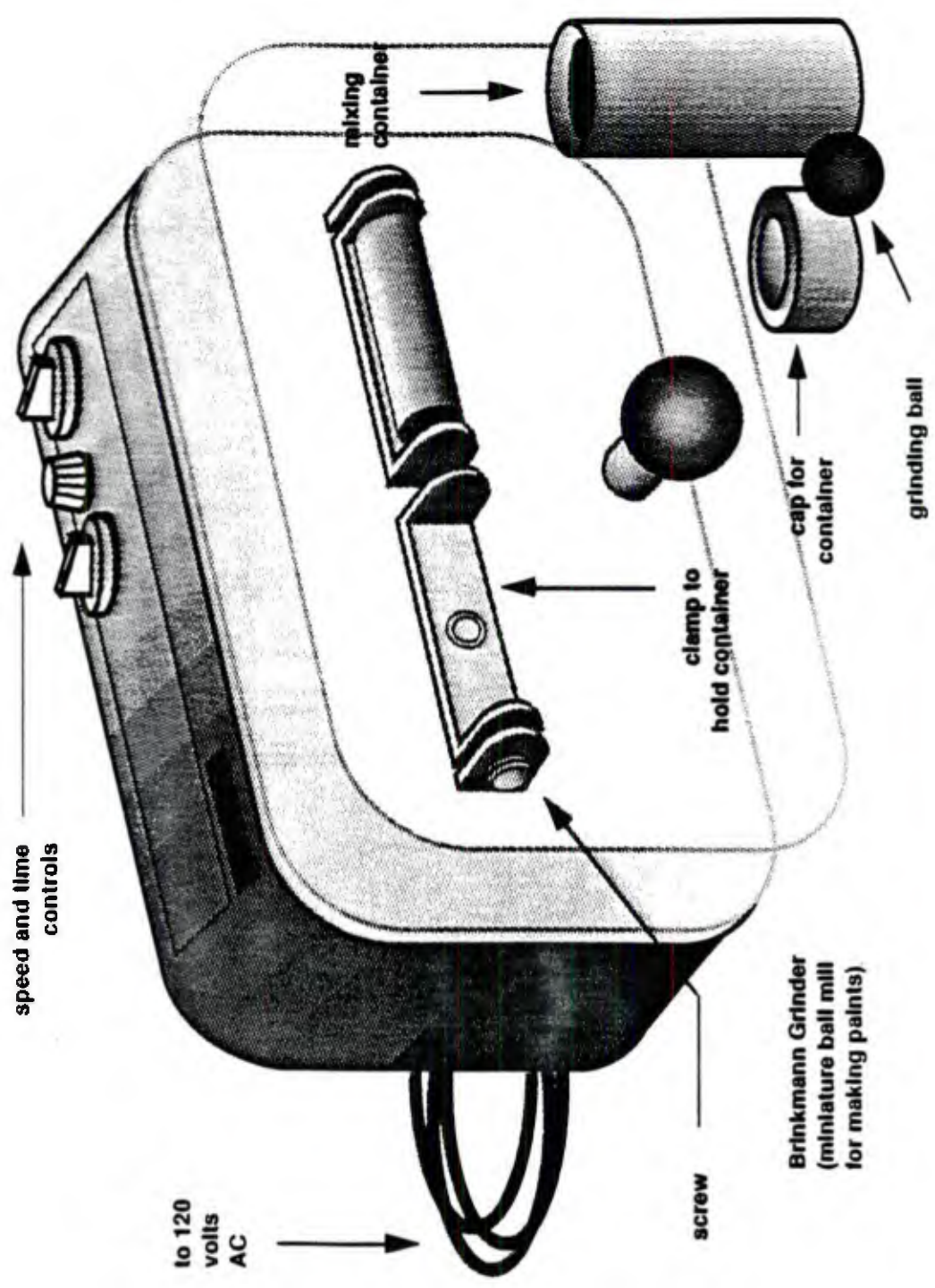


Figure 3. Apparatus for making the paints.

Section 1

Section 2

Section 3

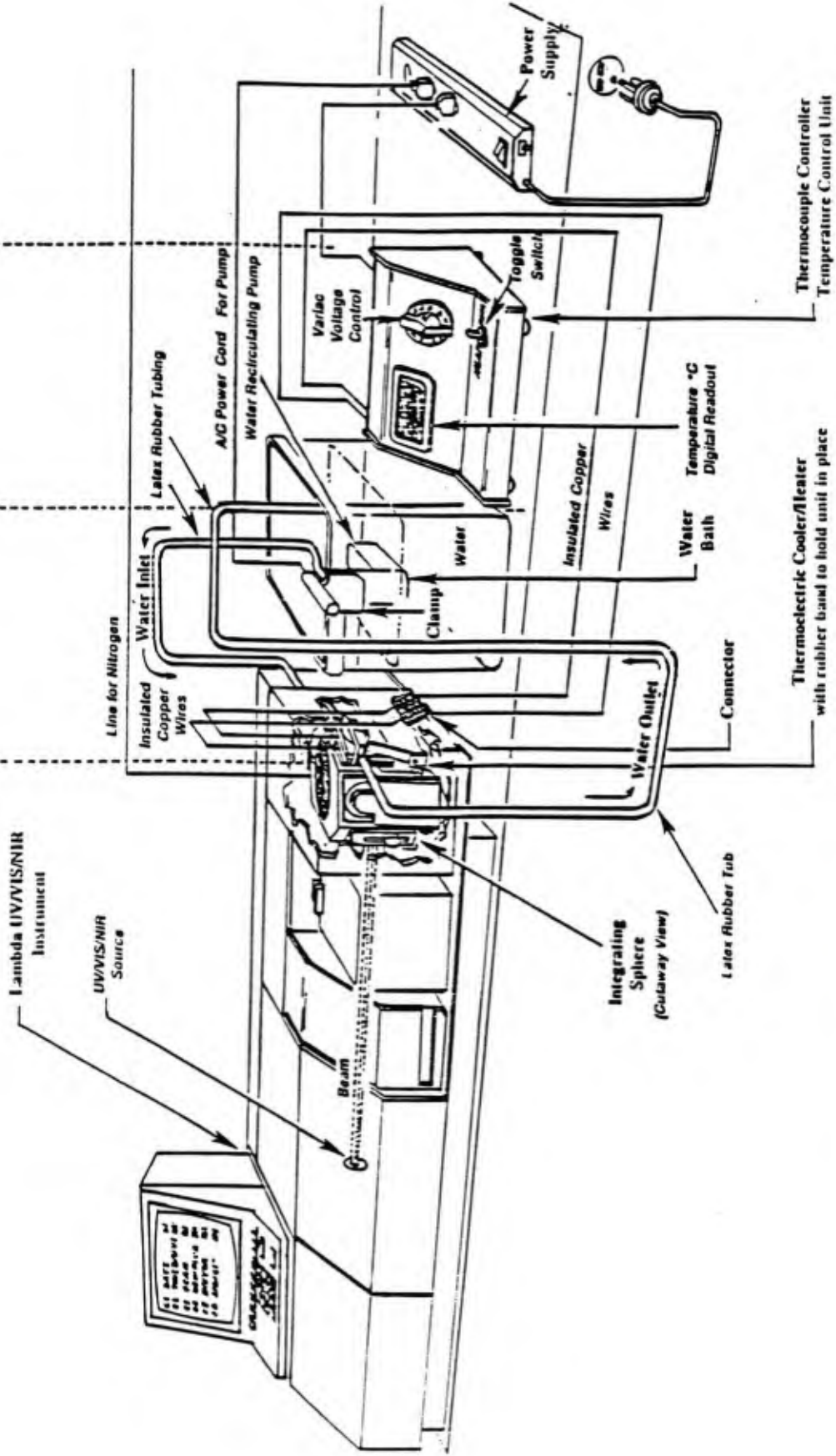


Figure 4 Overall view of Spectrophotometer and Thermoelectric Device.

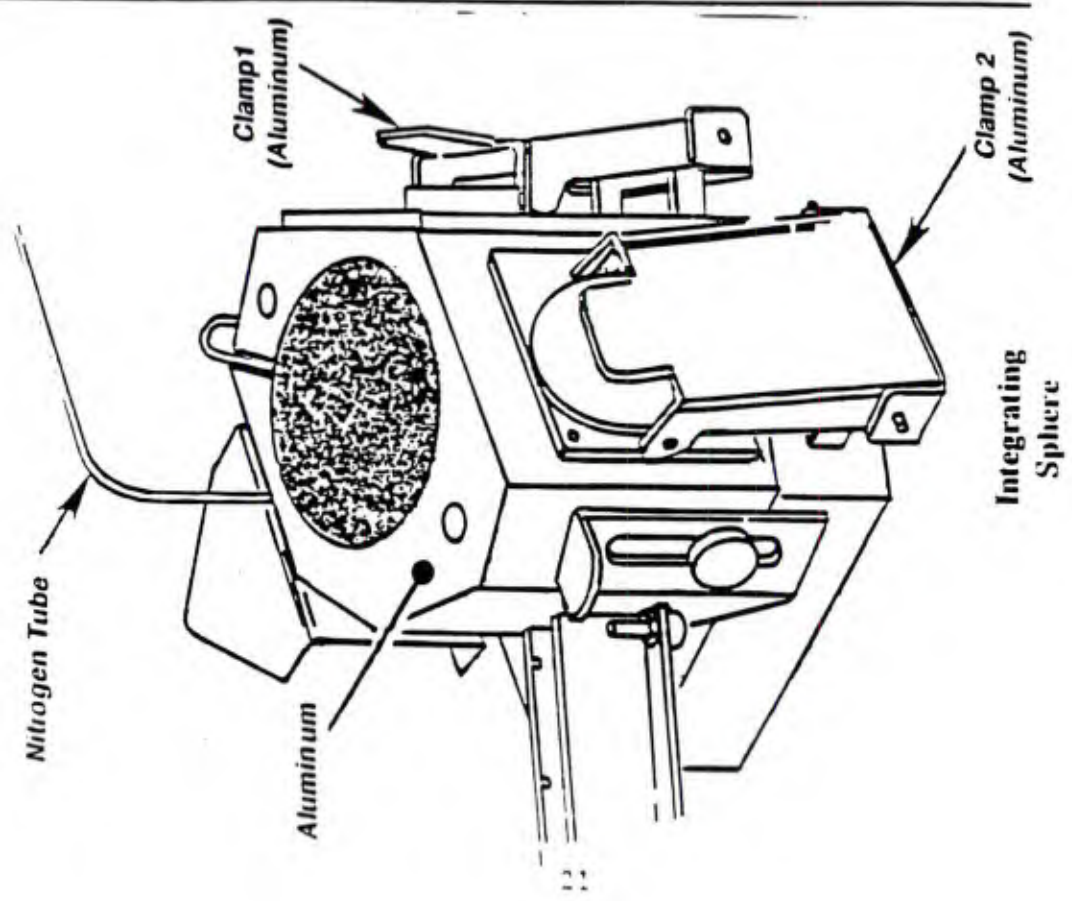
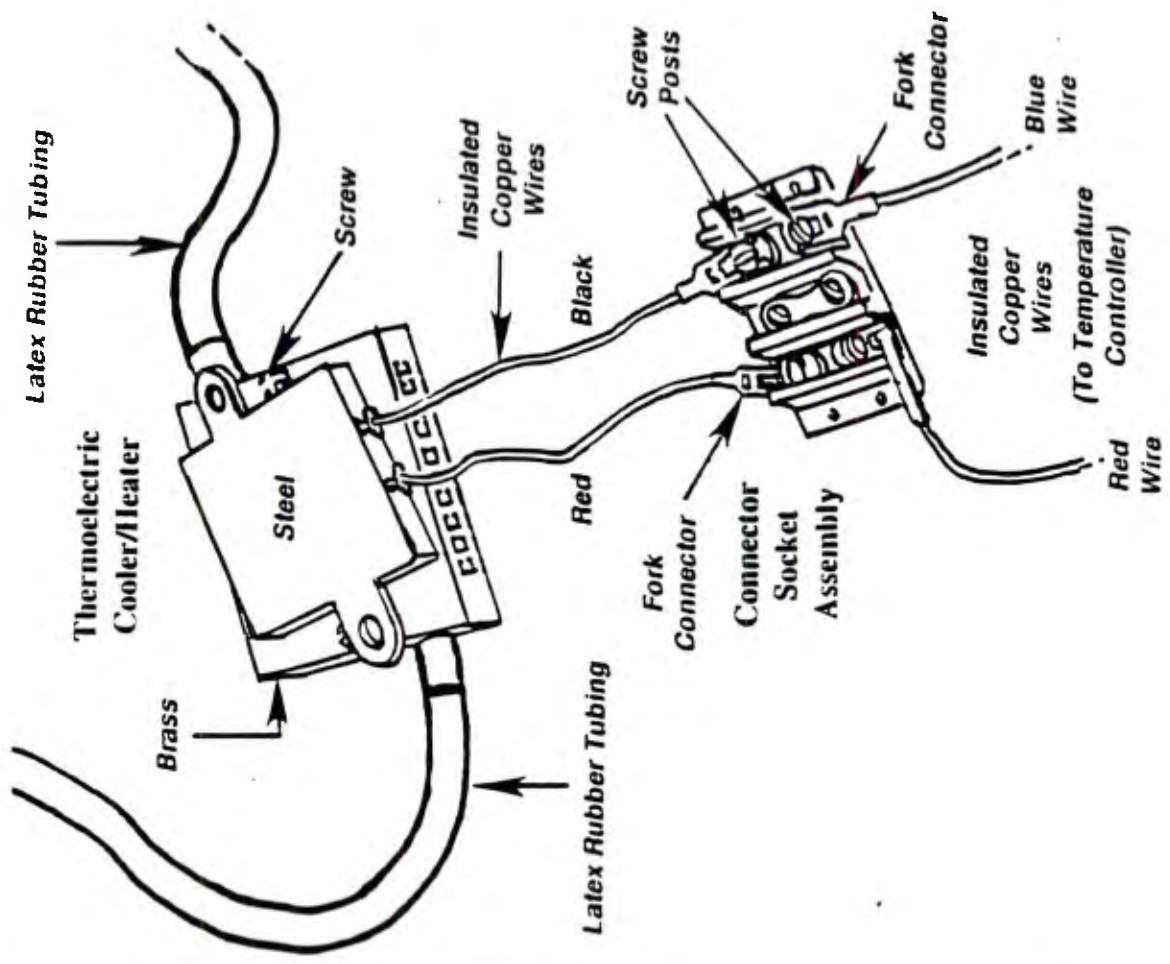
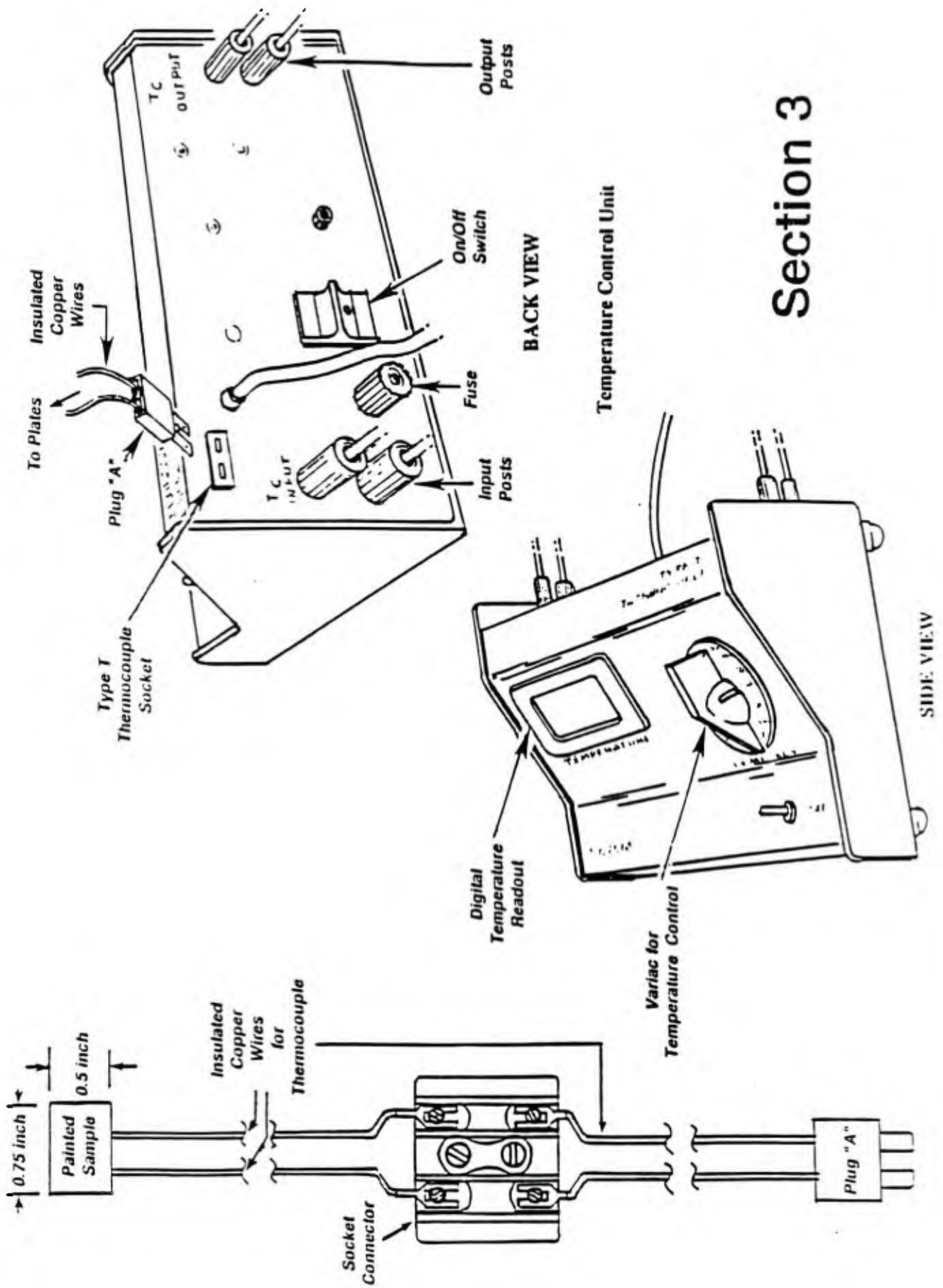


Figure 5 Details of Optical and Thermoelectric Devices.



Section 3

Figure 6 Details of Thermoelectric and Thermocouple Control Devices.

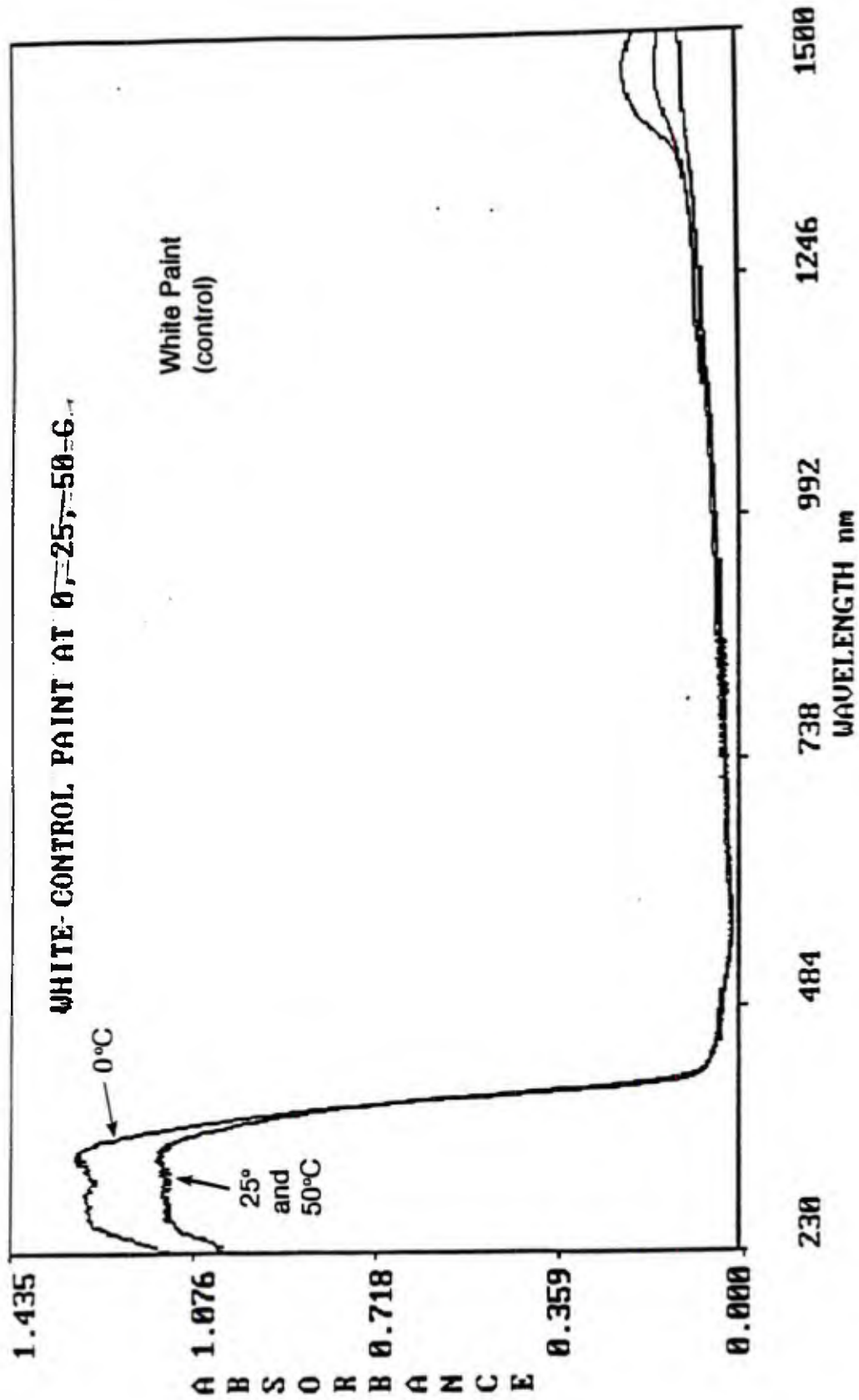


Figure 7 Spectra of conventional white paint (titanium dioxide) at 0°, 25°, and 50°C.

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1.468

A 1.101

B S O R H A N C E

0.734

0.367

0.000

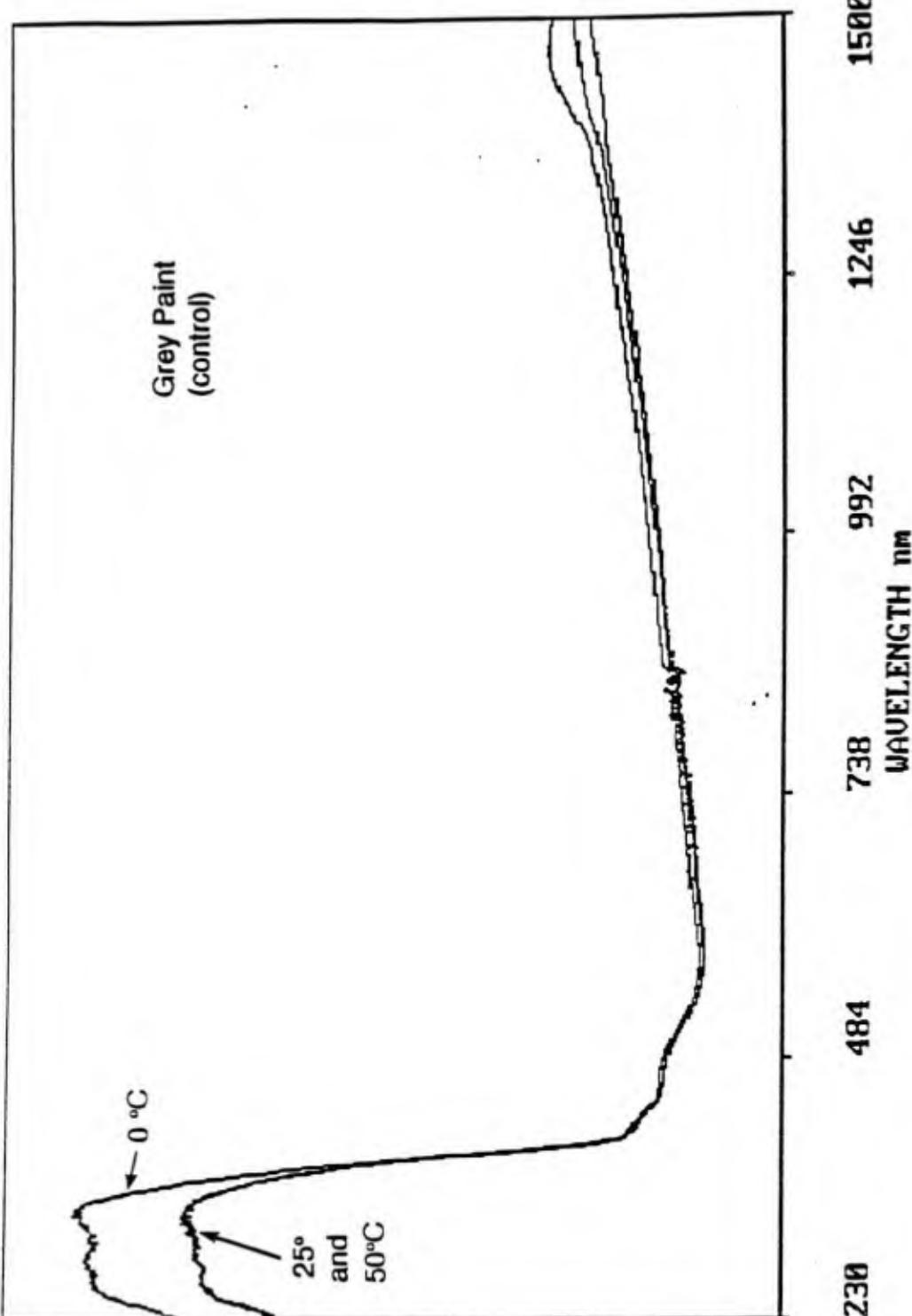


Figure 8 Spectra of conventional gray paint (titanium dioxide-carbon) at 0°, 25°, and 50°C.

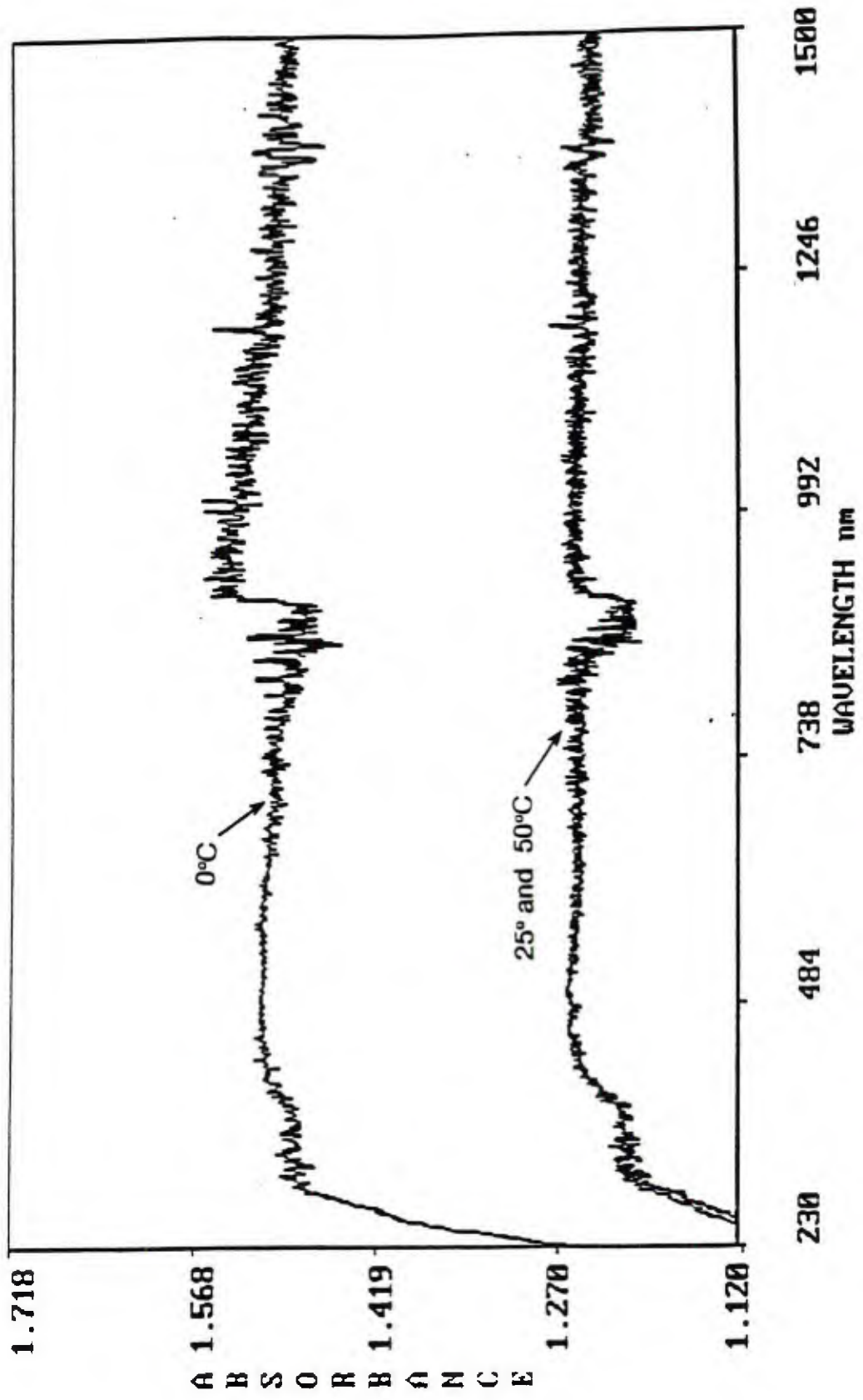


Figure 9 Spectra of conventional black paint (carbon) at 0°, 25°, and 50°C.

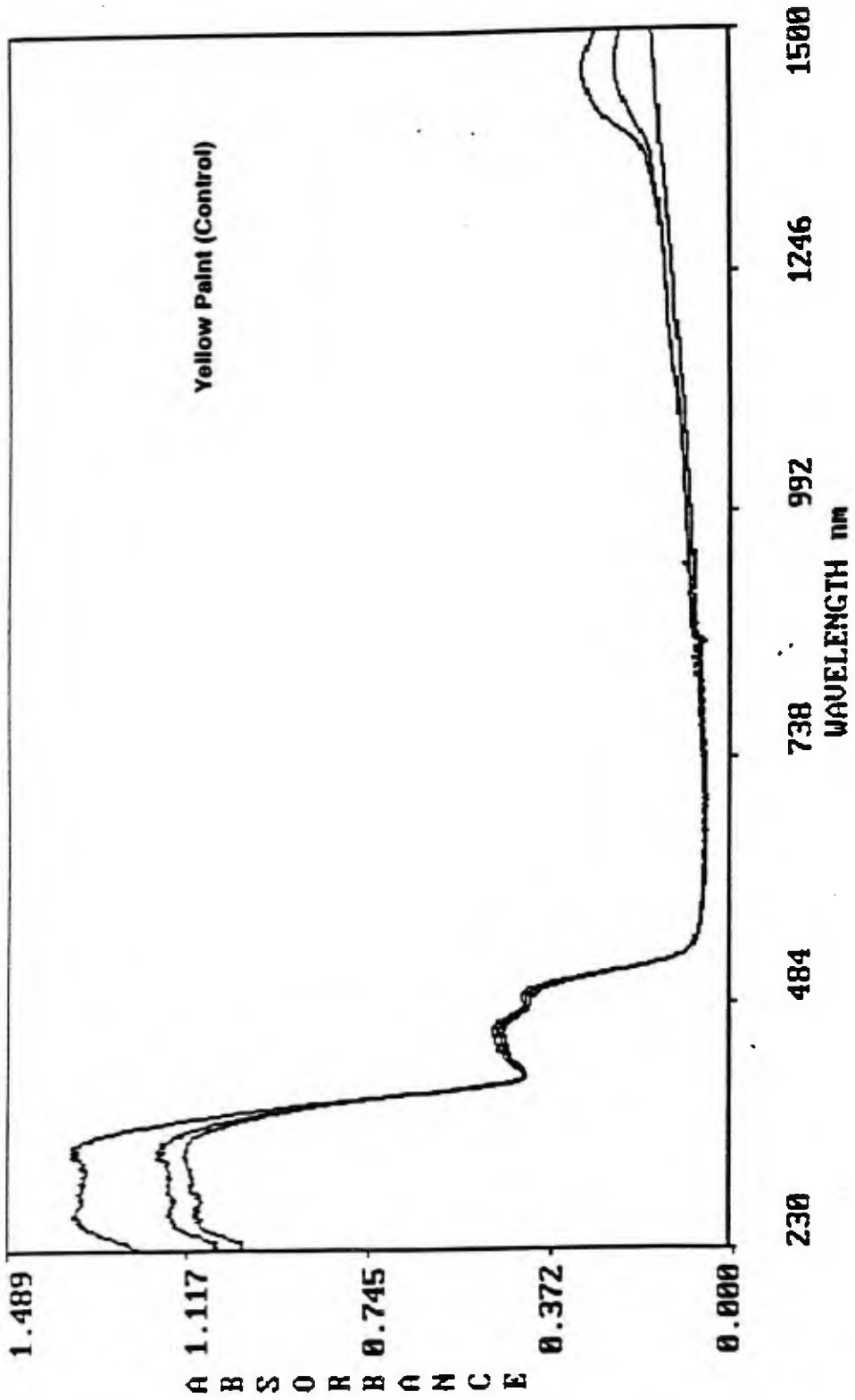


Fig 10 Spectra of Yellow Paint (Lead Chromate)
at 0°, 25° and 50°C

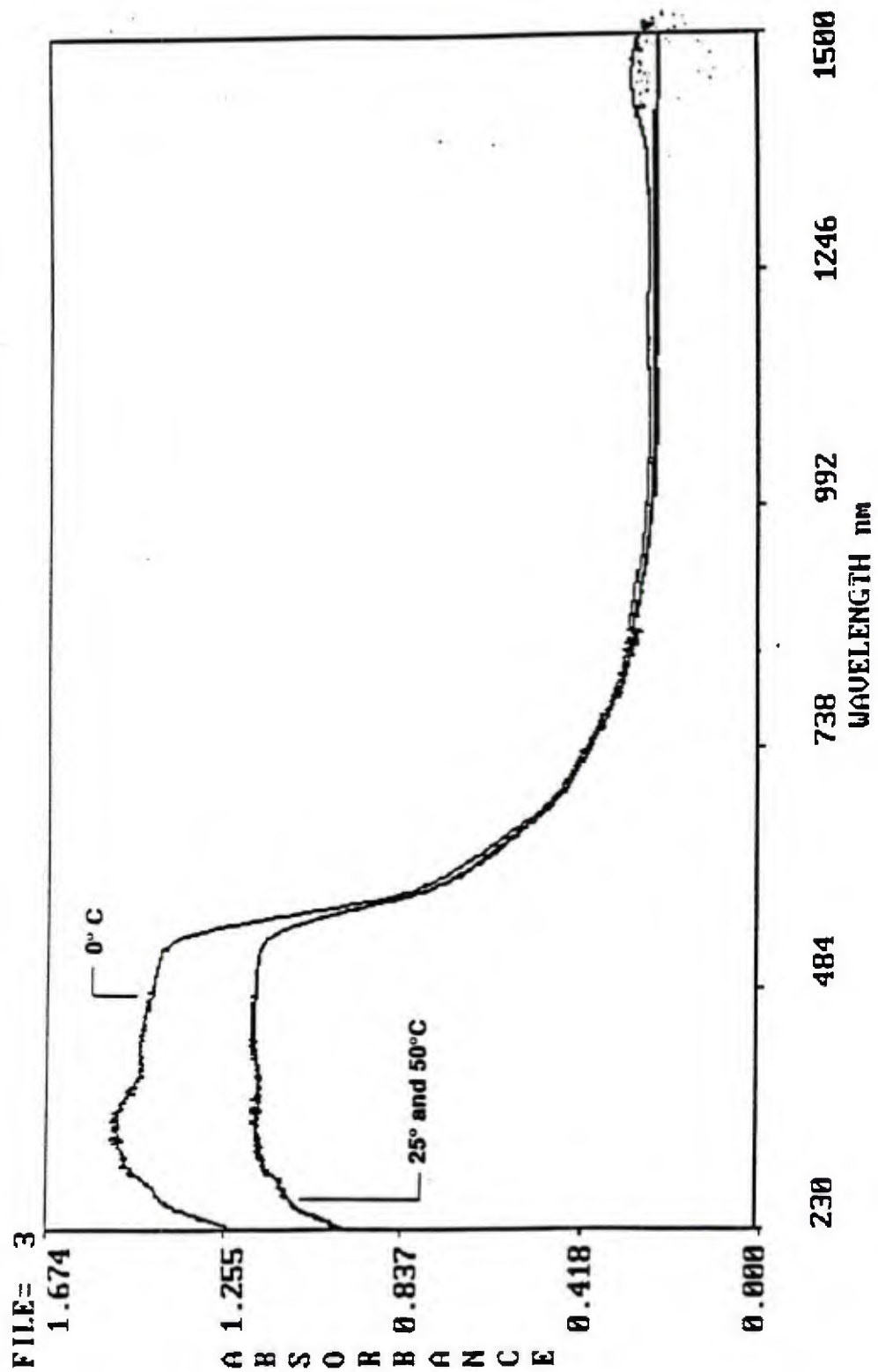


Fig 11 Spectra of Orange Paint (Cadmium Sulfide)
at 0°, 25° and 50° C

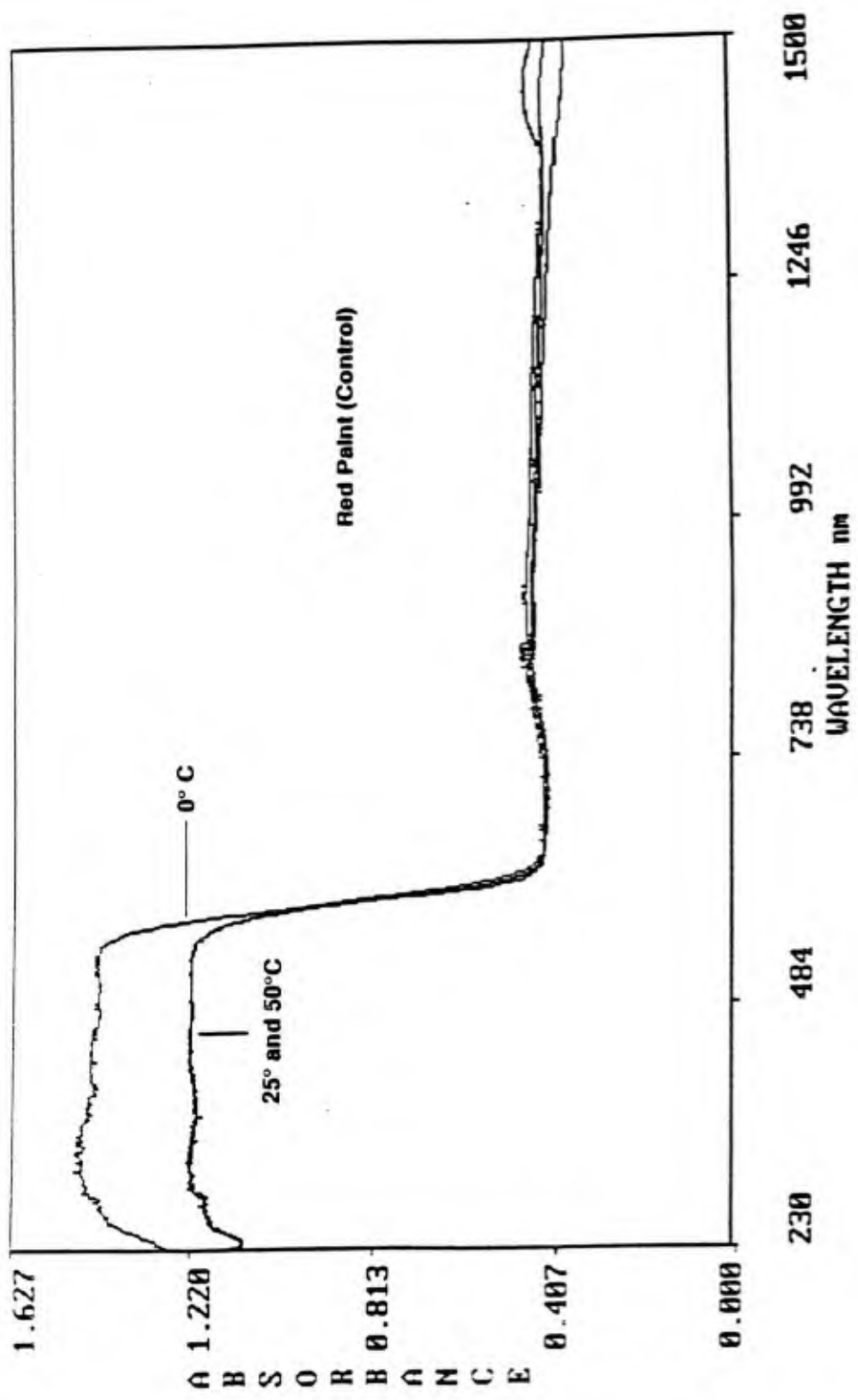


Fig 12 Spectra of Red Paint (Ferric Oxide) at 0°, 25° and 50° C

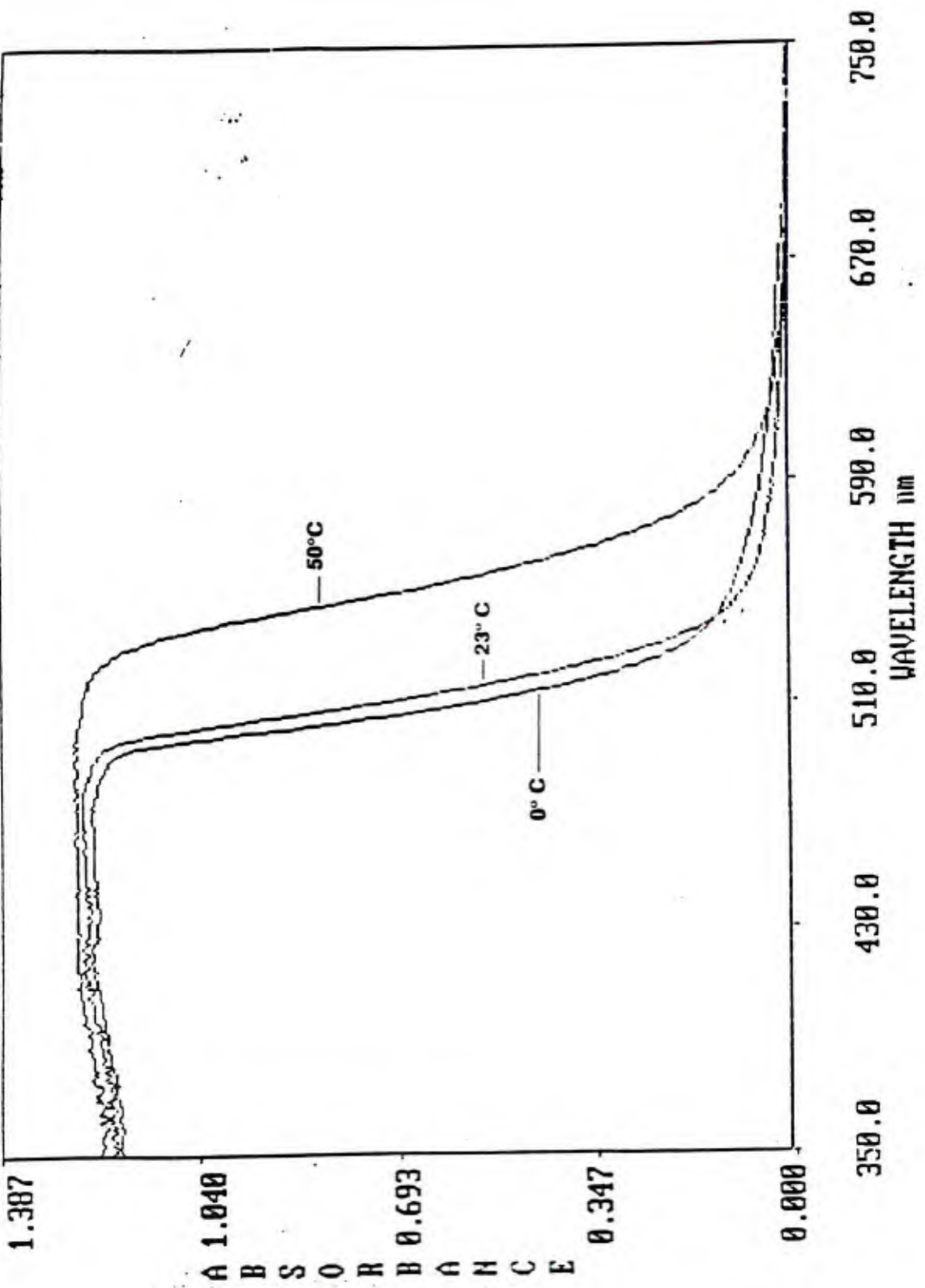


Fig 13 Spectra of Silver Mercury Iodide Paint at 0°, 23° and 50° C

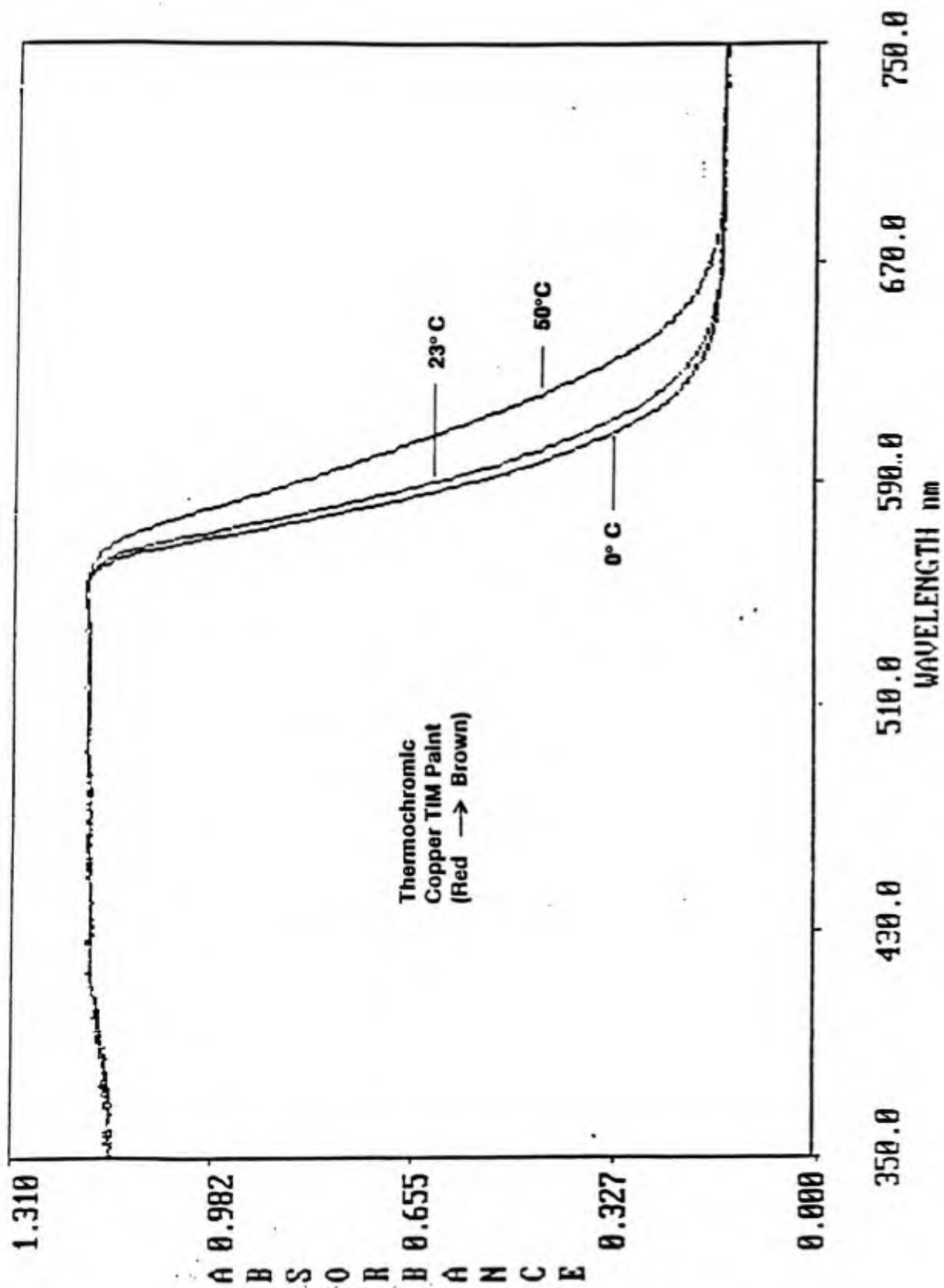


Fig 14 Spectra of Copper Mercury Iodide Paint at 0°, 23° and 50° C

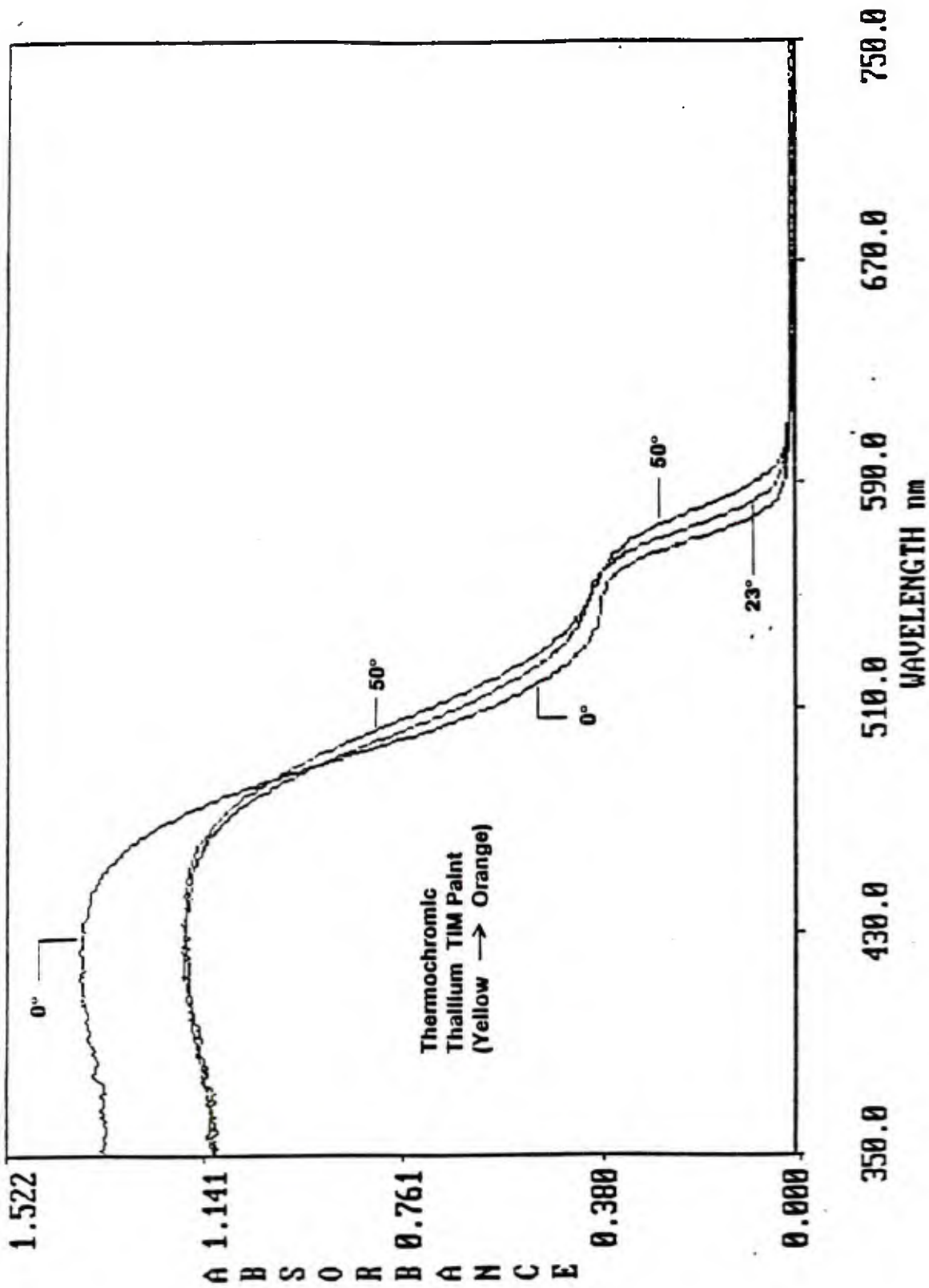


Fig 15 Spectra of Tetrathallium Mercury Hexalodide Paint at 0°, 23° and 50° C

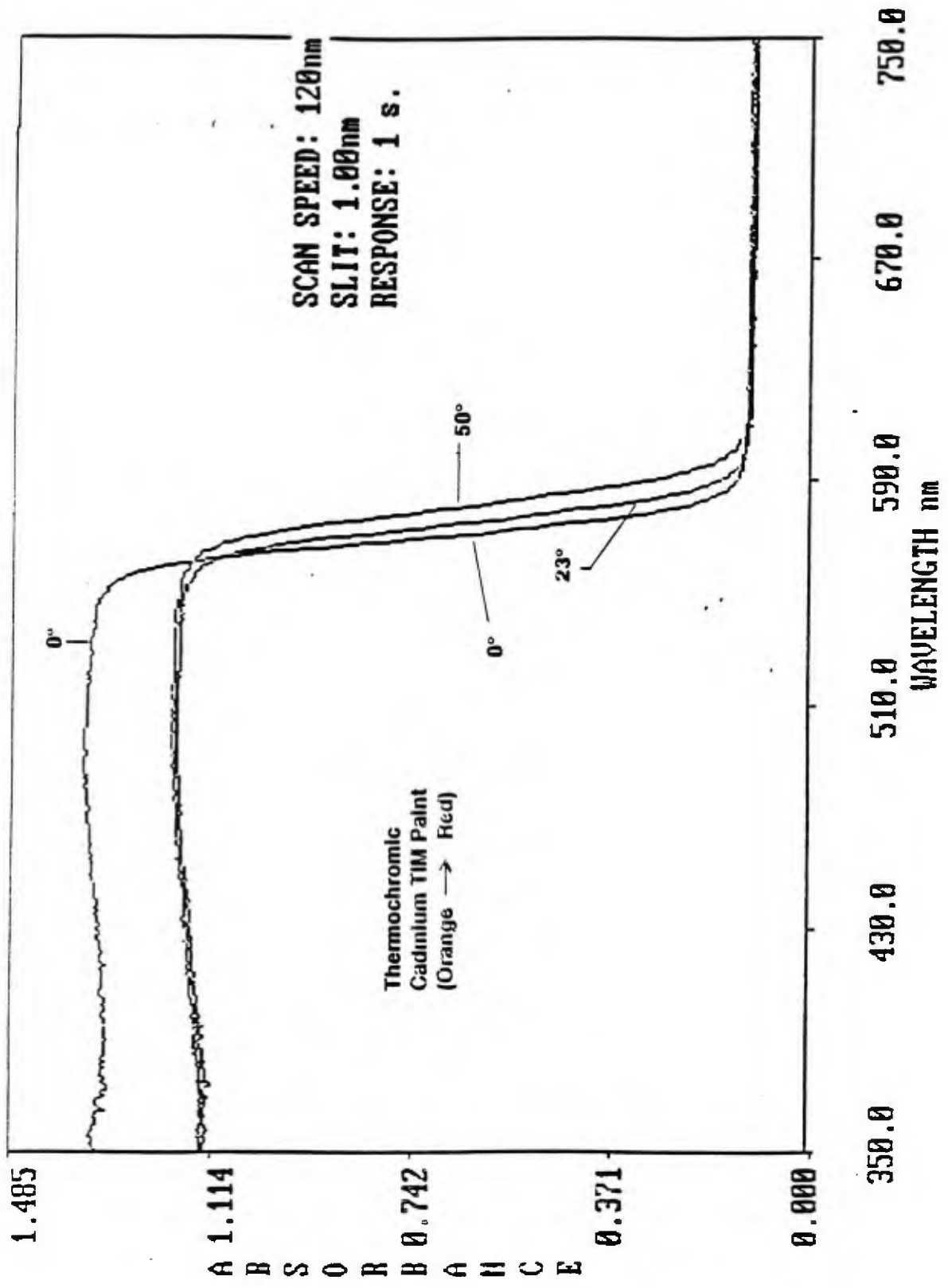


Fig 16 Spectra of Cadmium Mercury Iodide Paint at 0°, 23° and 50°C

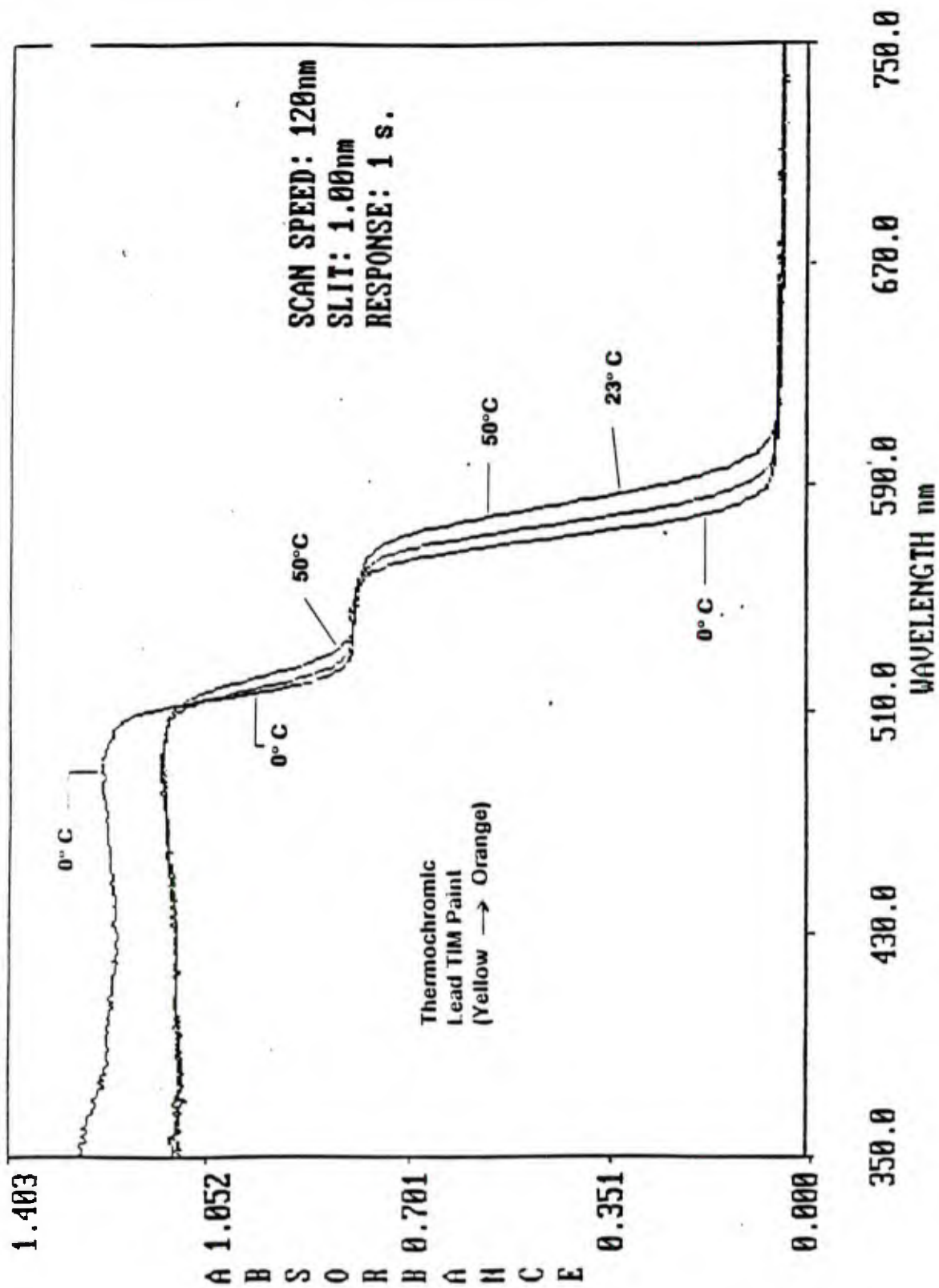


Fig 17 Spectra of Lead Mercury Iodide at 0°, 23° and 50° C

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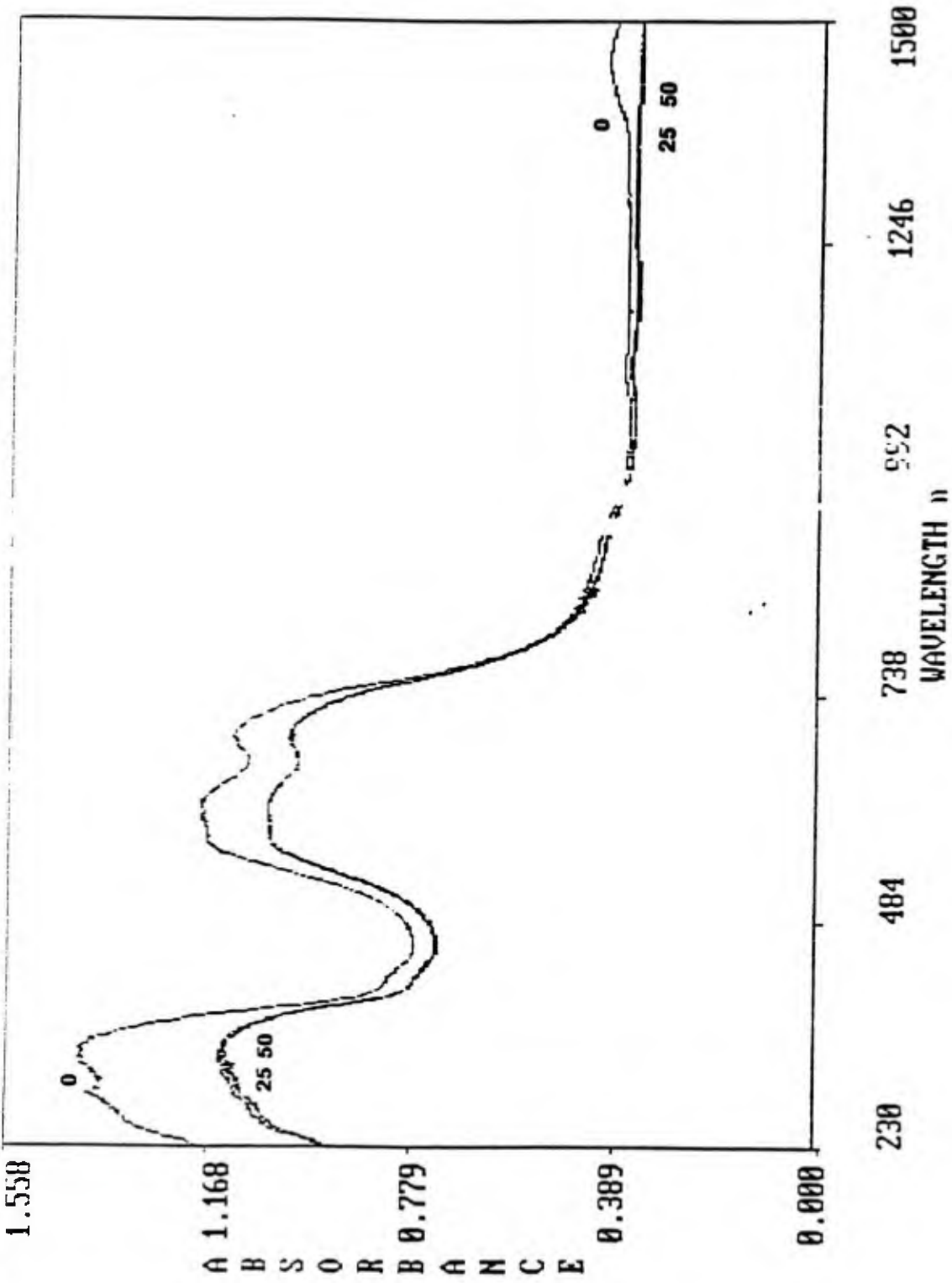


Fig 18 Spectra of Conventional Blue Paint at 0°, 25° and 50° C

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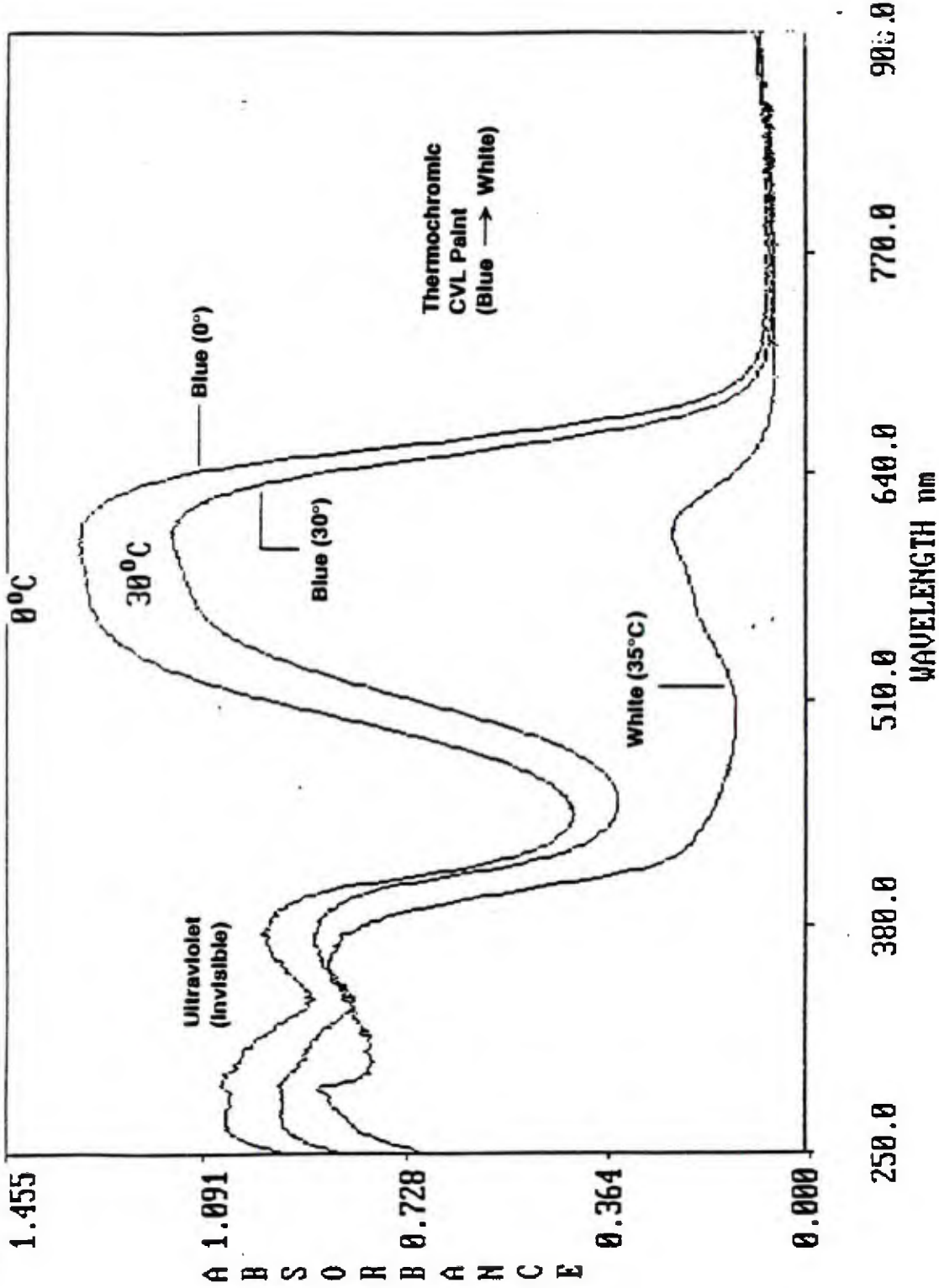


Fig 19 Spectra of Reversible Color (Blue → White)
CVL Mixture at 0°, 25° and 50°C

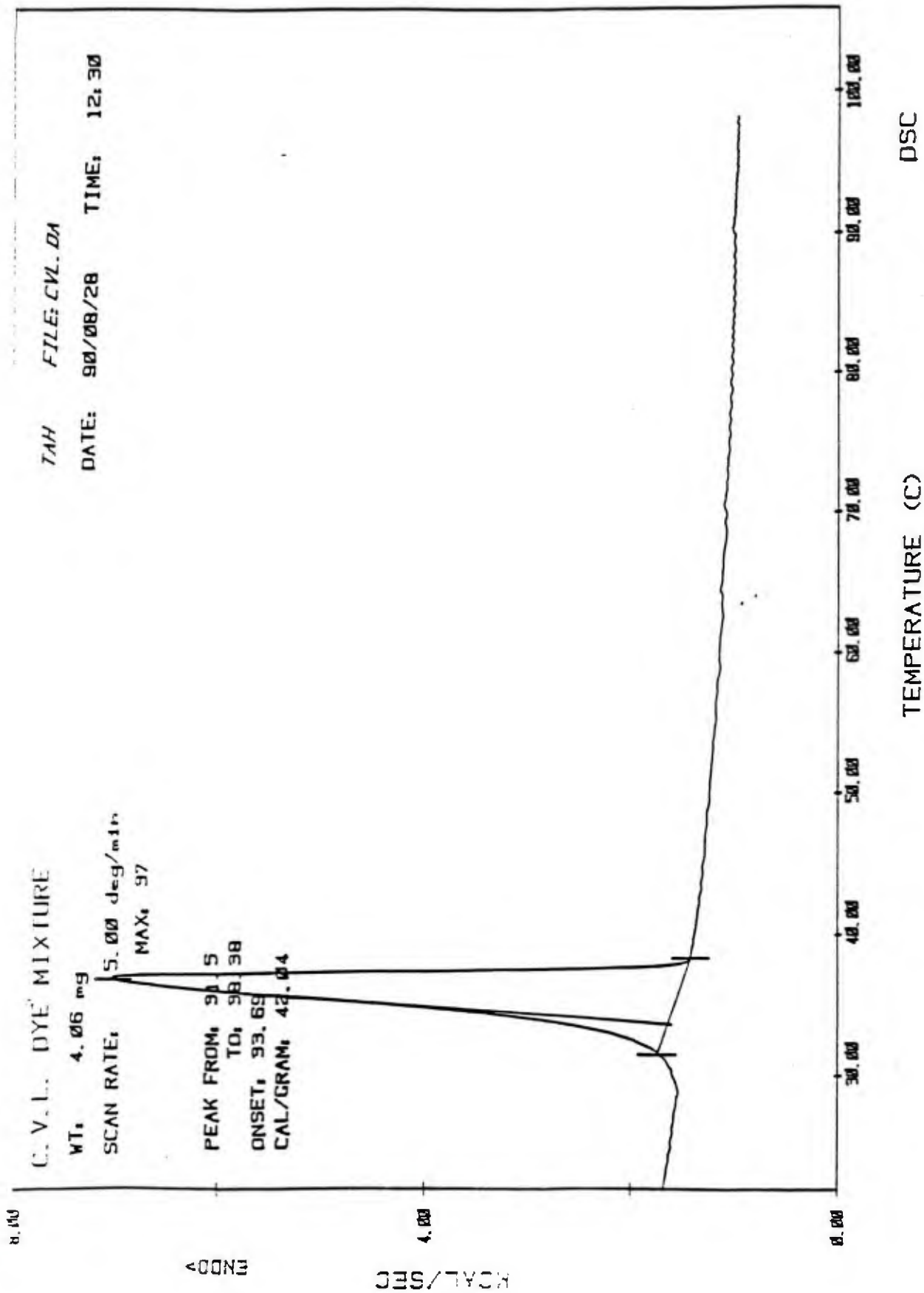


Fig 20 Thermal Plot (DSC) of Thermochromic CVL Dye Mixture

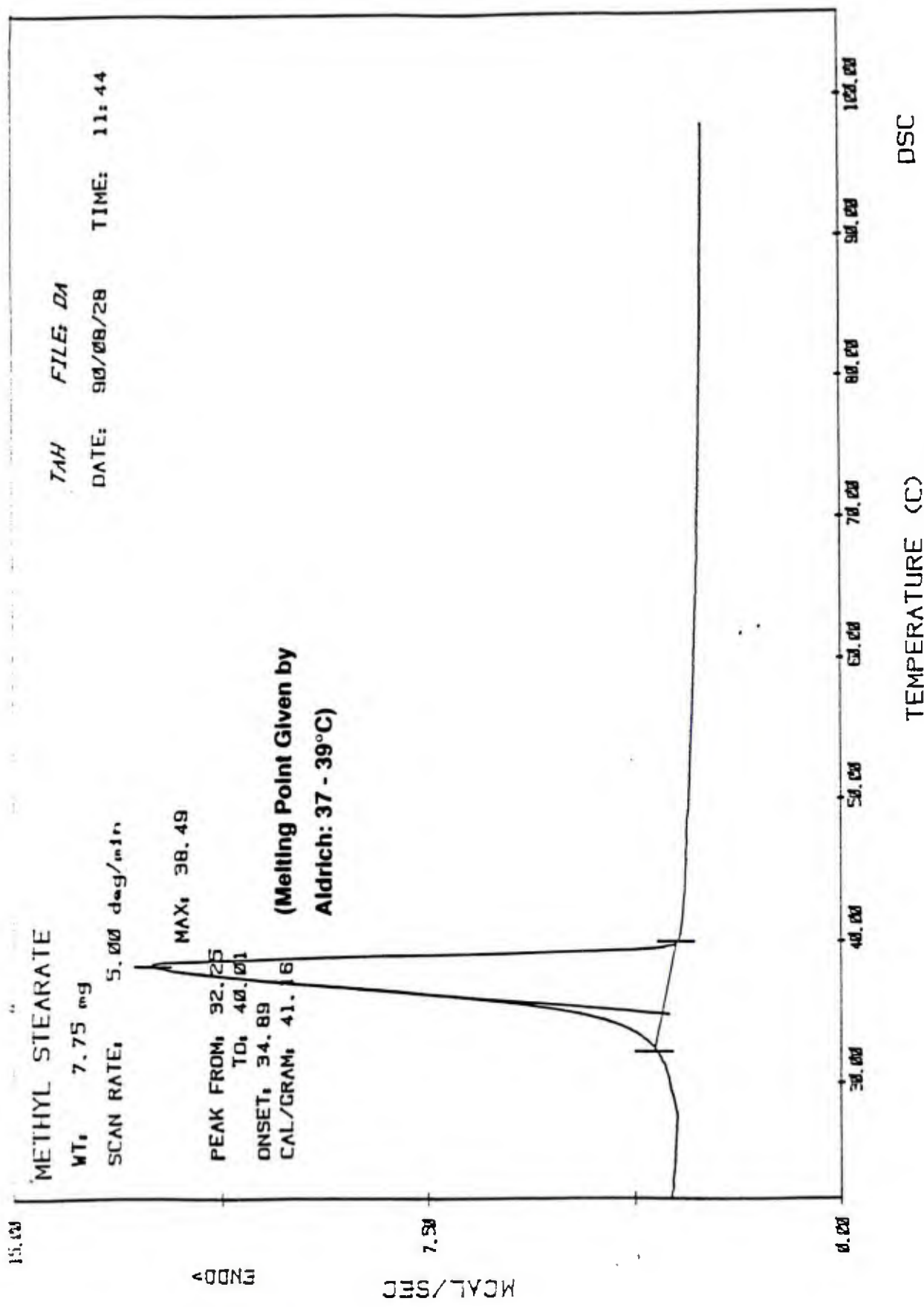


Fig 21 Thermal Plot (DSC) of Methyl Stearate

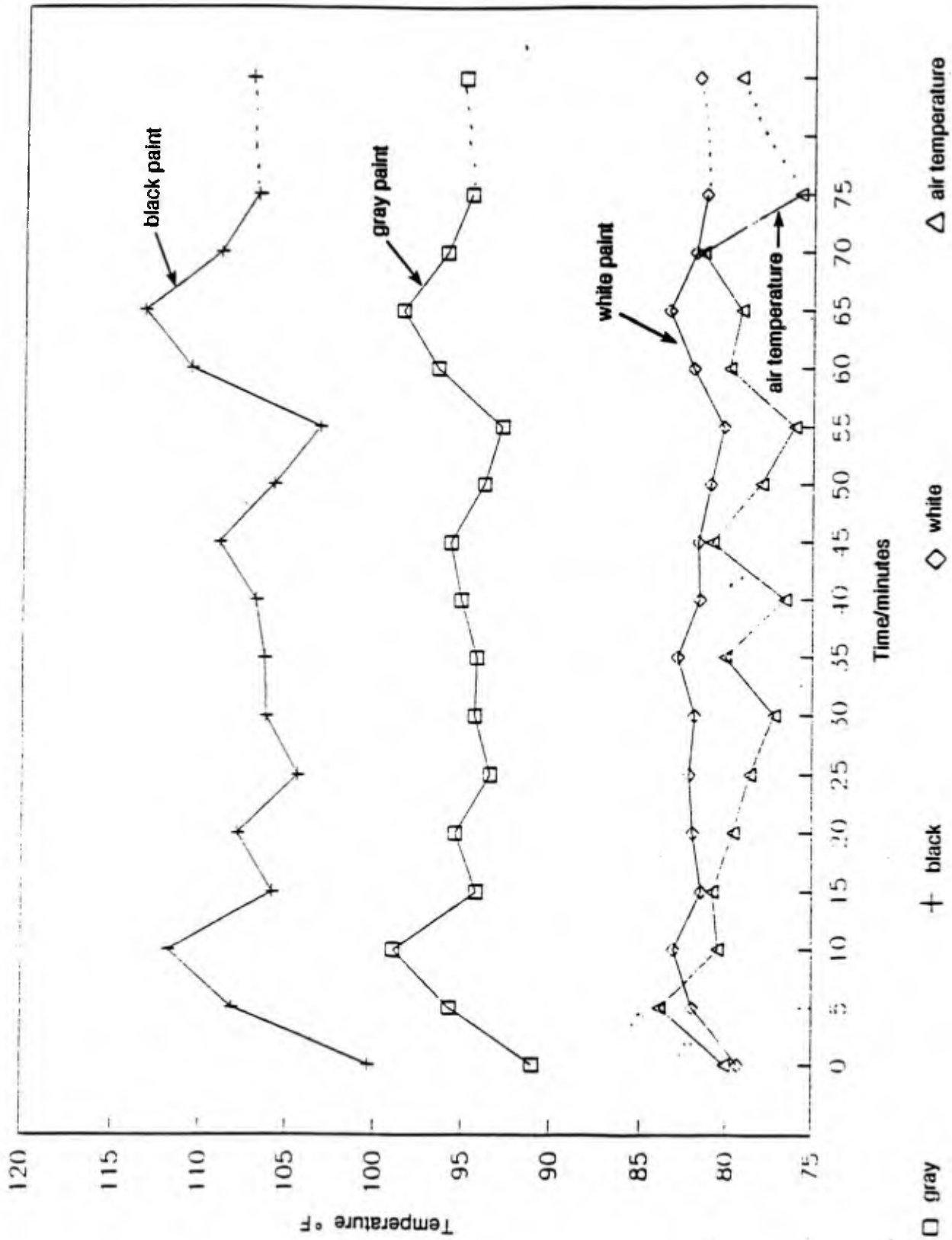


Figure 22 Thermal absorbance of black, gray and white painted panels exposed to sunlight for 75 minutes.

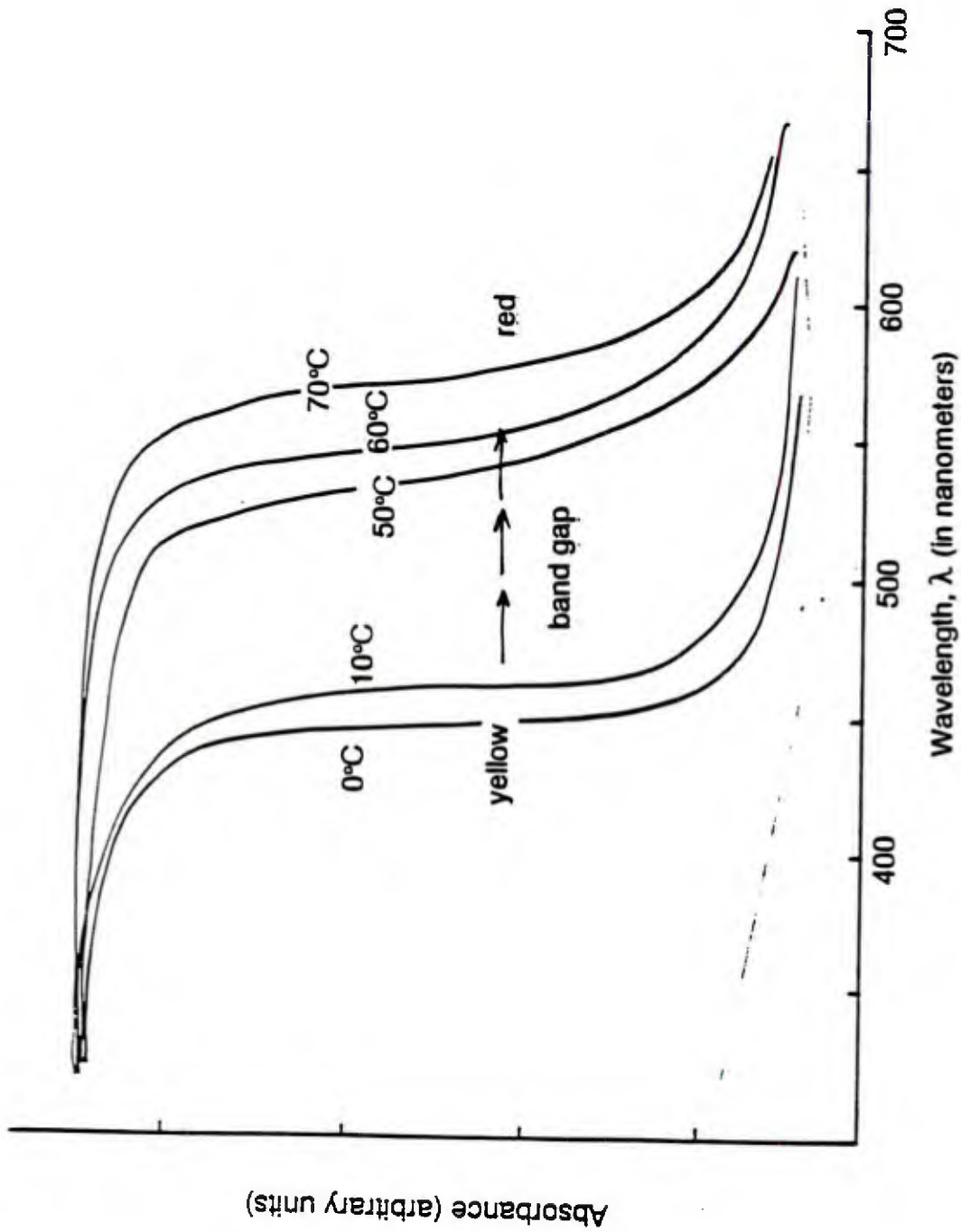


Figure 23 Type A Spectral Change (wavelength shift).

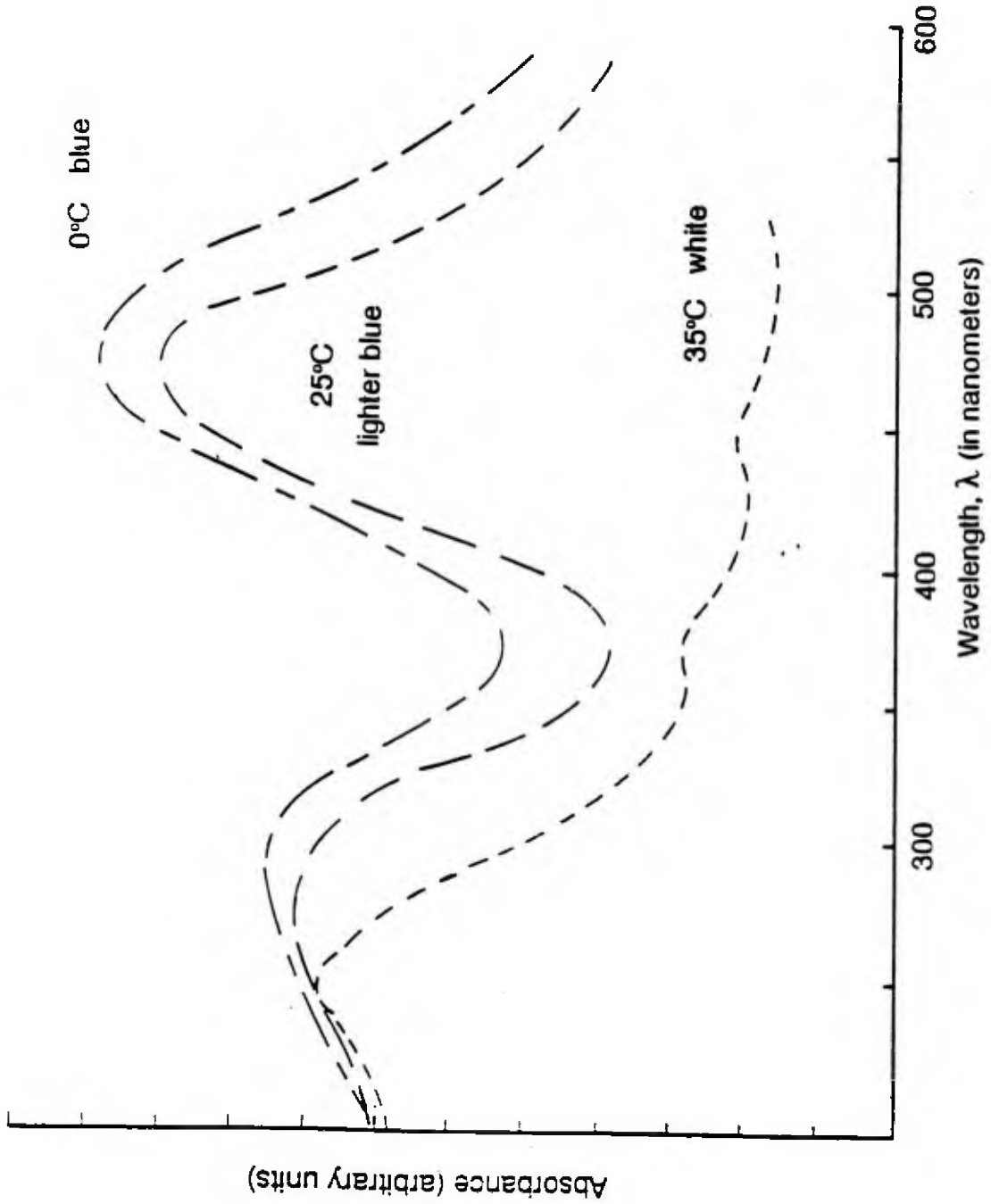


Figure 24 Type B Spectral Change (disappearance of absorbance peak).

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