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MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

Purdue Research Foundation

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JPL Flat Plate Solar Array Project

July 1, 1985

"The JPL Flat Plate Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of flat plate solar arrays. This work was performed by agreement between NASA and DOE."

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FOREWORD

The research described in this report represents 18 months of effort on Contract No. 956097 with the Jet Propulsion Laboratory, Pasadena, CA, under the technical cognizance of Brian Gallagher. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, W. Lafayette, IN under the direction of G.M. Vest and R.W. Vest. The research was carried out by Dr. S. Singaram, Mr. C.J. Sabo and Mr. J.D. Mis with assistance from Mr. R.L. Reed.

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1. ABSTRACT AND SUMMARY

This was a study to investigate the feasibility of utilizing metallo-organic decomposition (MOD) silver inks for front contact metallization of solar cells. Generic synthesis procedures were developed for all metallo-organic compounds investigated. The results of this study led to a number of conclusions. Silver neodecanoate was found to be the most suitable silver metallo-organic compound for use in thick film inks, but the quality of inks was found to be highly dependent on its purity. Benzene was the most suitable solvent investigated for silver neodecanoate, and tetrahydrofuran was a less desirable alternative. A combination of neodecanoic acid and butyl carbitol acetate, in an amount no greater than 40 w/o of the silver neodecanoate present, imparted suitable rheology to silver MOD inks for screen printing. A permanent binding agent was found to be necessary to obtain reproducible, long term adhesion. Bismuth 2-ethylhexanoate, which decomposes to bismuth oxide upon firing, was shown to be suitable for this purpose. Both platinum 2-ethylhexanoate and bismuth 2-ethylhexanoate, which respectively decompose to platinum and bismuth oxide, were suitable for imparting solder leach resistance to the silver films. Platinum and/or bismuth oxide additions degrade the sheet resistance of pure silver films and were minimized, without sacrificing their ability to impart desired properties to the films. Ink SC-10Y, which produces fired films of theoretical metallic composition 99 w/o Ag-1 w/o Bi, was the most suitable of all inks developed for solar cell front contact metallization. The contacts fabricated with it exhibited long term adhesion, excellent solderability and solder leach resistance, and a dense micros-

tructure. The preferred firing sequence for ink SC-10Y involves a 70 minute cycle with a maximum temperature of 292°C. The combination of HF cleaning and the preferred firing sequence produced a high resistance back contact with certain lots of solar cells. This observation requires that changes be made either in the metallurgy of the back contact or in the processing of the MOD inks. Although neither the process nor inks were completely optimized for solar cell front contact metallization, they show great promise for this application.

2. INTRODUCTION AND OBJECTIVES

Photovoltaic cells require back side metallization and a collector grid system on the front surface. Both front and back surface metallizations should have good adhesion, low contact resistance, low sheet resistance, long term stability, and their deposition methods should not degrade the n-p junction. In addition, the metallization for the collector grid should be capable of producing small grid spacings and grid widths. For the terrestrial flat-plate solar array project, low cost of the metallization is also a very important requirement. One of the dominant systems in use today is screen printed thick film silver conductors. When such conductors are used in hybrid microelectronics they are typically fired at temperatures from 650-850°C for 10-15 minutes, but for solar cells they must be rapidly fired in order to avoid degradation of the junction. This rapid firing compared to the conditions for which the inks were developed often leads to poor adhesion, and porous silver films are always the result.

Metallo-organic compounds (MOC's) are ones in which a metal atom is linked to a long chain carbon ligand through a hetero atom such as O, S, N, P or As. In order that the products of decomposition contain only CO_2, H_2O and perhaps nitrogen compounds, Purdue's Turner Laboratory pioneered the use of a set of MOC's for ink fabrication where the linking hetero atom was oxygen. Films produced by the metallo-organic decomposition (MOD) process have a number of advantages compared to conventional thick films. The approach followed at Purdue leads to generic inks because all of the compounds used are either purchased as pure materials or synthesized from commonly available reagents. Even if conventional inks did not contain proprietary additives they still could not be duplicated in the user's laboratory because film properties are dependent on characteristics of the particulates (average particle size, particle size distribution, particle shape, etc.) in addition to their chemical composition. All chemical compounds are in solution in inks for the MOD process, which means the mixing of the constituents is achieved on an atomic scale, and films produced after decomposition of the organic compounds reflect this uniformity. The uniformity of conventional thick films is a strong function of the degree of blending of the particulates in the organic screening agents, and there is always an inherent nonuniformity due to the finite particle sizes of the different constituents in the inks. Fired films produced by the MOD process are always thinner than films produced by conventional thick film technology. This can be a disadvantage if very high conductance is required, but can partially be overcome by deposition of thicker films or multilayer films.

MOD silver films have the potential for eliminating most of the present problems with silver conductors. The MOD silver films can be produced at much lower firing temperatures (e.g. 300°C), which should reduce chemical interaction effects as well as deterimental thermal effects on the junction. Because of their extremely high reactivity, MOD silver films with near theoretical density can be produced, which would overcome the porosity problem experienced with conventional thick film conductors.

The specific technological objectives of this project were to identify and characterize suitable MOC's, develop generic synthesis procedures for the MOC's, develop generic fabrication procedures for screen printable MOD silver inks, and optimize processing conditions to produce grid patterns on photovoltaic cells. The metallizations were evaluated as to their appearance, line definition, adhesion, sheet resistance and microstructure. Some metallized cells were evaluated at JPL as to their performance as solar cells, although initial photovoltaic evaluation were done at Purdue. Another objective of the program was to develop a model which describes the adhesion between the fired silver film and the silicon surface.

3. EXPERIMENTAL PROCEDURES

3.1 Identification and Synthesis of Metallo-Organic Compounds

3.1.1 General

Metallo-organic compounds are a subclass of organometallic com-

pounds. The structure of organometallic compounds is such that a central metal atom is bonded directly to the carbon atom of the organic ligands. Metallo-organic compounds, on the other hand, are ones in which the metal atom is linked to the organic ligand through a hetero atom such as oxygen, sulfur, nitrogen, phosphorus or arsenic. Along with the halogens, these are the only atoms which can form a strong covalent bond with carbon. The halogens are not useful as hetero atoms however, since they are monovalent and therefore cannot form a complete bridge between the carbon chain and metal atom.

In order that the products of decomposition of the metallo-organic compounds contain only CO_2, and H_2O, the preferable hetero atom is oxygen. Of special importance to the current research effort were the metal salts of carboxylic acid (soaps), since the silver metallo-organic compounds most suitable for formulation of thick film inks, fell into this class. The general formula for these soaps is

$$(R - \overset{\overset{O}{\|}}{C} - O)_n M$$

where R is a hydrocarbon usually containing from 5 to 20 carbon atoms and M^{+n} is a central metal ion with valence +n. The R can be either a straight chain hydrocarbon such as an octanoate, or a secondary or tertiary "branched" hydrocarbon such as a 2-ethylhexanoate or neodecanoate. As the chain length of R increases, the solubility of the metallo-organic compound in hydrocarbon solvents increases, but the metal content decreases. Therefore, the choice of metallo-organic compounds from the soaps involves a tradeoff between solubility and metal content. Another important consideration is the degree of branching, since

solubility is also known to increase as the degree of branching of the carbon ligand increases. In many cases the decomposition temperature of a metallo-organic compound is also dependent on the nature of R. The basic criteria used in metallo-organic compound selection were:

A. The compound should have oxygen as its hetero atom linking the hydrocarbon ligand to the metal atom.

B. The compound must thermally decompose to the metal or metal oxide without melting or subliming.

C. The compound should thermally decompose below 400°C.

D. The compound should have as high a metal content as possible.

E. The compound must be soluble in common hydrocarbon.

F. The compound must be stable in air.

Once a compound was synthesized, it was characterized by thermogravimetric analysis (TGA). A DuPont thermobalance (model #951), in conjunction with a Barber Coleman programmable temperature and heating rate controller (model # UP-55-0) was used for TGA. In all cases the samples were subjected to a heating rate of 10°C/min in air at a flow rate of 70 cc/min, usually from room temperature to 500°C. This was done by placing a few milligrams of sample on an alumina pan, which was then suspended next to a thermocouple from the fused quartz beam of the TGA's balance. The sample was heated in a furnace at the programmed rate and both the sample weight and its rate of change were recorded on a chart recorder as percent changes as a function of temperature. (The TGA is

also capable of recording these changes as a function of time at constant temperature.)

By studying the TGA results, the weight percent inorganics in a MOC or a MOD ink was determined. Also, the smoothness and rate of decomposition was noted as well as the decomposition temperature, which is the temperature at which the last of the organics were removed. A typical TGA is shown in Figure 3.1.

3.1.2 Silver Compounds

Based on the criteria discussed in 3.1.1, five silver metallo-organic compounds (all carboxylates) were selected for evaluation so that the most suitable for use in a thick film MOD ink could be selected. These were silver neodecanoate, silver neopentanoate, silver 2-ethylhexanoate, silver-ethylbutyrate and silver monomethylsuccinate. Silver carboxylates were selected because they meet criteria A and C in 3.1.1. These five specific compounds were chosen from the carboxylates because they contain primary, secondary and tertiary ligands and had chain lengths varying from five to ten carbons. These are important considerations if criteria D and E in 3.1.1 are to be met.

All five of these silver compounds were synthesized following the same procedure. As an example, the synthesis of silver neodecanoate will be described. The synthesis was done by a two step process for which the reactions were:

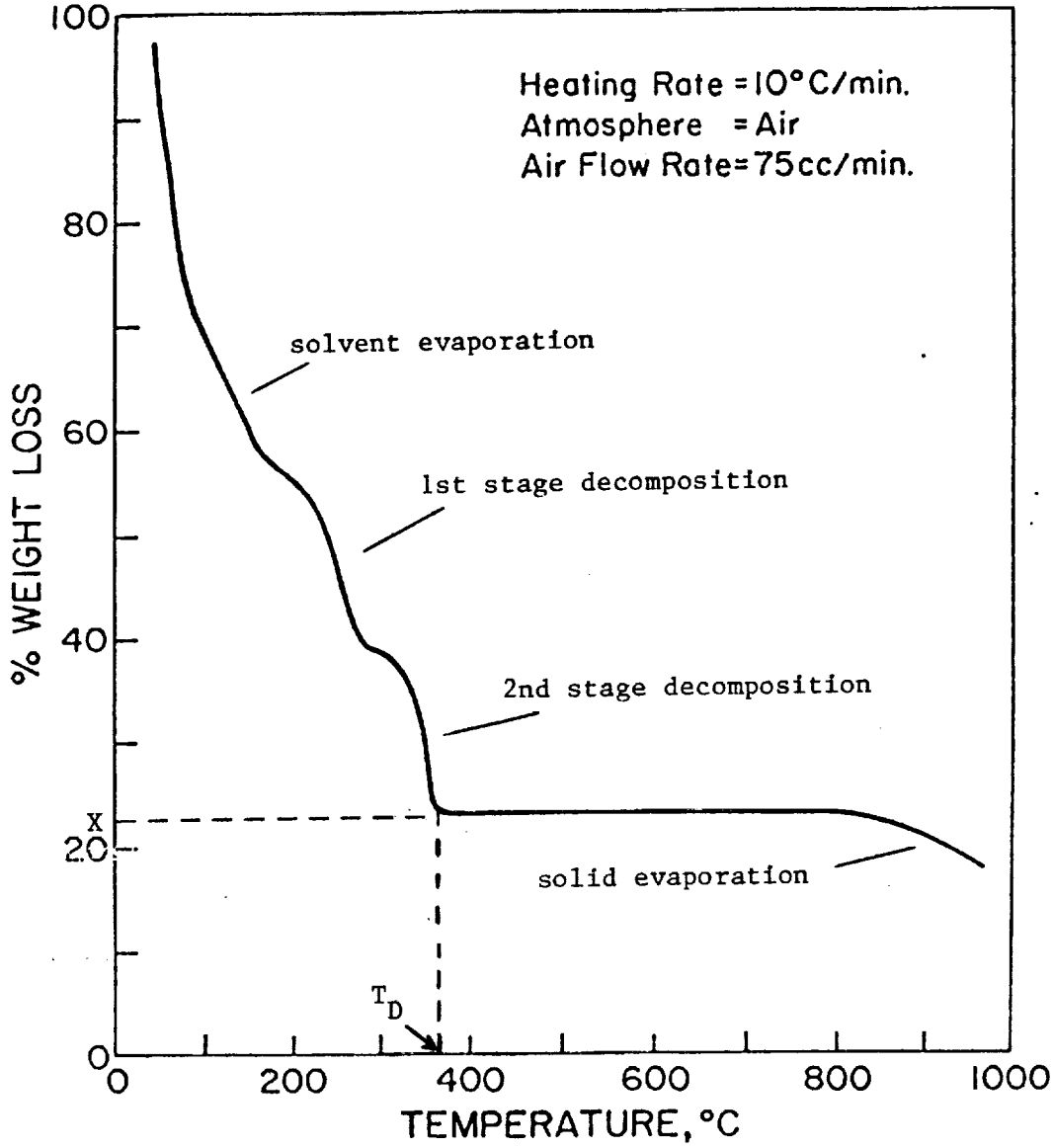
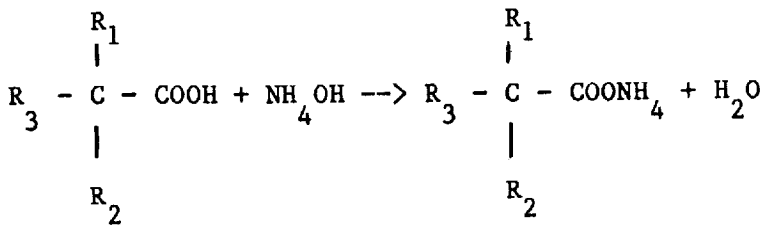
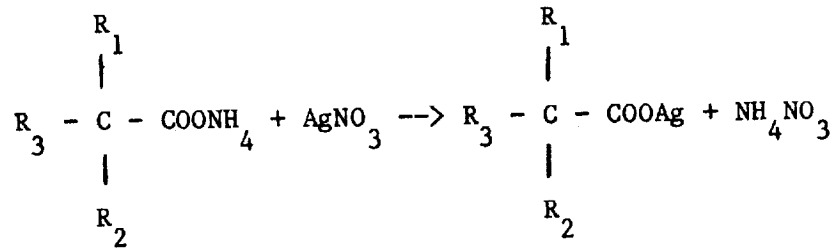


Figure 3.1 Typical thermogram from TGA evaluation where X = final wt. % inorganics in the compound or ink.



(1)

where $R_3 + R_2 + R_1 = C_8H_{19}$, and



(2)

In reaction (1), an equimolar mixture of 95% pure neodecanoic acid (103.2 g = 0.6 moles) and 58% ammonium hydroxide (36.26 g = 40.29 ml = 0.6 moles) was made with 200 ml of deionized water. The ammonium hydroxide was added slowly since an exothermic reaction took place. The resulting ammonium neodecanoate soap was stirred for 1 1/2 hours before reaction (2) was carried out by slowly adding an aqueous solution of silver nitrate(101.94 g = 0.6 moles) with constant stirring. (It is important that all glassware used has been rinsed thoroughly in deionized water, since the presence of any chlorine in the water will cause silver chloride to precipitate.) A semi-solid white precipitate was formed (impure silver neodecanoate) which was rinsed four times with cold deionized water and four times with warm (40-50^{o}C) deionized water. Enough methanol was then added with stirring (approximately 400 ml) until the silver neodecanoate had a "cottage cheese like" texture. The white solid and any remaining liquid was filtered through a buchner funnel and the solid was examined after one hour. If it had a yellow appearance, an additional 200 ml of methanol was added, followed by a

second filtering. The white powdery solid was placed in a flask under reduced pressure to remove any traces of methanol and then stored in dark bottles. The yield by this procedure was 70% of theoretical.

The only difference between this synthesis and that of the other four silver carboxylates was the acid used in reaction number (1). For instance, whereas neodecanoic acid was used to make silver neodecanoate, 2-ethylhexanoic acid would be used to make silver 2-ethylhexanoate, 2-ethylbutyric acid would be used to make silver 2-ethylbutyrate, etc. All five silver metallo-organic compounds were then evaluated to determine which one best met criteria B and D-F. This was done primarily by checking their respective solubilities in some common hydrocarbon solvents and by performing thermogravimetric analysis. The latter determined silver content, decomposition temperature and whether or not the compound decomposed smoothly and cleanly without evaporation.

3.1.3 Platinum Compounds

As is often required in conventional silver conductor inks, platinum may be added to the MOD silver conductor inks, in the form of a metallo-organic compound, should the fired silver films not possess good solder leach resistance without it. In the event that a platinum compound was needed, several were synthesized and evaluated for potential use. The selection of an appropriate platinum compound depended on the list of criteria for selecting metallo-organic compounds given in Section 3.1.1. Five platinum compounds were synthesized, which would hopefully decompose smoothly in the required temperature range without producing any toxic vapors or leaving behind a carbon residue. These were

platinum (II) 2-ethylhexanoate, platinum (IV) amine 2-ethylhexanoate, diglycine platinum (II), platinum (II) 2,4-pentanedionate, and bis-dimethylglyoxime platinum (II). With the exception of the last two, all have a carboxylate unit in their structure. Platinum (II) 2,4-pentanedionate is a β-diketone complex and the bis-dimethylglyoxime platinum (II) is a nitrogen compound. Unlike the silver compounds, the synthesis of these five platinum compounds varied, so each will be briefly described.

For platinum (IV) amine 2-ethylhexanoate, the two ingredients used, namely tetrachloro-platinum diaminopropane (a) and ammonium 2-ethylhexanoate (b), were prepared by the following reactions.

$$\underset{\text{(a)}}{H_2PtCl_6 \cdot 6H_2O + 4C_3H_{10}N_2 \rightarrow Pt(C_3H_{10}N_2)_2Cl_4} +$$

$$2C_3H_{10}N_2 \cdot HCl + 6H_2O \qquad (3)$$

$$\underset{\text{(b)}}{C_7H_{15}COOH + NH_4OH \rightarrow C_7H_{15}COONH_4} + H_2O \qquad (4)$$

For reaction (3), chloroplatinic acid hexahydrate (1.54 g = 2.9 mmoles) (37% Pt) was dissolved in absolute methanol (8 ml) and cooled in an ice bath. To this solution, 1,2-diaminopropane (1.28 g = 17.4 mmoles) was added dropwise with stirring. The reaction was exothermic, and a yellow precipitate separated immediately. The solution was further stirred for 0.5 hr, suction filtered and the precipitate was washed with methanol (5 ml) and dissolved in 10 ml water. For reaction (4), 2-ethylhexanoic

acid (2.7 g = 19 mmoles), 5 ml water and ammonium hydroxide (1.25 g = 20 mmoles) were mixed to form the desired product.

The products (a and b only) of reactions (3) and (4) were then combined by the following reaction to produce the platinum (IV) amine 2-ethylhexanoate.

$$Pt(C_3H_{10}N_2)_2Cl_4 + 4C_7H_{15}COONH_4 \rightarrow Pt(C_3H_{10}N_2)_2(C_7H_{15}COO)_4 + 4NH_4Cl \quad (5)$$

This was done by adding the tetrachloro-platinum-diaminopropane dropwise to the ammonium salt of 2-ethylhexanoic acid. A cloudy precipitate formed and coagulated immediately into a yellow oil which settled to the bottom. After 2 hours stirring and 4 hours settling time, the clear supernatent liquid was decanted off. The remaining residue was washed 3 times with water, extracted in xylene, and dried over molecular sieves. Evaporation of most of the xylene left a viscous, yellow, oily residue of platinum amine 2-ethylhexanoate.

For diglycine platinum (II) the synthesis reaction was:

$$K_2PtCl_4 + 4C_2H_5O_2N \rightarrow 2KCl + Pt(C_2H_4O_2N)_2 + 2C_2H_5O_2N \cdot HCl. \quad (6)$$

This reaction was carried out by warming a mixture of potassium tetrachloroplatinate (II) (0.8862 g = 0.0021 moles) and aqueous glycine (0.8862 g = 0.0021 moles in 1 ml water) over a water bath for approximately one hour. Colorless crystals of diglycine platinum (II) separated from the hot solution and upon cooling an additional crop separated. These crystals were then recrystallized for purification by dissolving them in room temperature water and collecting them when they

separated from the solution after heating and cooling back to room temperature.

For platinum (II) 2,4-pentanedionate the synthesis reaction was:

$$K_2PtCl_4 + 2C_5H_8O_2 + 2KOH \rightarrow Pt(C_5H_7O_2)_2 + 4KCl + 2H_2O. \qquad (7)$$

This reaction was carried out by dissolving potassium tetrachloroplatinate (II) (1.377 g = 0.0033 moles) in 8 ml hot water and stirring in potassium hydroxide (0.600 g = 0.010 moles) dissolved in 2 ml water. This solution was warmed slightly until it became yellow at which time acetylacetone (1.2 ml = 0.0115 moles) was added. The mixture was heated to $50^{o}C$ with frequent shaking which caused a pale yellow precipitate of platinum 2,4-pentanedionate to gradually form at an increasing rate. Precipitation was completed by holding the temperature at $50^{o}C$ for 1 to 1.5 hours. The mixture was cooled and the crystalline precipitate filtered off. To the remaining liquid a solution of potassium hydroxide (0.2 g in 1 ml water) and acetylacetone (0.6 ml) was added. After heating for one hour this solution produced a second batch of precipitate which was filtered out and combined with the initial batch. These platinum 2,4-pentanedionate crystals were then washed with water and dried in a dessicator.

The synthesis reaction for bis-dimethylglyoxime platinum was:

$$K_2PtCl_4 + C_4H_8N_2O_2 \rightarrow 2KCl + Pt(C_4H_7N_2O_2)_2 + 2HCl. \qquad (8)$$

This compound was prepared by mixing an aqueous solution of potassium tetrachloroplatinate (0.5466 g = 0.0013 moles dissolved in 3 ml water)

with a solution of dimethylglyoxime (0.3 g = 0.0026 moles dissolved in 60 ml of 50% ethanol). The resulting reddish orange homogeneous solution was stirred at room temperature for 30 minutes, but no visible reaction took place. The solution was then refluxed at 78 °C for 2 hours which caused a dark grey/blue precipitate to separate. This bis-dimethylglyoxime platinum (II) solid was suction filtered off, washed with water and 50% alcohol, and dried.

The final platinum metallo-organic compound synthesized was platinum (II) 2-ethylhexanoate which was prepared by carrying out the following two reactions simultaneously:

$$C_7H_{15}COOH + (C_2H_5)_3N \xrightarrow[R.T.]{H_2O} (C_7H_{15}COO(C_2H_5)_3NH \qquad (9)$$

$$K_2PtCl_4 + 2C_7H_{15}COO(C_2H_5)_3NH \xrightarrow[50^oC]{H_2O} Pt(C_7H_{15}COO)_2 + 2KCl + 2(C_2H_5)_3NHCl \qquad (10)$$

This was done by slowly stirring a solution of potassium tetrachloroplatinate (5.0 g = 0.021 moles dissolved in 100 ml water) into an equimolar mixture of 2-ethylhexanoic acid (10.38 g = 0.072 moles) and triethylamine (7.28 g = 0.072 moles dissolved in 50 ml water). The resulting homogeneous, honey colored solution was stirred at room temperature for one hour and then heated to 50°C in a water bath and stirred at this temperature for 2 to 3 hours. When a black oil separated, it was removed (leaving behind a clear aqueous solution), washed with cold water and then warm water(50-60°C). The washings were repeated until no silver chloride precipitate formed when silver nitrate was added to a

small amount of the wash water (this insured that no chlorine was present in the compound). The black oil was then extracted in ~ 40 ml benzene and dried over molecular sieves.

All five platinum metallo-organic compounds were then evaluated, after the silver compound was selected, to determine which one would be most compatible with it.

3.1.4 Compounds for Use as Adhesion Promoters

In addition to selecting an appropriate platinum metallo-organic compound, various metallo-organic compounds were prepared which could potentially increase the fired film to silicon solar cell adhesion, if necessary. Of the three classes of thick film bonders, reactive bonders were eliminated since they are used only for alumina substrates, and frit bonders could not be used since a glass can not be formed at the firing temperatures used in this research ($< 400^{o}C$). For these reasons, eight metallo-organic compounds, which would decompose to compounds often used as flux bonders in conventional or other MOD thick film ink systems, were evaluated. It was hoped that these compounds would act in the same role in fired silver MOD films. These compounds were boron-bis-n-propoxy-2-ethylbutyrate, boron-n-propoxy diacetate, ethoxy-silicon-tri 2-ethylhexanoate, bismuth 2-ethylhexanoate, chromium 2-ethylhexanoate, chromium (III) 2,4-pentanedionate, nickel 2-ethylhexanoate and cobalt 2-ethylhexanoate. All eight compounds formed the corresponding metal oxides on decomposition.

The synthesis for the two boron and one silicon metallo-organic

compounds was performed in-house for a research project dealing with thick film resistors formed from metallo-organic precursors. The special apparatus designed specifically for these syntheses and the synthesis procedures are described in the final report from that research*. The last 3 compounds were purchased; the chromium 2,4 pentanedionate from Alfa Products, and the nickel and cobalt 2-ethylhexanoates from Pfaltz and Bauer, Inc. Synthesis procedures for the remaining two compounds are described below.

The synthesis reactions for bismuth 2-ethylhexanoate were:

$$C_7H_{15}COOH + NH_4OH \rightarrow C_7H_{15}COONH_4 + H_2O \qquad (11)$$

and

$$Bi(NO_3)_3 \cdot 5H_2O + 3C_7H_{15}COONH_4 \rightarrow Bi(C_7H_{15}COO)_3 + 3NH_4NO_3 + 5H_2O \qquad (12)$$

For reaction (11), ammonium 2-ethylhexanoate soap was prepared by mixing 2-ethylhexanoic acid (26.73 g = 0.1854 moles), 58% ammonium hydroxide (15.27 g = 0.2530 moles) and 75 ml of water. To this soap, a clear solution of bismuth nitrate (15 g = 0.0309 moles) dissolved in 10% nitric acid (30 ml contains 4.26 g HNO_3 = 0.0676 moles) was slowly added to affect reaction (12). At the end of the addition a white oil of bismuth 2-ethylhexanoate separated and stirring was continued for 30 minutes. The oil was then extracted in 40 ml of benzene and dried over

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* R.W. Vest and G.M. Vest, "Metallo-organic Materials for Improved Thick Film Reliability", Final Report on NAC Contract No. N00163-83-C-0167, 4 April 1985.

molecular sieves to remove any moisture.

The synthesis reaction for chromium 2-ethylhexanoate was:

$$Cr(CH_3COO)_3.H_2O + 3C_7H_{15}COOH \rightarrow$$
$$Cr(C_7H_{15}COO)_3 + 3CH_3COOH + 3H_2O \qquad (13)$$

A mixture of chromic acetate, 2-ethylhexanoic acid and ethanol (40 ml) was taken in a large porcelain evaporating dish and kept on a steam bath stirring for ~2 hours. The chromic acetate slowly started to dissolve and the alcohol and byproduct acetic acid evaporated leaving behind some unreacted chromic acetate. More ethanol (40 ml) was added and the process was continued for another ~2 hours. At the end there was no solid chromic acetate left and chromic 2-ethylhexanoate was obtained as a heavy green syrupy liquid, which was taken up in benzene (~30 ml). The yield was quantitative.

3.2 Ink Formulation

Having synthesized or purchased all of the necessary ingredients for a silver MOD thick film ink, they were mixed in many combinations and processed into formulations suitable for screen printing. This was done by following the generic procedure illustrated in Figure 3.2. Usually this resulted in a homogeneous, low viscosity solution after the formulation step in the diagram. Provided this was the case, the solution was processed into a thick film ink using a Brinkman rotavapor

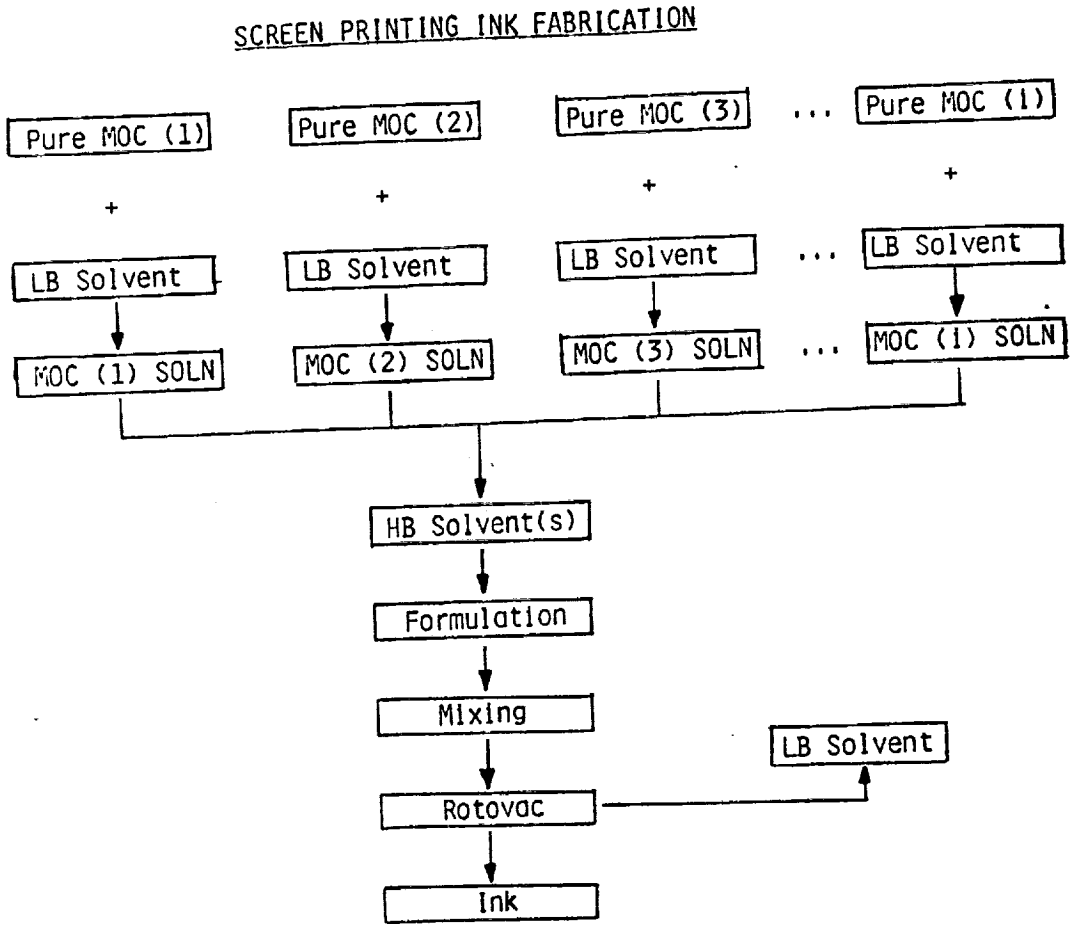


Figure 3.2 Generic fabrication procedure for MOD thick film inks where

MOD = Metallo-organic compound
LB Solvent = Low boiling point (high vapor pressure) solvent
HB Solvent = High boiling point solvent (rheology adjustors)

(model #R-110). The rotavapor essentially performs a solvent exchange operation in which the high vapor pressure solvents are removed in favor of the higher boiling point(lower vapor pressure) rheology adjusters. This was done by connecting a flask containing the homogeneous ink solution to a condenser through a drive unit which continuously rotated the flask. A vacuum was applied by a water pump exerting approximately 12-14 mm of mercury pressure and the flask was placed in a warm water bath of 30-60^{o}C, with the temperature used dependent on the boiling point of the solvent to be removed. A receiving flask was connected to the condenser to collect the condensed solvent after it was removed as a vapor from the solution. The majority of the solvent in ~25 ml of ink solution was removed by this process within 30 minutes. Provided the proper selection of types and amounts of rheology adjusters was made, the product was usually an ink suitable for screen printing.

The amounts of the various ingredients used in an ink were dependent, by convention, on the silver compound used since the silver compound made up the bulk of any given ink. Once the amount of ink needed was determined (depending on the number of substrates to be printed), the amount of silver compound needed was calculated based on the convention that all inks should be 30% silver by weight. From thermogravimetric analysis, the percent silver in a given silver metallo-organic compound was determined, so the amount of compound needed to produce an ink of 30 w/o silver could be calculated. All other ingredient amounts were calculated based on the amount of silver compound used. Any additional active ingredient amounts (such as platinum or binder compounds) were determined based on the desired ratio of inorganic constituents in

the fired films. For instance, if a fired film of metallic composition 91 wt.% Ag, 4 wt.% Pt and 5 wt.% Bi was desired, the amounts of platinum and bismuth compounds were calculated based on the amount of platinum or bismuth they contained (determined by thermogravimetric analysis) and the respective desired ratios of the platinum or bismuth content to the silver content in the fired film. Similarly, the appropriate amounts of rheology adjusters and solvents for an ink were determined by trial and error as a percent of the silver compound used in the ink. Once the amounts of the various constituents were determined, the procedure shown in Figure 3.2 was followed.

3.3 Substrates

The substrates used were silicon solar cells supplied by Jet Propulsion Laboratory, although some AlSiMag 838 substrates (99.5% alumina) were used during ink constituent evaluation. The solar cells were 2 cm square, approximately 300 μm thick with a shallow p-n junction depth (varied between cell batches) of roughly 0.25 μm. Their top surface texture was changed at one point during this study from a rougher alkali etched to a smoother acid etched surface (in no cases was the surface polished smooth). The surface roughness, although never measured, was clearly significant based on visual and microscopic examination. The cells had already received back side metallization prior to their arrival at Purdue, and each lot was assigned a batch number, which is important for identifying how the cells were made and for photovoltaic evaluation which requires a standardized cell (kept at JPL) from the same batch.

Initially the solar cells were printed as received, but JPL requested that they be cleaned to remove the native SiO_2 from the surface prior to printing. The cleaning process suggested by JPL was as follows

1. Dip the cell in a 10:1 dilution of deionized water and hydrofluoric acid for 10 seconds.

2. Thoroughly rinse the cell with deionized water

3. Blow dry the cell with inert gas

This process was referred to as the HF cleaning procedure. Prior to printing, all solar cells were further dried for at least 30 minutes at $65^{o}C$ to remove any remaining moisture. The removal of the oxide allows for better contact between the solar cell and soon-to-be deposited metal film.

For some experiments, the solar cells were cleaned with methanol followed by rinsing with deionized water and drying prior to printing. Although methanol will not remove any SiO_2 from the solar cell surface, it does remove dust and other contaminants.

3.4 Screen Printing

The screen printing machine used to deposit the MOD inks on the substrate in a desired pattern was a modified version of the Aremco 3100. All motions were controlled by air actuated hydraulic cylinders, and the overall mechanical construction was adequately rigid and repeatable. The machine was adjustable with squeegee speeds of 2.5-25 cm/s,

squeegee overtravel of 0-2.5 mm and screen-to-substrate spacing of 0 (contact printing) to 2.5 mm. The machine was operated at a constant pressure of 655 kPa maintained by a two stage regulator. The substrate was rigidly supported in place using a vacuum stage which had a slightly indented region in which the substrate was indexed. The machine was equipped with two microswitches for safely and automatically initiating the printing cycle.

The squeegee shape used was rectangular, except for the bottom side which had a 60^{o} trailing, sharp printing edge. The polyurethane blade was held between two parallel plates with rigid spacers that limited compression of the blade. The mechanism that held the squeegee assembly in the machine allowed limited rotation along the vertical axis so that the printing edge was always free to align flush with the screen surface.

The screen printing process can be easily modified to find the best parameters for printing a given ink, and the machine in the Turner Laboratory had been rigorously tested to find a set of parameters which generally allow good printing of most conventional inks. However, this machine had not been similarly tested for MOD inks which print quite differently. Such a calibration became even more difficult while ink development was being carried out since variations in viscosity are a major source of printing process variation. Nonetheless, a set of boundary conditions for the printer were used in order to keep the process as constant as possible. These are presented in Table 3.1. Note that two of the important variables, squeegee overtravel (which is proportional to the amount of downward pressure exerted by the squeegee) and

Table 3.1 Boundary Conditions for AREMCO 3100 for Silver MOD Screen Printing

Screen*	Squeegee
Material - ASTM 304 stainless steel	Material - polyurethane
Mesh - 325	Hardness - 70 durometer
Wire diameter - 25μm min./30μm max.	Angle of attach - 60^{o}
Size - 17 cm X 20 cm I.D.	Print direction - foward
Weave - plain	Squeegee speed - 14 cm/sec.
Emulsion type - MS-1(general purpose)	Squeegee overtravel - varies
Emulsion thickness - 0	Screen to substrate distance - varies < 0.50 mm max.

*Screens manufactured by Micro-screen precision products, South Bend, IN 46618

screen-to-substrate distance were not held constant, but were varied so that the prints obtained on the substrates were as complete and dense as possible for each ink printed.

Two screen patterns were used for printing films during this project. The first one is one of the Turner Laboratory standard conductor patterns which is illustrated in Figure 3.3. This was employed early in the research when ink constituent evaluation was extensively carried out by printing and firing inks on alumina substrates. The pattern has a 103 square serpentine conductor, three different sizes of adhesion test pads and a series of conductor lines for quantitative line definition measurements. Once research commenced on actual solar cell metallization, the pattern used was one supplied by Jet Propulsion Laboratory. It was a standard test pattern for solar cell front contact metallization which is illustrated in Figure 3.4. It has 230.4 squares in the conductor area connecting points A, B, C and D in the Figure.

3.5 Drying and Firing

Once printed, all wet films underwent some type of heat treatment to produce the final conductor. The heat treatment used during metallization of solar cells varied in both the type of furnaces used and the time/temperature profiles employed in the various furnaces. The basic requirements for selecting a heat treatment process were:

A. It must be capable of allowing for smooth decomposition in air of the printed films to dense, homogeneous silver conductors without cracking, the presence of any decomposition by-products, or oxida-

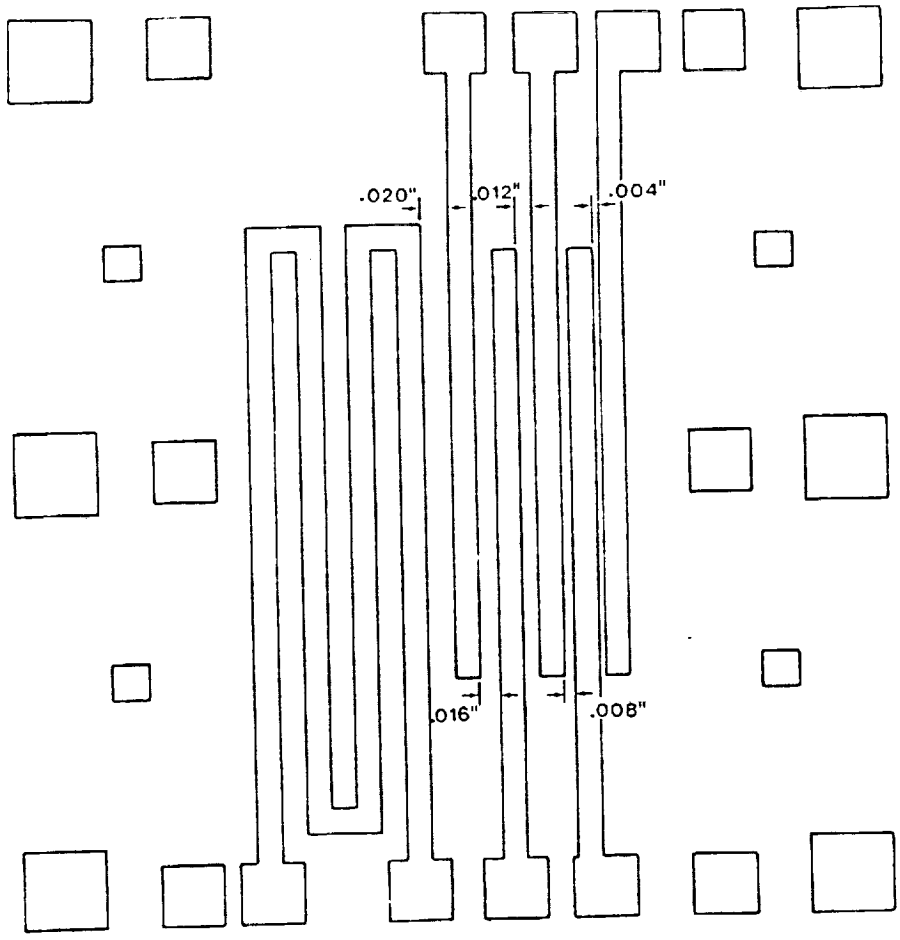


Figure 3.3 Turner Laboratory standard conductor screen printing test pattern.

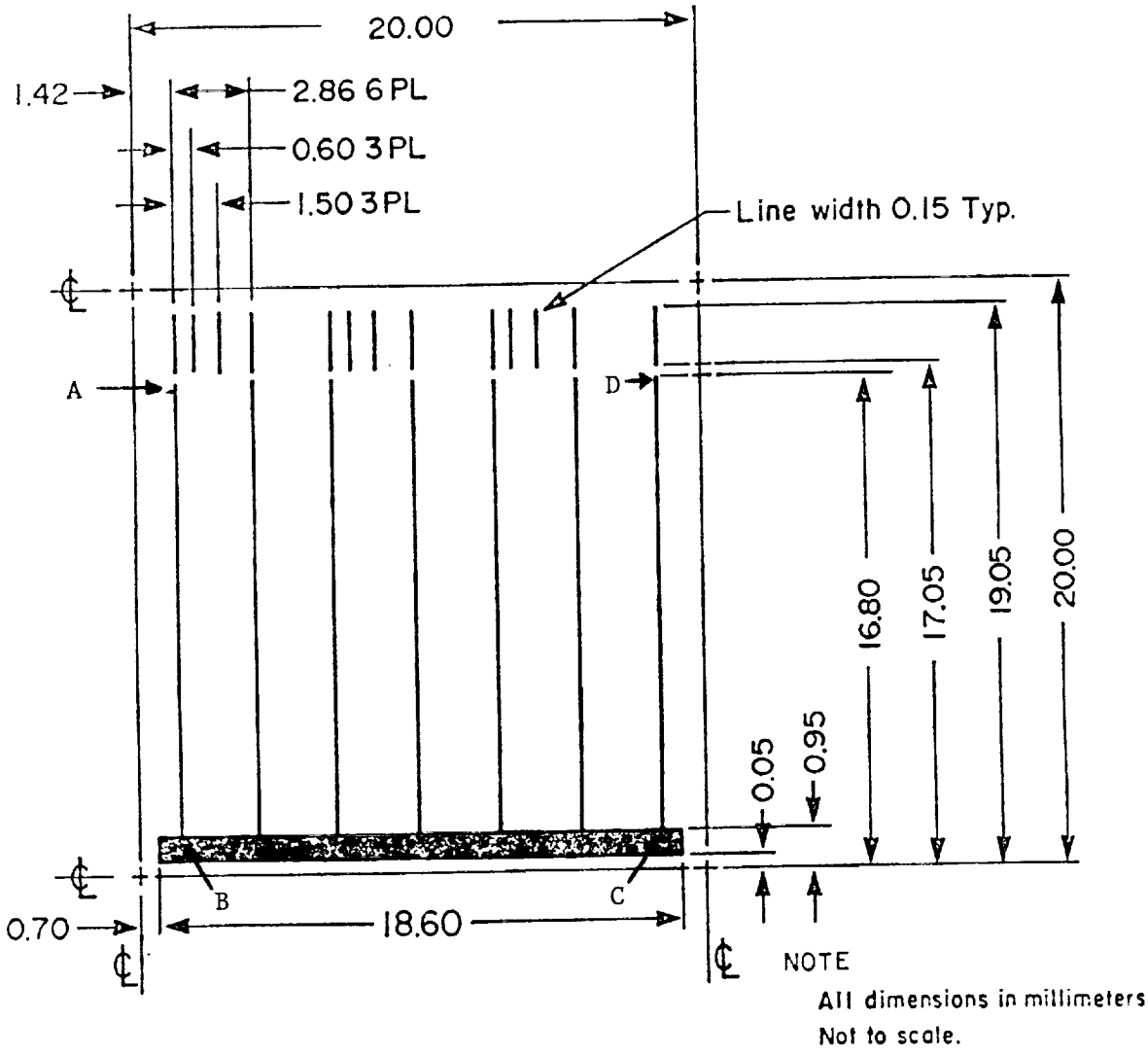


Figure 3.4 Blueprint representation of the front contact pattern used for screen printing solar cells as supplied by JPL.

tion of the silver.

B. It must not cause degradation of the solar cell performance.

C. It must be accurately reproducible.

D. It should be compatible to a production type setting.

The three types of firing investigated under these criteria were:

1. A series of muffle furnaces with the temperature successively increased from one furnace to the next.

2. A Turner Laboratory designed furnace with time-temperature programming and controlled air flow.

3. A thick film belt furnace with variable time-temperature profiles and natural convection.

In all cases, the firing was preceeded by drying in a gravity oven. In an attempt to meet requirement B above, the maximum firing temperature used was 350°C if the time of exposure was to be more than a few minutes. For firing temperatures higher than 350°C, thermal spiking, similar to that done to fire conventional silver contacts on solar cells, was used either alone or to compliment another heat treatment. Thermal spiking was done between 600-800°C for 30-90 seconds in an IR or batch muffle furnace at constant temperature.

3.6 Evaluation of Fired Films

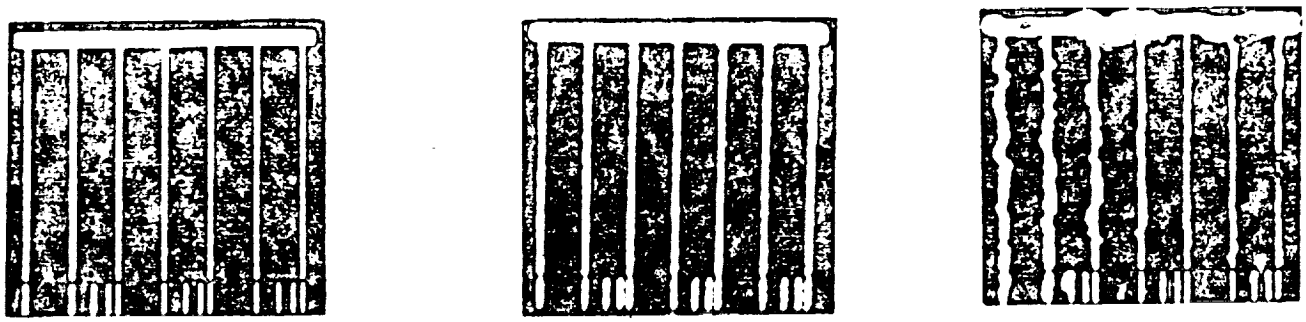
3.6.1 Film Appearance and Line Definition

Both of these metallization properties were evaluated qualitatively. The film appearance was judged primarily by color, although film homogeneity and smoothness were also observed. Table 3.2 lists some of the common film appearances with possible reasons for the appearance. There were some cases where the film appearance illustrated more than one of these conditions or where it exhibited other characteristics. For these cases, special mention of the probable cause will be made in later sections.

The line definition for the JPL metallization pattern was evaluated according to the rating system illustrated in Figure 3.5. The fired films shown in this figure are silver/platinum fired films produced from the same ink at the same time, but under different processing conditions. When a set of films showed varying line definitions (which may be the case if the ink viscosity changed during printing) a combination rating of A/B or B/C was given. Because of the wide spacing between the fingers (2860 μm) and between the closest segments (600 μm) quantitative measurements were not practical. When the test pattern shown in Figure 3.3 was used, quantitative line definitions were measured using the series of five isolated conductor lines and the leg of the serpentine conductor pattern closest to them. Note that the spacing between these lines increases in increments of 4 mils (≃100 μm) from 4-20 mils. When an electrical contact was made to opposite ends of adjacent lines and the contacts were connected to a resistance meter, either an infinite or some positive finite value of resistance was measured by the meter. A positive value meant the lines were connected at at least one point and

Table 3.2 Correlation of Various Film Appearances to Probably Causes

Appearance	Probable Cause
Dark black, brown or grey fired films	Incomplete decomposition resulted in the presence of residual carbon or other by-products of decomposition.
Spotty, multi-color films	Poor, inhomogeneous ink. Possible incomplete decomposition.
Yellowish (pure silver films)	Impure silver neodecanoate used to formulate ink.
Silver (appears white on silicon)	No problem with such films. Desired decomposition took place.
Unexpected (different from normal for a given ink)	Potential shelf-life problem with ink or one or more of its constituents.
Cracked	Too rapid or multi-stage decomposition took place disrupting previously formed film.



(a) (b) (c)

Figure 3.5 Line definition rating system used for JPL solar cell front grid pattern

(a) excellent
(b) acceptable
(c) unacceptable

therefore the line definition was worse than that particular spacing. In this manner, the line definition was determined as <4, 4, 8, 12, 16, 20 or > 20 mils. The distance between the end of the fingers and the small (2000 μm length) segments in the JPL pattern was only 250 μm (~ 10 mils), but since this distance did not vary in the pattern, the line definition could be stated as only greater than or less than 10 mils when a similar quantitative approach was used. For these reasons, a qualitative determination of line definition was used almost exclusively throughout this study.

3.6.2 Sheet Resistance

Whether sheet resistance or resistivity was used as an evaluation of the metallization's electrical properties, the first measurement needed was the series resistance in the fired contact. This was measured by placing probes at opposite ends of either the serpentine conductor on the Turner standard conductor pattern (Figure 3.3) or at the ends of the outside fingers on the JPL collector grid pattern (Figure 3.4). The probes were connected to a Keithly digital multimeter which automatically gave a measure of the resistance between the probes, provided a good contact was made to the conductor line. The sheet resistance (in ohms/square) was calculated by

$$R_s = R/n \tag{14}$$

where n (the number of squares) was 103 for the serpentine pattern in Figure 3.3 and 230.4 for the JPL pattern in Figure 3.4 between the ends of the outside fingers. If a resistivity value was desired, a fired

film thickness (t) was calculated by measuring the cross sectional area of the film and dividing by the design line width at the point in the pattern. This method eliminated errors due to bleed-out. The resistivity was then calculated by

$$\rho = R_s t \tag{15}$$

Caution had to be used in placing the probes on either circuit, since the resistance value varied with probe location. Since the number of squares was held constant, care was taken to always place the probes on the same spot on the circuit, although there was considerable operator judgement required for this. Any films with breaks received special consideration since breaks cause an open-circuit. In these cases the probes were placed at different locations and an appropriate adjustment was made in the value of n for R_s calculations. Finally, standard deviations (σ's) were calculated for groups of solar cells which were metallized under the same conditions, so that statistically valid comparisons could be made.

3.6.3 Solderability

Solder acceptance and leach resistance were evaluated using a laboratory size melting (solder) pot with 62 w/o Sn-36 w/o Pb-2 w/o Ag solder at $230^{o}C \pm 10^{o}C$. The films were dipped in the solder for either 5 or 10 seconds and a qualitative judgement was made of both percent solder acceptance and percent of film which resisted leaching. This test was a modified version of a DuPont test developed for conventional

silver/platinum thick film conductors.

Usually, a fluxing step was required prior to dipping in the solder. The flux removes any naturally formed protective layer, such as an oxide or sulphide, from the film which would prevent both solder acceptance and film leaching. A fluxing step was not always used with the MOD films until a suitably mild flux was found which could be used without causing total, instantaneous film dissolution upon dipping in the solder. A 15:1 dilution of Alpha 611 flux in methanol was found to be suitable as a fluxing agent for some MOD films. The final requirement for the test was the use of 2-layer or greater films as single layer films were too thin (< .5 μm) to use for accurate testing.

3.6.4 Adhesion

All adhesion testing was done by the Scotch tape test, which is a qualitative threshold test. This test was performed by pressing a piece of fresh cellophane tape onto a not previously tested film. (3M's Scotch brand 810 magic transparent tape was used). Care was taken to insure no air bubbles were trapped underneath the tape and to smooth the tape out without fracturing the brittle solar cells. The tape was then pulled up briskly, but uniformly.

This applied a force of 6 ± 0.5 lbs per inch of width*. The percentage of film remaining intact after the test was qualitatively judged and the

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* L. Jacobson, Proc. IEEE Electronic Components Conference, 1971, pp. 474-479.

adhesion was reported according to the following rating system.

Percent film adhering	Adhesion rating
95-100%	excellent
75-95%	good
50-75%	fair
0-50%	poor

Generally, this test was useful for rejecting poorly adherent films, and an excellent rating on the Scotch tape test was considered to be a minimum specification for metallized contacts on solar cells. Other tests to determine quantitative adhesion strengths were not performed.

For long term adhesion studies, a set of metallized solar cells, which were fabricated at the same time and had excellent initial adhesion, were stored either in the laboratory environment or in a dessicator to protect them from any environmental effects. Either one or two films were removed at pre-determined intervals and Scotch tape tests performed. The length of time between tests (in days) gradually increased during the duration of the test as long as the adhesion remained excellent. The long term adhesion was reported as the number of days the adhesion remained excellent.

3.6.5 Film Thickness

Film thicknesses were measured using either a light section microscope or a moving stylus profilometer. The light section microscope offers the following advantages over most alternative methods of film thickness measurement:

1. It is nondestructive;
2. It is a simple and rapid method of measurement; and
3. Since there is no direct contact between the instrument and film, wet film thickness measurements could be made.

The principle used by the light section microscope is simple, planar beam light reflection. A powerful fiber optic light source was used to reduce absorption, transmission and scattering of the incident light, which would otherwise restrict the equipment's usefulness. When a sample was placed in the microscope and illuminated by the light source, the reflected light was non-planar and an image was formed which corresponded to the cross section of the contoured surface being measured. Since the films measured were opaque, no correction factor was needed and the fired film thickness value (in μm to the nearest 0.25 μm) was read directly by measuring the contour differences in the reflected image using an internal measuring system.

The thicknesses which could be measured in the light section microscope were limited by the requirement of obtaining the image in the

field of view. This eliminated measurement of very thick films (~ > 200 μm) and very thin films (<1 μm). The profilometer was used for the very thin films, and had the added advantage of giving a calculated cross sectional area of the film. Measurements were always made at more than one point on the films due to variations in film thickness resulting from the screen printing process and roughness of the solar cell surface. For the JPL metallization pattern, separate average measurements were made for the fingers and the bus bar. Figure 3.6 shows the 10 standard points chosen for film thickness measurements on the metallized solar cell collector grid. Points A-C were averaged for the bus bar dried film thickness and points D-J were averaged for the finger dried film thickness.

3.6.6 Film and Interface Microstructure Evaluation

Microstructure evaluation was done on the fired solar cell contacts using a scanning electron microscope and an EDAX energy dispersive spectrometer to evaluate the density and homogeneity of the contacts up to 20,000 magnification and to roughly correlate actual and expected fired contact chemistries. The metallized solar cells were mounted directly on aluminum cylinders using wax which formed a solid, but non-permanent bond, so the cell remained stationary when tilted during evaluation. When the silicon solar cell or interface between the contact and solar cell was examined, a thin layer (~100 angstroms) of aluminum was applied by vacuum evaporation prior to observation, so that the sample would not charge.

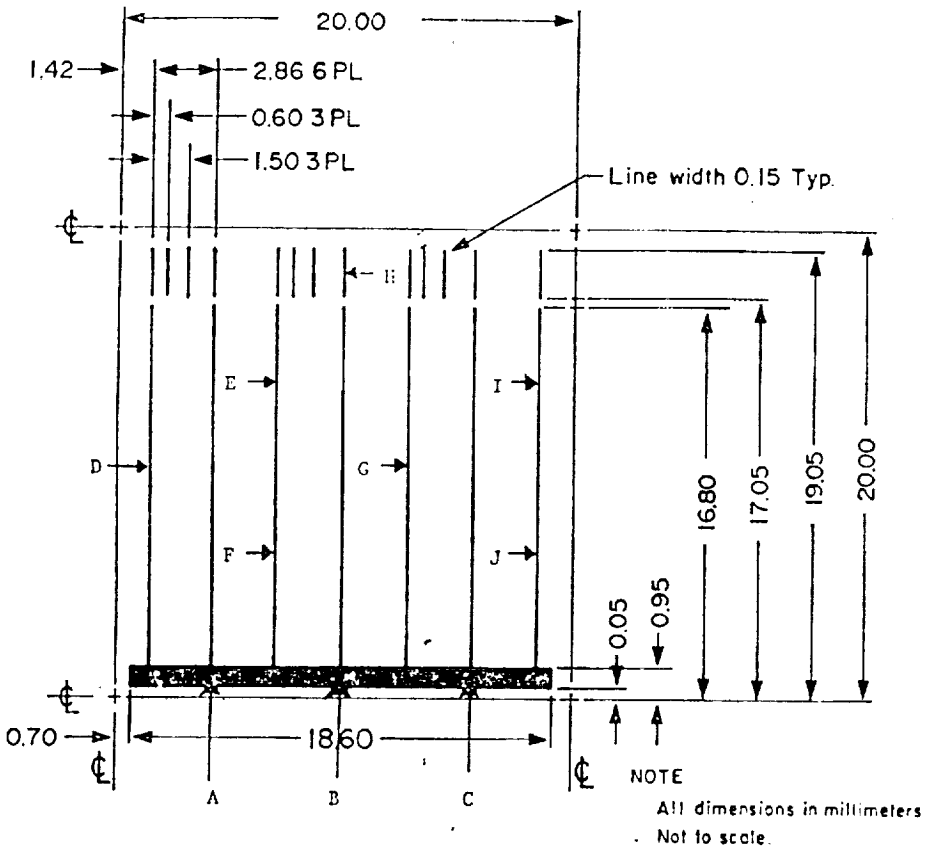


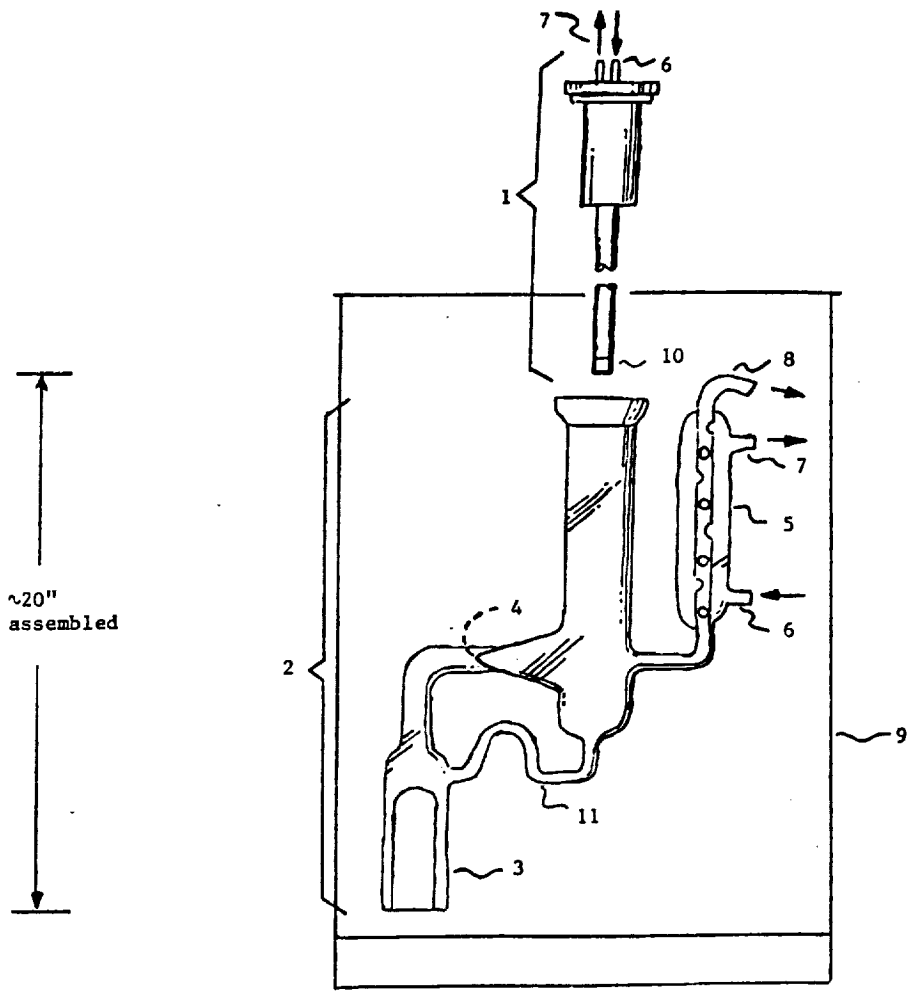
Figure 3.6 JPL screen pattern showing the ten points at which film thickness measurements are made.

In order to aid in the determination of the adhesion mechanisms responsible for adhesion of the silver contacts to the silicon solar cells, it was necessary to examine the interface between the two. This was done by selectively removing the fired contact by mercury vapor leaching and examining the interface using the SEM. The mercury vapor leaching setup is illustrated in Figure 3.7. Liquid mercury was placed in the boiler and heated to produce mercury vapor which passed through the jet aimed at the fired film on the solar cell mounted on a water cooled sample holder. The mercury vapor condensed on the sample and formed an amalgam with the film, provided the mercury/film eutectic temperature was lower than the boiling point of mercury (as were the silver/mercury and platinum/mercury eutectic temperatures). The amalgam was collected and recycled in a bath below the sample holder and a condenser prevented any mercury vapor from escaping.

The film was slowly removed in a manner similar to the way a mild acid attacks a metal. The process of single layer silver MOD film removal took approximately one hour. After cooling, the samples were removed, so that the interface could be examined. The mercury vapor leaching process is selective, as it only attacks the metal film and not any atomic species or oxides which have diffused into the silicon surface or any oxides present at the interface.

3.6.7 Photovoltaic Response

The most important property of the metallized contacts is how well they transfer current from the solar cell to the "outside" world. This is best evaluated by studying the photovoltaic response of solar cells



1. Specimen Holder (Stainless Steel)
2. Main Glass Body
3. Boiler
4. Mercury Vapor Jet
5. Glass Condenser
6. Cold Water Inlets
7. Drain Outlets
8. Vacuum Line Connection
9. Mounting Board
10. Sample Mounting Area (One Each Front and Back)
11. Siphon

Figure 3.7 Schematic representation of the experimental apparatus used for mercury vapor leaching.

metallized by the MOD process and comparing this response to that of solar cells metallized by other methods.

All quantitative photovoltaic evaluations were carried out at Jet Propulsion Laboratory for solar cells metallized during this study, but qualitative measurements for comparison purposes were conducted in-house. The solar cell to be evaluated was illuminated with a light source of constant but unknown intensity, and an alternating current was applied to the solar cell through connections to its front and back contacts. A current-voltage (IV) curve was then monitored for the solar cell using a curve tracer oscilloscope. This curve shows the voltage output of the solar cell resulting from the alternating current. Typical IV curves for a practical and ideal solar cell are shown in Figure 3.8.

Four important points on the IV curve are used to evaluate the solar cell performance. These are the short-circuit current (I_{sc}), the open-circuit voltage (V_{oc}), the maximum power current (I_{mp}) and the maximum power voltage (V_{mp}). All four points are shown in Figure 3.8. (Note that $I_{sc} = I_{mp}$ and $V_{oc} = V_{mp}$ for an ideal solar cell.) The short circuit current is that which flows through a wire connected directly between the front and back contacts of the cell. The open circuit voltage results when there is no external circuit and the number of current carriers being generated equals the number being annihilated by recombination. The two maximum power points (V_{mp} and I_{mp}) are those corresponding to the maximum solar cell power output which occurs when the resistance of the external circuit equals the internal resistance of the solar cell. Since an alternating current is applied to the solar

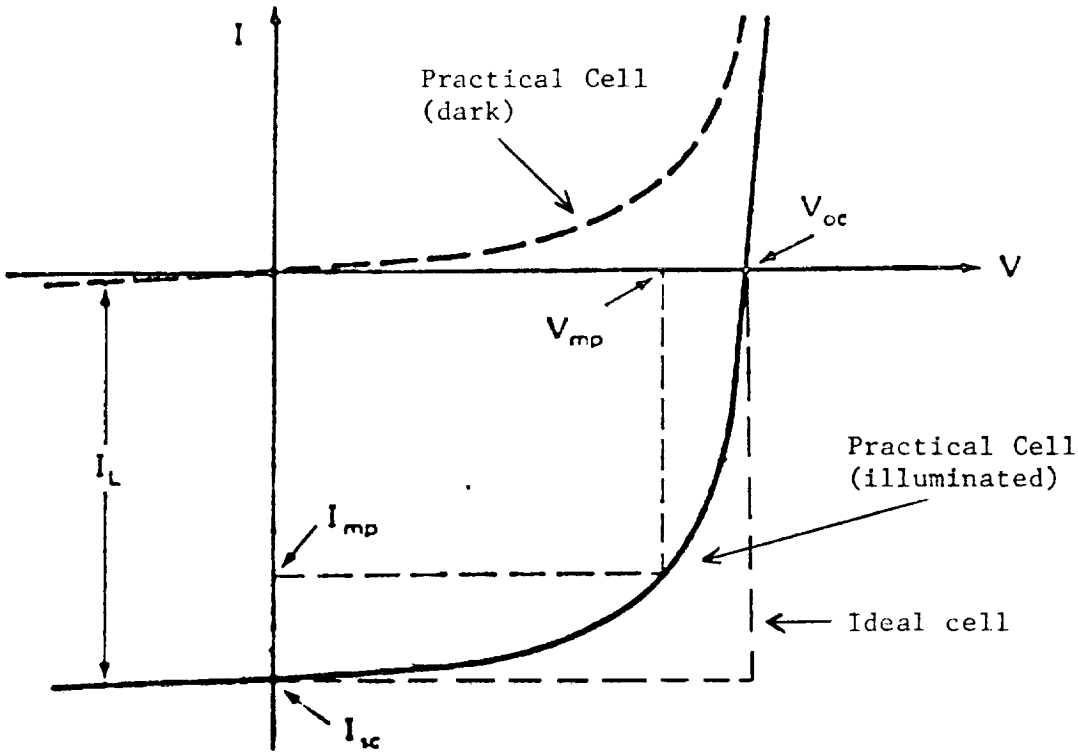


Figure 3.8 IV curves for a practical solar cell illuminated and in the dark as well as that for an "ideal" cell.

cell during evaluation, the IV curve is being continually retraced, so that at various instantaneous points in time all four of these critical parameters are repeatedly generated and can be read directly from the IV curve.

These four parameters were used to calculate the fill factor (FF), which is the decimal equivalent of how well the IV curve fills the area under an ideal curve for the same cell. It is calculated by

$$FF = \frac{V_{mp} I_{mp}}{V_{oc} I_{sc}} \tag{16}$$

and is typically equal to between 0.7 - 0.85 for cells of reasonably good efficiency. The efficiency, which is the measure of how efficiently the solar cell converts the power in the light illuminating the cell to useable power, could not be determined because a standard lamp was not available.

4. RESULTS AND DISCUSSION

4.1 Evaluation of Potential Ink Constituents

4.1.1 Silver Compounds

After synthesizing the five silver metallo-organic carboxylates, as described in Section 3.1.2, they were evaluated by checking their solubility in xylene, toluene, benzene, and tetrahydrofuran, and by subjecting them to thermogravimetric analysis to determine silver content, decomposition temperature and to observe decomposition behavior. The

results of this evaluation are presented in Table 4.1. The thermograms of these five compounds are given in the Appendix.

Of the five compounds studied, only silver neodecanoate showed appreciable solubility in any of the hydrocarbon solvents (it was soluble in all four). This observation is in general agreement with the rule-of-thumb that solubility increases with chain length and degree of branching. The amount of silver produced upon decomposition of the compounds was close to the theoretical values calculated from the formulae. Silver neodecanoate had the lowest silver content of the five, which was expected, because the metal content decreases as the chain length increases. All of the compounds had approximately the same decomposition temperature (230-240^{o}C), even though their molecular weights and degrees of branching varied considerably. This suggests that the decomposition is initiated in all of the compounds by breaking of the silver-oxygen (metal-hetero atom) bond. If this is true, than all silver carboxylates will decompose between 230-240^{o}C. As for the decomposition behavior of the compounds, all five decomposed very smoothly, although silver monomethyl succinate and silver 2-ethylhexanoate showed an additional small weight change above their decomposition temperatures between 295-335^{o}C. This indicated that their decompositions are not as clean as the other compounds, possibly as a result of some impurities present in them.

Based on the combined results of the silver compound evaluation, silver neodecanoate was selected as the most suitable compound. Despite its lower silver content, it is superior primarily due to its excellent solubility in the hydrocarbon solvents. Silver neodecanoate's

Table 4.1 TGA Results for Five Silver Compounds

Silver Compound	Formula	Molecular Weight	w/o Ag (theo)	w/o Ag (expl)	T_d (°C)	Solubility Rating[a]
Mono-methyl succinate	$CH_3OOC \cdot C_2H_4 \cdot COOAg$	238.99	45	46	230	none
2-Ethyl butyrate	$C_2H_5 - \underset{\displaystyle H}{\overset{\displaystyle C_2H_5}{C}} - COOAg$	223.03	48	58	235	none
2-Ethyl hexanoate	$C_4H_9 - \underset{\displaystyle C_2H_5}{\overset{\displaystyle H}{C}} - COOAg$	251.08	43	42	235	none
Noepentanoate	$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - COOAg$	208.87	52	55	230	none
Neodecanoate	$R_3 - \underset{\displaystyle R_2}{\overset{\displaystyle R_1}{C}} - COOAg$ $[R_1 + R_2 + R_3 = C_8H_{19}]$	278.87	38.6	38	230	all four

(a) Complete solubility in xylene, toluene, benzene, and tetrahydrofuran.

thermogram and important properties are illustrated in Figure 4.1. One important experimental observation made during thermogravimetric analysis of silver neodecanoate was the strong odor of the off gases produced. The smell was similar to that of propane (C_3H_8). This indicated that metallo-organic compounds which decompose below 250°C do not simply decompose to CO_2 and H_2O. Rather, decomposition of such compounds most likely results in the production of a variety of volatile non-toxic hydrocarbons and oxygen containing compounds.

The synthesis procedure described in Section 3.1.2 for silver neodecanoate was derived after research with silver inks had begun. Initially, silver neodecanoate was synthesized as a pasty, off white semi-solid of 35 w/o Ag before it was discovered that it is a white powder in its pure form. The washings in methanol described in Section 3.1.2 were added after this discovery. Also, the warm water washing temperature was lowered from 80°C to 50°C. Since there is always the possibility of impurities being carried over into both the inks and fired films made from an impure compound, it is essential to insure as high a degree of purity as possible in all metallo-organic compound synthesis.

4.1.2 Platinum Compounds

The five candidate platinum compounds discussed in Section 3.1.3 were evaluated for possible addition to silver neodecanoate to produce an ink, which upon printing and firing would decompose to a Ag/Pt film with good solder leach resistance. The order of evaluation was to first check the compounds for solubility in the solvents which dissolve silver neodecanoate, then to evaluate their decomposition behavior and

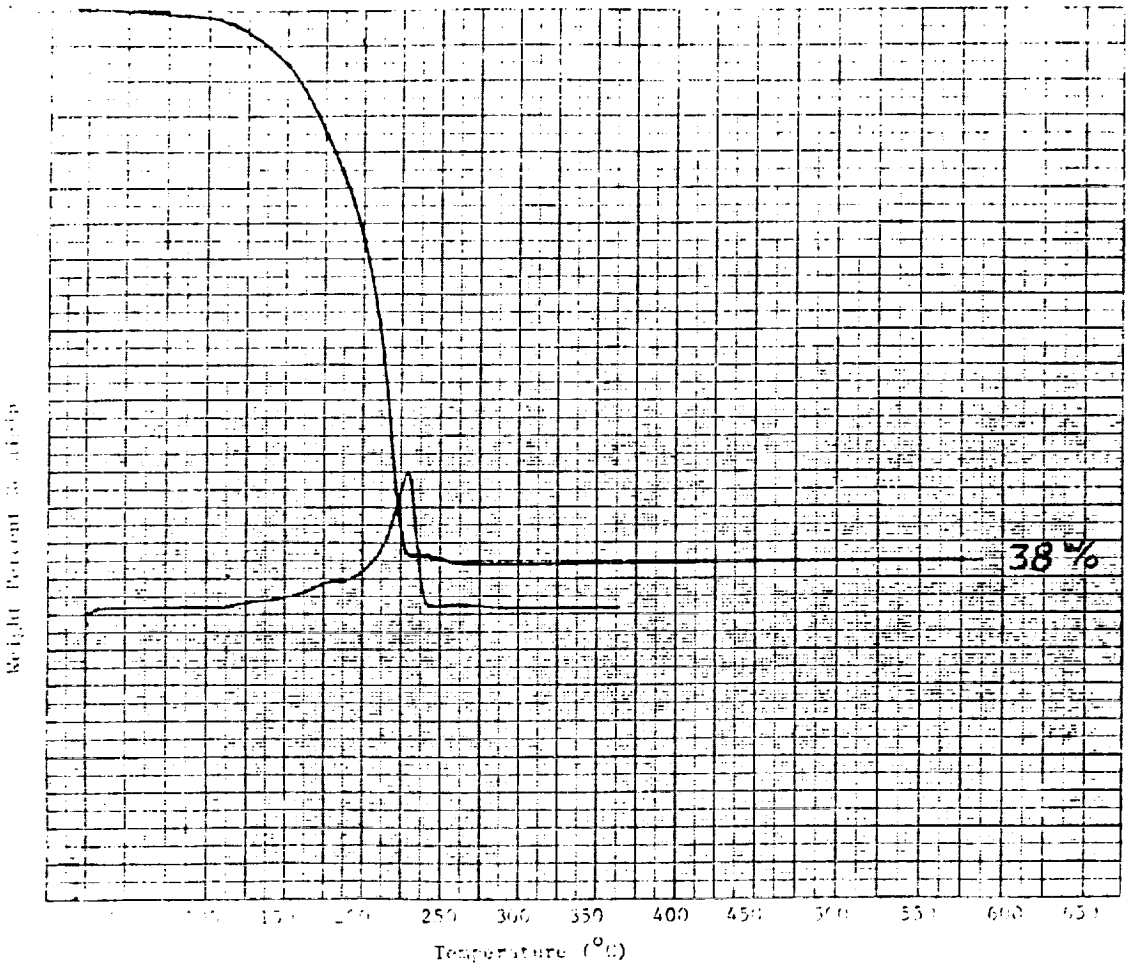


Figure 4.1 Thermogram of solid silver neodecanoate.

Important Properties

T_D: 230°C

Silver Content: 38.6%

Chemical Formula: $C_9H_{19}COOAg$

Molecular Weight: 278.87

Degree of Branching: tertiary

Compatible Solvents: aromatic and tetrahydrofuran

temperature by TGA. Complete decomposition must occur at a temperature low enough so that it does not disrupt the silver film which forms completely by 250°C. The results of the evaluation are presented in Table 4.2 and the thermograms of the five compounds are given in the Appendix. If a platinum compound was insoluble in all four of the solvents used for silver neodecanoate, it was eliminated from consideration. As long as the majority of a compound's decomposition occurred below 350°C, it was retained for ink studies, since it is possible that the decomposition of silver neodecanoate would trigger the platinum compound decomposition in an ink at a lower temperature than when it was alone.

Based on the results in Table 4.2, platinum amine 2-ethylhexanoate, platinum (II) 2,4-pentanedionate and platinum 2-ethylhexanoate were retained for ink studies. Of the three, the latter was felt to be the most promising, since it had the lowest decomposition temperature and it decomposed smoothly and cleanly without evaporation. It should be mentioned that although platinum neodecanoate was not synthesized, it would probably have similar characteristics as platinum 2-ethylhexanoate, but with a lower platinum content.

4.1.3 Adhesion Promoters

The eight metallo-organic compounds discussed in Section 3.1.4 as potential adhesion promoters were boron-bis-n-propoxy-2-ethylbutyrate (BBPE), boron-n-propoxy diacetate (BPDA), ethoxy-silicon-tri 2-ethylhexanoate (ESIE), chromium (III) 2,4 pentanedionate (CrPD), and the 2-ethylhexanoates of bismuth (Bi2EH), chromium (Cr2EH), nickel (Ni2EH) and cobalt (Co2EH). Since their primary role was to promote adhesion,

Table 4.2 TGA Analysis of Platinum Compounds in Air at $10^{o}C$/minute.

Compound	Form	Amt. Inorganics (wt. %)	T_D (^{o}C)	Comments
Pt (IV) amine 2-ethylhexanoate	xylene solution	13.5	430	high T_D
Diglycine Platinum (II)	solid	56.0	255	insoluble in common solvents
Pt (II) 2,4-pentanedionate	solid	27.0	215	partial sublimation before decomposition
Pt bis-dimethylglyoxime	solid	37.0	375	insoluble in common solvents
Pt 2-ethylhexanoate	benzene solution	13.4	235	very soluble in common solvents

extensive evaluation of the compounds was not done prior to actual ink formulation. However, thermogravimetric analysis was done on each to insure decomposition below 350°C (see the Appendix for the eight thermograms), as well as quick solubility tests in a silver neodecanoate/xylene solution and some limited solution firing studies on alumina, glass and polished silicon substrates.

The results from these tests are presented in Table 4.3. All decomposition temperatures were low enough to merit further consideration of the compounds. The lone silicon compound was eliminated from consideration when it was fired on various substrates and found to be very volatile; considerable evaporation occurred and the compound that remained was a flaky powder after decomposition. The other seven compounds were then mixed with a silver neodecanoate in xylene solution, and all except CrPD dissolved after thorough mixing. The CrPD compound was eliminated from further consideration because it was not soluble. Based on these results, the six remaining compounds were used in silver inks to assess their adhesion promoting capabilities.

4.1.4 Solvents and Rheology Adjusters

4.1.4.1 General

Although separate evaluation of all metallo-organic compounds is both useful and necessary prior to ink formulation, past research in the Turner Laboratory with both silver and other ink systems has shown that compounds may perform quite differently as part of an ink than alone. Unless a compound's initial evaluation gave poor results, it was gen-

Table 4.3 Properties of the Eight Compounds Evaluated as Potential Adhesion Promoters.

Compound	Solvent	Product	Wt.% Product	T_D (°C)	Comments
BBPE	none	B_2O_3	4.9	110	promising
PBDA	none	B_2O_3	3.5	100	promising
ESIE	toluene	SiO_2	6.5	140	evaporates
Bi2EH	benzene	Bi_2O_3	14.4	340	promising
Cr2EH	none	Cr_2O_3	14.7	168	insoluble
CrPD	none	Cr_2O_3	4.2	270	promising
Ni2EH	benzene	NiO	5.0	323	promising
Co2EH	benzene	CoO	8.4	292	promising

BBPE = Boron-bis-n-propoxy-2-ethylbutryrate
PBDA = Boron-n-propoxy diacetate
ESIE = Ethoxy-silicon-tri 2-ethylhexanoate
Bi2EH = Bismuth 2-ethylhexanoate
Cr2EH = chromium 2-ethylhexanoate
CrPD = chromium (III) 2,4 pentanedionate
Ni2EH = nickel 2-ethylhexanoate
Co2EH = cobalt 2-ethylhexanoate

erally formulated into an ink before any final decisions were made concerning its potential. Before considerable ink evaluation was carried out, both high vapor pressure (low boiling point) solvents to serve as compound mixing aids, and low vapor pressure (high boiling point) solvents to serve as rheology adjusters for imparting proper screen printing characteristics, were selected. Both types of solvents were required for the ink processing procedure described in Section 3.2. Often, especially in the case of rheology adjusters, inks were made, screen printed and fired to evaluate the solvents and rheology adjusters. However, these inks will not be described in detail, since they would not be suitable for photovoltaic metallization or other applications.

4.1.4.2 Low Boiling Solvents

In order to formulate inks comprised mainly of silver neodecanoate, a proper solvent had to be selected to put it into solution, as it is a white, powdery solid in its pure form. Without first dissolving it, homogeneous mixing with the other ink constituents would not be possible. Once selected, this solvent was used in the synthesis of all metallo-organic compounds, since extraction in a solvent was usually required. The metallo-organic compunds are also easier to measure and handle as low viscosity solutions.

In order to chose the best solvent from among those suitable for silver neodecanoate (xylene, toluene, benzene and tetrahydrofuran), four experimental inks were prepared, printed and fired. The processing of all four inks was held as constant as possible, so a direct comparison

could be made among the four solvents. The four inks were prepared by dissolving some silver neodecanoate in one of solvents to give a 15 ± 2 w/o silver solution. The same amount of butyl carbitol acetate (BCA) was added to each solution as a rheology adjuster. Most of the high vapor pressure solvents were then removed from the solutions using the rotavapor apparatus. The resulting inks were then printed on alumina substrates using the Turner Laboratory standard conductor pattern (Figure 3.3) and fired in the belt furnace to 290°C maximum temperature using a 30 minute cycle. The properties of the inks and fired films produced from them are presented in Table 4.4.

The most important results for low boiling solvent selection were the film appearance and electrical properties. Clearly, there were impurities or solvent removal problems (due to higher boiling points) associated with xylene and toluene, which did not exist with benzene and tetrahydrofuran. Also, the sheet resistances for films produced from inks using these latter two solvents were significantly lower, most likely as a direct result of improved film quality. The adhesion results are given as an illustration of the lack of initial adhesion for silver films, which was often observed during early ink research. Since the primary goal of this phase of the research was ingredient selection, these adhesion results were not a major concern, but they illustrated the potential need for some type of binder in the fired silver films.

These results left the solvent choice as benzene or tetrahydrofuran. Despite its carcinogenic nature, benzene was selected, since it was the more versatile of the two as far as being a suitable solvent for a wider range of compounds. Also, tetrahydrofuran is not as stable as

Table 4.4 Experimental Inks and Properties of Fired Films Fabricated with them for Solvent Selection.

Ink #	Solvent and Boiling Pt.	w/o Ag	Surface Appearance	Line Defin. (in.)	# of Samples	Sheet Resis. ($m\Omega$/sq. $\bar{+}\sigma$)	Initial Adhesion
SS-1[(a)]	xylene 138°C	26.4	yellowish grey/silver	.012 - .016	6	99.4 $\bar{+}$ 10.5	fair to good
SS-2	toluene 110°C	21.0	spotty silverish	>.020	4	61.9 $\bar{+}$ 14.8	poor
SS-3	benzene 80°C	26.0	silver	.016	3	16.9 $\bar{+}$ 0.7	fair to good
SS-4	tetra-hydrofuran 66°C	24.4	silver	.016	3	17.5 $\bar{+}$ 0.8	fair to good

(a) This ink was formulated with dodecane as the screening agent instead of BCA. No inks were ever formulated from purified Ag neodecanoate in xylene soln. and BCA.

benzene and it must be distilled often and stored under nitrogen to prevent peroxide formation. However, tetrahydrofuran remains a potential suitable solvent for use in silver metallo-organic inks, although it was not used further in the studies conducted for this project.

4.1.4.3 High Boiling Solvents

Table 4.5 lists the various rheology adjusters which were used in various inks throughout this study. For the most part, they cannot be directly compared, since they were used in different proportions and the experimental inks made with them were often processed differently. However, individual results from each one (see comments in Table 4.5), were of considerable importance in choosing a combination of neodecanoic acid (NDA) and butyl carbitol acetate (BCA) as the rheology adjusters for MOD silver inks.

The choice was based primarily on their individual properties. Smooth, stable, screen printable inks were made using BCA, but too much was needed to do so, resulting in decreased ink silver content and quality of the fired films. Neodecanoic acid was found to be highly absorbent of silver neodecanoate, therefore making very little necessary to impart the proper rheology, but its acidic nature, although mild, requires that it not be used alone. Fortunately, a combination of BCA with NDA gave the best properties and thus a screening agent was discovered for future inks. An interesting observation about boiling points is that these two solvents have two of the higher boiling points of any of the rheology adjusters evaluated and both are above the decomposition temperature of silver neodecanoate. However, their thermograms

Table 4.5 Rheology Adjustors Evaluated

Chemical Name	Classification	Boiling Pt. or Range (°C)	Comments
α-terpineol	alcohol	217-218	Ink formulated with it has too high T_D.
2-(2-butoxyethoxy) ethyl acetate[a]	ester	236-249	Good, but too much is needed to impart proper ink rheology.
Diphenyl ether	ether	259	Apparently forms an organic reaction product in an ink, which has too high a T_D.
Dodecane	hydrocarbon	215-217	Too much needed to impart proper ink rheology (more than BCA).
2-methoxy ethyl ether (diglyme)	ether	162	Vaporizes during screen printing (inks become non-printable quickly).
Tri ethylene glycol dimethyl ether (triglyme)	ether	216	Inks formulated with it were very poor in texture and appearance.
Neodecanoic Acid[b]	acid	250-257	Good, but should not be used alone due to acidic nature.
Decahydronaphthalene	hydrocarbon	189-191	Inks fabricated with it had tacky quality which made screen printing difficult.

(a) Commonly known as butyl carbitol acetate (BCA).

(b) Henceforth referred to as NDA.

(see the Appendix) show that both vaporize completely nearly 100°C below their respective boiling points when heated at 10°C/minute.

The neodecanoic acid used as a rheology adjuster was a purified version of that used in the synthesis of silver neodecanoate. It was rendered 99+% pure by performing a two stage, reduced pressure, fractional distillation on the impure NDA by heating it to 145°C, which is the boiling point under a pressure of 12-14 mm Hg. Any vapors which formed and were condensed from the NDA prior to 145°C were discarded as impurities, while pure NDA distilled beginning at 145°C. The temperature was held at 145°C until most of the impure NDA had been distilled, with the last few milliliters discarded as potential impurities with lower vapor pressures than NDA.

The necessary amounts of NDA and BCA to impart proper rheology were determined for each ink system as a decimal percent of the weight of silver neodecanoate (AGND) to formulate a given ink. These results are presented in Table 4.6. The amount of NDA was always twice the amount BCA used. This conforms to their respective roles as NDA is the major absorber of the silver neodecanoate and BCA is present to offset the acidic quality of NDA. It was discovered that the amount of bismuth compound used in an ink did not noticably affect the ink rheology, as rheology adjuster amounts did not need to be varied for inks which produce from 1-5 w/o Bi in the fired films. The platinum compound on the other hand, was much more viscous and therefore its inclusion in a ink to produce 4 w/o Pt in the fired films, required the use of an additional 6 w/o NDA and 3 w/o BCA, relative to the amount of silver neodecanoate used in the ink.

Table 4.6 Amounts of BCA & NDA Needed for Various Metallo-Organic Ink Systems

Ink System	Expected Metallic Fired Film Composition	Amt. BCA (% of AGND)	Amt. NDA (% of AGND)
Ag	100 wt.% Ag	10	20
Ag/Pt	96 wt.% Ag-4 wt.% Pt	13	26
Ag/Pt/Bi	91 wt.% Ag-4 wt.% Pt-5 wt.% Bi	13	26
Ag/Bi	97 wt.% Ag-3 wt.% Bi	10	20

*Ratio does not effect amounts of NDA & BCA needed for 0-5 w/o Bi.

4.2 Film Deposition and Processing

4.2.1 Screen Printing

Since many different inks were developed during the course of this study, the screen printing process was not studied in detail nor optimized, but rather was used only as a means of film deposition which varied from ink to ink. For this reason, the effects of two of the primary machine parameters, namely screen-to-substrate distance and squeegee overtravel, were not investigated for the MOD silver inks as they usually are for completely developed ink systems deposited by screen printing. The third main machine parameter, squeegee speed, was set at a constant 14 cm/s. The first two parameters were adjusted in order to obtain complete, dense, wet prints as judged by 40X microscopic examination.

There were no problems encountered in printing MOD inks of suitable viscosity and stability, provided careful adjustments were made to the screen-to-substrate distance and squeegee overtravel. The proper amounts of neodecanoic acid and butyl carbitol acetate provided ink viscosity suitable for screen printing, and both short term stability during screen printing and long term storage stability. Occasionally, the initial ink viscosity was too low for printing, even though previous batches of the ink had printed well. This was a result of insufficient solvent exchange in the rotavapor, which resulted in too much benzene being left in the ink. In these cases, the inks were either dried naturally on the screen (the benzene evaporates in air) or they were

dried by blowing an inert gas on the ink which quickly removed any excess benzene.

4.2.2 Drying and Firing

Most of the initial printed film heat treatments were carried out batchwise in a series of muffle furnaces, where the maximum temperature was above the ink's final decomposition temperature, as determined by thermogravimetric analysis. However, once more advanced ink compositions were developed after metallo-organic compound, solvent and rheology adjuster selection, there was a need for a more versatile heat treatment. The best choice for two reasons was a thick film belt furnace which had three independently controlled zones. First, belt firing is the accepted production heat treatment method, so photovoltaic metallization systems developed for potential production use are best fired by this method. Secondly, belt furnaces allow for completely adjustable time-temperature profiles and variable atmosphere (although air was used for this study). A Turner Laboratory designed batch furnace with adjustable time-temperature profiles and variable atmospheres was also tried, but deemed impractical since only 4-6 cells could be fired at one time.

The choice of an appropriate firing profile in the belt conveyor furnace was made by combining the thermodynamic requirements of the silver/carbon system (to insure only Ag, CO and CO_2 as the thermodynamically stable phases), the decomposition behavior of the films as judged by thermogravimetric analysis of bulk samples of the inks, and a suitably slow firing cycle to allow for smooth decomposition. The desired

maximum temperature for the firing profile was set around 300°C, since complete decomposition of silver metallo-organic inks formulated with silver neodecanoate occurs by 250°C. The desired maximum temperature was set 50°C higher to allow for the somewhat higher decomposition temperatures expected when platinum or adhesion promoting compounds are added to the ink. Finally, a firing cycle of 70 minutes was selected to allow adequate time for organic removal. It was observed that fired films cracked if any decomposition that produces gases occured after the metal film formed. A maximum firing temperature of approximately 300°C with a 70 minute firing cycle is standard firing sequence No. 1, and is illustrated in Figure 4.2.

Prior to firing in the belt furnace under standard firing sequence No. 1, the heat treatment also consisted of a drying step following the printing. This was done below 70°C, which is the temperature at which silver neodecanoate begins to slowly decompose to metallic silver. The drying step was done batch wise for 30 minutes to initiate solvent removal, so that less organics needed to be removed during firing. This was found to be helpful in producing higher quality films with excellent initial adhesion, without the use of a binder. The 30 minute length of the drying step was chosen based on thermogravimetric analysis of neodecanoic acid and butyl carbitol acetate. Bulk samples of each of these could be totally vaporized within 15 minutes.

Levelling of the somewhat thixotropic ink was done at room temperature to remove any memory of the screen mesh marks left after the printing operation. A microscopic examination of the wet films at 100X showed that levelling occurred very quickly at room temperature.

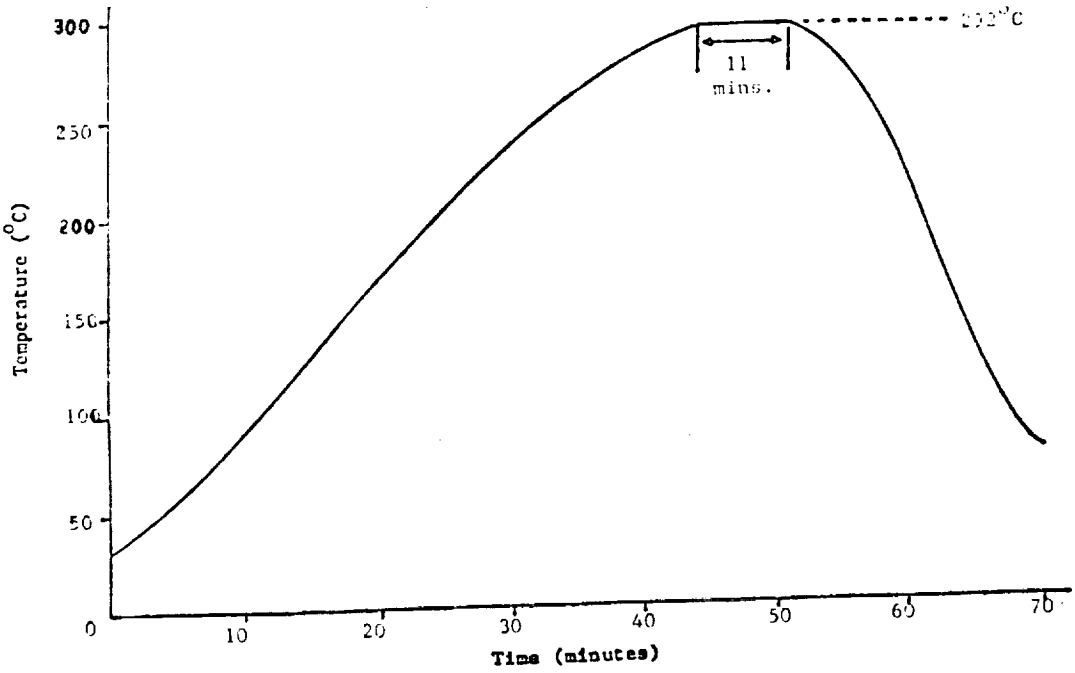


Figure 4.2 Time-temperature profile for standard firing sequence no. 1.

4.3 Pure Silver Inks

In addition to numerous inks formulated to determine the proper solvents, rheology adjusters and firing profiles, one ink (SC-1Y) was formulated to produce pure silver front contacts on solar cells. The Y in the ink code refers to the batch number. It was formulated with silver neodecanoate dissolved in benzene with 10 w/o BCA and 20 w/o NDA (relative to the amount of silver neodecanoate) as the rheology adjusters. The two drawbacks to pure silver contacts are their lack of both consistent initial and reliable long term adhesion, and their lack of solder leach resistance. The main purpose in fabricating some solar cells with pure silver front contacts was to verify these shortcomings and to compare their properties to fired contacts produced from other ink systems, which attempt to overcome these two drawbacks. Two batches of ink SC-1Y were formulated, and the properties of single and double layer fired films produced from them, are presented in Tables 4.7a and 4.7b. The thermogram of one of these inks is in the Appendix.

The most important result in Tables 4.7(a) is the resistivity calculated from the sheet resistance and average film thickness measured with the profilometer. The value is very close to the resistivity of bulk silver (1.59 μΩ-cm), which indicated that the film was near theoretical density. The excellent initial adhesion observed with single layer films was found to degrade with time indicating a lack of long term adhesion. The lack of results on SC-1A single layer films is due to the fact that a second layer was immediately printed on all films except one, since they were fabricated for solder leach testing. As will be seen when the results from alloyed fired films are presented in

Table 4.7 Properties of Pure Silver Ink SC-1Y and the Single Layer Solar Cell Front Contacts Produced from it

Ink #	Solar Cell Batch #	Fired Film Properties					
		Surface Appearance	Line Defin.	# of Samples	Sheet Resist. (mΩ/sq)	Resist (μΩ-cm)	Initial Adhesion
SC-1A	346-193	smooth, bright white silverish	A	-	-	-	-
SC-1B	346-208	inhomogeneous whitish silver w/ yellow tint	B	8	26.2 ± 3.9	1.99 ± 0.30	Excellent

Table 4.7 Properties of Double Layer Solar Cell Front Contacts Fabricated with Ink SC-1Y

Ink #	Cell Batch #	Surface Appearance	Line Defin.	# of Samples	Sheet Resist. (mΩ/sq)	Initial Adhesion
SC-1A	346-193	smooth, bright whitish silver	B	6	14.5 ± 1.5	good
SC-1B	346-208	inhomogeneous whitish silver w/ yellow tint	B	6	20.2 ± 1.6	excellent

later sections, the sheet resistances for these single and double layer pure silver films were lower than any other single or double layer films fabricated on solar cells during this study. This was expected since any alloying of the pure silver films would adversely affect their sheet resistances.

4.4 Silver/Platinum System

4.4.1 Platinum Compound Selection

Three inks were formulated in order to choose one of the promising platinum compounds discussed in Section 4.1.2 as a solder leach resistance promoter. Ink SC-4Y contained Pt amine 2-ethylhexanoate, ink SC-5Y contained Pt (II) 2,4-pentanedionate and ink SC-6Y contained Pt 2-ethylhexanoate. All inks were formulated to produce fired films of theoretical composition 96 w/o Ag-4 w/o Pt. The thermograms of these inks are given in the Appendix. The properties of these inks are presented in Table 4.8 and the properties of single layer films produced from them on alumina substrates are presented in Table 4.9. The results in Table 4.8 are almost sufficient to separate the platinum (II) 2-ethylhexanoate used in ink SC-6Y as the most suitable platinum compound. The high final decomposition temperature of ink SC-4Y containing Pt amine 2-ethylhexanoate and the formation of a small amount of precipitate during ink formulation (possibly a AgCl complex, since Pt amine 2-ethylhexanoate contains 0.5% Cl) are enough to eliminate it from consideration. The somewhat lower final decomposition temperature, better stability and smooth decomposition without the possibility of sublimation, clearly make Pt 2-ethylhexanoate used in ink SC-6Y, the better of

Table 4.8 Ink Properties of SC-4, SC-5 and SC-6

Ink #	w/o Ag + Pt	T_D	Comments
SC-4A	23.0	530°C(a)	Small amt. of precipitate formed with Pt and Ag compounds were mixed. Possibly AgCl complex.
SC-5A	26.0	310°C	Ink stability was short term. Compound sublimation before decomposition not observed when used in an ink.
SC-6A	24.6	285°C(b)	Excellent long term ink stability. Smoothest decomposition of the 3 inks.

(a) all but 2 w/o of organics decomposed by 245°C.

(b) all but 1 w/o of organics decomposed by 215°C.

Table 4.9 Fired Film Properties of Films Fabricated on Alumina Substrates from Inks SC-4, SC-5 and SC-6

Ink #	Surface Appearance	Line Defin.	# of Samples	Sheet Resist. (mΩ/sq)	Initial Adhesion
SC-4A	copperish gold	.016"(a)	3	687.4 ± 297.7	fair
SC-5A	whitish silver	B	2	39.3 ± 1.4	excellent
SC-6A(b)	whitish silver	A/B	3	77.3 ± 7.6 (c)	excellent

(a) Ink printed with Turner Laboratory standard conductor pattern, which allowed for quantitative line definition determination.

(b) Fired under std. firing sequence No. 1. Inks SC-4A and SC-5A were also belt fired, but to a maximum temperature of 334°C instead of 292°C as employed in std. firing sequence No. 1.

(c) Values were obtained as low as 56.3 ± 6.0 mΩ/sq. for an earlier printing of SC-6A when the only difference was heat treatment in a series of two batch muffle furnaces.

the two remaining compounds.

These advantages are important, since fired films produced from inks SC-5Y and SC-6Y have similar properties as illustrated in Table 4.9. The fired film properties of films fabricated from ink SC-4Y are far worse, which further eliminates Pt amine 2-ethylhexanote from consideration. It would appear that the films produced from ink SC-5A are somewhat superior to those produced from ink SC-6A, based on sheet resistance results. However, the lower sheet resistance for SC-5A films may be the result of a lower platinum content in the ink than the expected 4 w/o, due to possible sublimation during decomposition of Pt (II) 2,4-pentanedionate. Based on all of the above results, platinum 2-ethylhexanoate was selected as the best platinum compound for the silver/platinum ink system.

4.4.2 Solderability Studies

The primary reason for adding platinum to the inks was to improve the solder leach resistance of the fired films. Four sets of solder leach resistance tests were conducted. Each test used two films, one pure silver (SC-1B) and one 96 w/o Ag-4 w/o Pt (SC-6B), and the films were dipped into the solder pot for equal amounts of time at 230^{o}C. The films were fabricated in as similar a manner as possible, so that a direct comparison of the results could be made. The films were evaluated for percent solder leach resistance, which is the amount of film remaining after one dip, and percent solder acceptance, which is the percent of film area tinned by the solder. The results given in Table 4.10 show that some degree of leaching occurred for all of the

Table 4.10 Solder Leach Resistance Testing Results for Films Produced from Inks SC-1Y and SC-6Y

Type of Film	Initial Film Adhesion	Dip Time (secs)	% Solder Leach Resist.	% Solder Acceptance	Comments
silver	excellent	5	75	98	Leaching occurred to the fingers leaving them ½ as wide as in their as-fired condition.
silver/plat.	excellent	5	100	55	Poor solder acceptance on bus bar.
silver	good[(a)]	5	45	100	Complete leaching of the fingers occurred, but none to bus bar.
silver/plat.	excellent	5	100	50	Poor solder acceptance on bus bar.
silver	excellent	10	20	100	Part of bus bar and all fingers completely leached.
silver/plat.	excellent	10	100	50	Poor acceptance on bus bar.
silver	good[(a)]	10	40	100	Complete leaching on fingers. None on bus bar.
silver/plat.	excellent	10	100	40	Poor acceptance on bus bar.

(a) The adhesion for two of the silver films was only good due a difference in processing, which was necessary to mimic the processing of the silver/plat. films to which they were compared. Apparently, the silver/platinum film adhesion was not sensitive to this difference in processing.

pure silver films, but none for the silver/platinum films. This clearly demonstrates the effectiveness of platinum as a solder leach resistance promoter. The results in Table 4.10 also show the excellent solderability of silver, since excellent solder acceptance on non-leached areas always occurred. The results also exhibited the necessity of a fluxing step in the testing as solder acceptance was only fair on the solder leach resistant silver/platinum films. This could be due to a protective oxide or sulphide on the film surface, which fluxing would normally remove. The side effect to poor solder acceptance is that this protective layer may be protecting the films from leaching as well. A mild flux should be used if a suitable one can be found. Preliminary studies with diluted Alpha 611 indicated that this flux was too strong at all dilution levels tested.

4.4.3 Processing Studies

Extensive processing studies were conducted with ink SC-6Y from different batches and after various shelf storage times. The results for single layer fired front photovoltaic contacts are presented in Table 4.11, and those for multi-layer fired films are presented in Table 4.12. All printing and firing was done on the JPL supplied silicon solar cells using standard firing sequence No. 1 as the final heat treatment. The film appearance for both single and multi-layer films was whitish silver in all cases, which demonstrated: (a) the benefits of using low boiling point benzene as a solvent; (b) the high purity of the metallo-organic compounds used and; (c) smooth, clean decomposition of the ink. The ink was very stable as evidenced by the fact that no

Table 4.11 Fired Solar Cell Front Contact Properties for Single Layer Films Produced from Ink SC-6Y

Test #	Ink # and Age	Solar Cell Batch #	Line Defin.	# of Samples	Sheet Resist (mΩ/sq)	Initial Adhesion
1	SC-6A 27 days	341-177	A	3	59.9 ± 6.9	good to excellent on fingers, fair to poor on bus bar
2	SC-6B 2 hrs.	341-177	B	8	54.0 ± 10.1	excellent
3	SC-6B 8 days	341-177	B	5	56.9 ± 1.5	excellent
4	SC-6B 15 days	341-177	B	9	51.7 ± 5.3	excellent
5	SC-6B 28 days	341-177	B	5	75.6 ± 12.3	excellent
6	SC-6B 28 days	346-193	B	13	72.1 ± 7.0	excellent
7	SC-6B 53 days	346-193	B	6	77.4 ± 4.2	excellent
8	SC-6B 53 days	346-193(a)	B	6	61.3 ± 2.6	excellent
9	SC-6B 53 days	346-193(b)	B	6	60.2 ± 3.4	excellent
10	SC-6C 6 hrs.	346-193(b)	A	4	56.6 ± 1.8	excellent
11	SC-6C 14 days	346-193(b)	A	3	44.1 ± 1.8	good
12	SC-6F 1½ hrs.	346-199(b)	A/B	12	51.6 ± 3.3	good

(a) methanol cleaned
(b) HF cleaned

Table 4.12 Fired Front Solar Cell Front Contact Properties for Multi-Layer Films Produced from Ink SC-6Y

Test #	Ink # and Age	# of Layers	Intermediate Heat Treatment	Line Defin.	# of Samples	Sheet Resist (mΩ/sq)	Initial Adhesion
1	SC-6B 2 hrs.	2	Batch Drying and Std. Firing Sequence No. 1	B	6	22.9 ± 1.0	poor to fair
2	SC-6B 8 days	2	None	C	4	47.0 ± 2.4	excellent
3	SC-6B 8 days	2	Batch Drying and Std. Firing Sequence No. 1.	B	5	23.7 ± 1.9	excellent
4	SC-6B 8 days	2	Std. Firing Sequence No. 1	B	4	23.7 ± 1.1	excellent
5	SC-6B 15 days	2	Batch Drying and Std. Firing Sequence No. 1	B	4	26.1 ± 5.2	excellent
6	SC-6B 28 days	2	Batch Drying Only	B	4	29.2 ± 1.8	excellent
7	SC-6C 8 hrs.	2	Batch Drying and Std. Firing Sequence No. 1	A/B	6	23.5 ± 0.7	poor
8	SC-6C 8 hrs.	3	Batch Drying and Std. Firing Sequence No. 1	A/B	6	14.9 ± 0.3	poor

correlation was found between ink age and fired film properties. The relative atmospheric humidity in the laboratory was monitored during the various printings and firings, which lasted over 3 months, but no correlation was discovered between film properties and humidity level. For multi-layer printing and firing, four different intermediate heat treatments between layers were used. These were drying only at 65^{o}C for 30 minutes, firing only under standard firing sequence No. 1, both drying and firing or no intermediate heat treatment.

Cleaning the solar cells in hydroflouric acid prior to printing was found to be non-detrimental to the film properties (Table 4.11). In fact, a statistically significant improvement in the film sheet resistance was observed for fired films fabricated on cleaned solar cells as compared to those on uncleaned solar cells fabricated at the same time (see test Nos. 7 and 9 in Table 4.11). Methanol cleaning (test No. 8) also resulted in a sheet resistance improvement similar to that for hydrofluoric acid cleaning, but hydroflouric acid cleaning was adopted as the standard cleaning procedure once these results were obtained, since it is the method used by Jet Propulsion Laboratory.

Another important result from Tables 4.11 and 4.12 was the inconsistent adhesion results obtained for single and multi-layer films. Even for some films showing excellent initial adhesion (tests 7-10 in Table 4.11), long term adhesion studies revealed the beginning of adhesion degradation between 4-18 days after fabrication.

The wide variation in sheet resistance values obtained for the single layer films in Table 4.11 cannot be explained by variations in film

thickness. As Table 4.13 shows, an increased sheet resistance did not necessarily correspond to a dried film thickness decrease, as measured using the light section microscope. The large standard deviation in the film thickness was mainly a function of the printing process, but the roughness of the solar cell surface was also a contributing factor. Because of results such as these, considerable emphasis was not placed or dried film thickness measurements. A more important result from the sheet resistance data is that the values for multi-layer films were consistently lower than those for single layer films. For two layer films the decrease was at least 50% in all cases and for the one three layer test the decrease was nearly 75% compared to their 1 layer counterparts. Also, the variability of the data decreased with multi-layers, most likely due to a levelling out and densification of the films with the addition of multiple layers.

Finally, the multiple layer results also showed that only a batch drying step should be needed between layers. No heat treatment at all (test No. 2 in Table 4.12) resulted in poor line definition and only a slight decrease in sheet resistance over its 1 layer counterpart. Complete drying and firing or firing alone between layers produced results similar to comparable multi-layer films which were only dried between layers (tests 4, 5 and 7). Since a simple low temperature batch drying step is quicker and much more cost effective than the two alternatives, only it needs to be used between layers in multi-layer screen printed films.

Table 4.13 Correlation Between Dried Film Thickness and Sheet Resistance

Test #[a]	Sheet Resist (mΩ/sq)	Dried Film Thickness (μm)
12	44.1 ± 1.8	17.6 ± 2.6
13	51.6 ± 3.3	18.9 ± 3.4
11	57.6 ± 1.8	13.75 ± 2.5
8	77.4 ± 4.2	15.3 ± 3.25

4.5 Adhesion Studies

4.5.1 Time Dependent Adhesion Tests

Silver or silver/platinum films with excellent adhesion to silicon could be achieved if the proper ink formulating and thermal processing procedures were followed, as demonstrated by the results given in Tables 4.11 and 4.12. However, some samples in Tables 4.11 and 4.12 with similar processing did not have excellent adhesion. Even more disturbing was the observation that some films from a processed batch that had excellent adhesion were found to have only good or fair adhesion when tested several weeks after the initial test. Because of these results, time dependent adhesion tests were conducted. Silver/platinum ink SC-6Y was used for these tests because of the extensive processing studies presented in Section 4.4.3.

The results from two adhesion/time studies are presented in Tables 4.14 and 4.15. Both studies produced similar results concerning the potential degradation of adhesion over time. When samples processed in the same way were tested by the Scotch tape test one by one over a period of 42 days in the first study (Table 4.14), the adhesion, which was initially excellent, was noticed to begin to degrade after 3-4 days. A summary of the initial properties of the films in Table 4.14 may be found under Test No. 5 in Table 4.11. The adhesion continued to degrade until only about 20% of the film was adhering on the 42nd day. In the second test (Table 4.15), which was designed to evaluate the effect of surface preparation of the silicon, the adhesion was noticed to begin to decrease from an excellent initial rating between the 5th and 7th days.

Table 4.14 Adhesion/Time Study with Single Layer Fired Films of Ink SC-6Y[(a)].

Time since printing & firing (days)	Relative humidity at time of test (%)	Adhesion (estimated % of total surface area)	Comments
0	54	100,100	
1	52	100	
2	53.5	100	
4	59.5	68,80	For two samples adhesion loss occurred on connecting bar only.
10	60.5	56.65	Nearly complete loss of adhesion on connecting bar. Adhesion beginning to degrade slightly on narrow lines.
10	60.5	2	Test done on one of the samples from day zero which had shown 100% adhesion after first test.
15	57.5	30.40	Complete adhesion loss on connecting bar and significant loss on narrow lines.
21	55	30,40	Complete adhesion loss on connecting bar and significant loss on narrow lines.
26	53.5	35,45	Same as for day 21 except less loss on narrow lines.
42	55.5	10,30	Considerable adhesion losses. Only small sections of some narrow lines are adhering.

(a) See Test No. 5 in Table 4.11 for the initial properties of these films.

Table 4.15 Adhesion/Tome Study with Single Layer Fired Films of Ink SC-6Y on Substrates Which Have Undergone 3 Types of Surface Preparation Prior to Printing

Time since printing & firing (days)	Cleaning Method	Relative Humidity at time of test (%)	Adhesion (estimated % of total surface area)	Comments
0	None[(a)]	60%	100	
0	HF[(b)]	60%	100	
0	MeOH[(c)]	60%	100	
1	None	56%	100	
1	HF	56%	100	
1	MeOH	56%	100	
3	None	53.5%	100	
3	HF	53.5%	100	
3	MeOH	53.5%	100	
5	None	54.5%	100	
5	HF	54.5%	100	
5	MeOH	54.5%	60	90% of connecting bar lifted. Still excellent adhesion of narrow lines.
6½	None	58%	100	
6½	HF	58%	70	Adhesion losses occurred about equally to connecting bar and narrow lines.
6½	MeOH	58%	100	Adhesion restored on this MeOH sample. No apparent visual difference between this and day 5 sample above.
18	None	55.5%	1	shortage of samples caused the delay between these last two sets of tests. Almost total loss of adhesion occurred between day 6½ and day 18.
18	HF	55.5%	2	
18	MeOH	55.5%	1	

(a) See Test No. 7 in Table 4.11 for the initial properties of these films.
(b) See Test No. 9 in Table 4.11 for the initial properties of these films.
(c) See Test No. 8 in Table 4.11 for the initial properties of these films.

The initial properties of the films used in this second study may be found under Tests 7-9 in Table 4.11. This second study was also helpful in determining whether or not a relationship existed between the humidity level and the adhesion. As can be seen from Table 4.15, the humidity varied between 53.5% and 60.0%. At least in this range, no correlation could be found connecting either increases or decreases in relative humidity with the degradation of adhesion over time. There had been some concern that such a correlation existed after the first study was completed, because a sharp rise in humidity between days 2 and 4 in Table 4.14 coincided with the first loss of adhesion. The results from the second study did not show any such connection.

The adhesion/time studies demonstrated that the excellent adhesion of the silver/platinum SC-6Y conductor films was not long term. Also, even though the initial adhesion was excellent in most cases, there were instances where the initial adhesion was poor. Inconsistencies such as these are not acceptable since they introduce too much uncertainty into the performance of the films in actual use. In order to insure initial as well as long term adhesion, it was apparent that there had to be a change in the ink chemistry to include a permanent bonding agent.

4.5.2 Selection of Adhesion Promoter

The potential adhesion promoting compounds discussed in Section 4.1.3 were evaluated as ink constituents. The first inks formulated with ingredients to enhance the adhesion of the silver films were SC-2A and SC-3A. These inks contained bis-propoxy-boron-2 ethylbutyrate and n-propoxy boron diacetate, respectively. Both of these compounds should

theoretically decompose to B_2O_3 in the fired films and promote adhesion by flux bonding with the silicon substrates. Butyl carbitol acetate was used alone in these two inks as the rheology adjuster. Ink SC-2A was formulated to produce fired films of theoretical composition 95w/o Ag-5w/o B_2O_3. The thermogram of the ink (see the Appendix) was very promising and showed complete decomposition by 215°C, although the inorganic content was only 12 w/o. Ink SC-3A was formulated to give fired films of theoretical composition 96.5w/o Ag-3.5w/o B_2O_3. The TGA of this ink (see the Appendix) showed majority decomposition by 245°C, although the last 1 w/o of the organics did not completely decompose until 425°C. The inorganic content of this ink was 30 wt.%.

The fired films made from either SC-1A or SC-2A were very dark in color, non-conducting, and non-adhering even though the firing was done well above the decomposition temperatures. The films fabricated with ink SC-2A also had a very oily texture which smudged easily and did not dry in air after 3 days. X-Ray diffraction of the SC-2A films revealed only silver peaks, so the composition responsible for the black/brown color remained unknown(B_2O_3 is either a colorless glass or a white powder). The potential of boron compounds to form boron oxide as a potential flux bonder was considered very remote and other bonding systems were investigated.

The other four compounds in Table 4.3 were then evaluated as potential adhesion promoters. Inks were made by first mixing a benzene solution of silver neodecanoate with a benzene solution of bismuth 2-ethylhexanoate, or chromium (III) 2,4, pentanedionate, or nickel 2-ethylhexanoate, or cobalt 2-ethylhexanoate. For each ink, the relative

amounts of the two solutions were adjusted so that the inorganic content was 97 w/o Ag and 3 w/o Bi, or Cr, or Ni or Co. Then, 10 w/o BCA and 20 w/o NDA (relative to the amount of silver neodecanoate) were added and solvent exchange affected on the rotavapor. Metallization patterns were printed on solar cells and fired using standard firing sequence No. 1. Some samples made from each of the inks were given an additional heat treatment of 60 seconds at 800°C. The results of these experiments are given in Table 4.16. Only the bismuth and nickel additions gave films with consistently excellent initial adhesion, and the bismuth addition had a smaller determinital effect on sheet resistance. Therefore, bismuth 2-ethylhexanoate was selected as the adhesion promoting additive for further testing.

4.5.3 Silver/Platinum/Bismuth Oxide System

Only one ink was formulated, printed and fired in this system, although several batches were used. This ink (SC-7Y) was prepared to test the ability of bismuth additions to promote adhesion in the fired films. The ink composition was such that the fired films were of theoretical metallic composition 91 w/o Ag-5 w/o Bi-4 w/o Pt. Bismuth 2-ethylhexanoate was the metallo-organic compound used in ink formulation which was expected to decompose to bismuth oxide in the fired films. The thermogram of ink SC-7Y in the Appendix shows 99% organic decomposition by 265°C with the last 1% decomposing by 307°C. Despite this higher than usual final decomposition temperature, standard firing sequence No. 1 was employed on the printed films because the much slower decomposition and smaller sample volume, compared to that used in the

Table 4.16 Fired Front Contact Properties of Inks with Four Different Compounds Added for Potential Adhesion Promotion.

Ink No.	Chemistry	Fired Film Appearance	Line Defin.	Sheet Resistance (mΩ/sq)			
				No. of Films	Initial Value	Value After 60 sec. Spike at	Initial Adhesion
SC-9A	Ag/Bi	silver with copperish tint	A	16	40.1 ± 3.9	24.9 ± 1.5	excellent
SC-11A	Ag/Cr	dark silver/ grey	A/B	7	89.0 ± 3.8	51.2	good to excellent
SC-12A	Ag/Ni	dark with purple tint	A	9	157.7 ± 7.5	91.3	excellent
SC-13A	Ag/Co	dark with greenish yellow tint	A	9	>860	98.3	fair to good

TGA, should allow for total decomposition at a temperature below 292°C (the maximum temperature under standard firing sequence No. 1). All firing was done on solar cells (batch #346-199) after cleaning them in hydrofluoric acid. The results for single layer fired films fabricated with ink SC-7Y are presented in Table 4.17. The film appearance was a greyish silver as opposed to the bright whitish silver for SC-6Y films, which was probably due to the presence of bismuth.

All the films produced in test No. 1 (Table 4.17) and those from test No. 2 not used for the multi-layer studies, were stored in a dessicator. Either one or two samples were removed for an adhesion test after 1, 2, 3, 5, 8, 10, 15, 21, 27, 35 and 65 days. The results of these tests need not be tabulated since the adhesion remained excellent (100%) throughout the entire test (the test was terminated when the films ran out). The long term adhesion tests (Tables 4.14 and 4.15) conducted with silver/platinum films made from ink SC-6Y were not done using a dessicator. In order to eliminate this variable, a set of films were printed (initial properties are under test No. 12 in Table 4.11) using ink SC-6Y and stored in a dessicator. This time one or two films were adhesion tested after 1, 3, 4, 5, 8, 12 18 and 26 days. The adhesion was initially good (85-95%) and remained good throughout this study (the 12 day film even showed an improvement to excellent adhesion), which may suggest that humidity or other atmospheric impurities may accelerate adhesion degradation. The storage in the relatively constant environment of the dessicator seemed to considerably slow the degradation of adhesion. However, for low cost processing of practical solar cells, the metallization would have to be exposed to normal atmosphere

Table 4.17 Single Layer Results for Fired Solar Cell Front Contacts Fabricated with Ink SC-7Y

Test #	Ink #	Ink Age	Line Defin.	# of Samples	Sheet Resist. ($m\Omega$/sq $\pm \sigma$)[a]	Initial Adhesion
1	SC-7A	16 days	A	14	173.2 ± 13.8	excellent
2	SC-7A	28 days	A	5	139.5 ± 8.9	excellent
3	SC-7B	18 days	B	2	79.9 ± 6.8	excellent
4	SC-7B	26 days	A	2	77.9 ± 3.4	excellent

(a) $\pm \sigma$ = 1 standard deviation

for some period of time. Therefore, the addition of bismuth to the ink was considered to be essential.

Besides the excellent long term adhesion results obtained for the fired films, the other important results in Table 4.17 are the very high sheet resistances of fired films with the bismuth addition. This could be decreased by either increasing the film thickness, optimizing and minimizing the additions to the silver films (especially bismuth) or both. A series of multi-layer films were fabricated with the goal of improving the poor sheet resistance results. Since bismuth oxide should only be needed for adhesion in the layer in contact with the solar cell, additional layers were added using ink SC-6Y, which did not contain bismuth. This should serve to decrease the high sheet resistances of single layer SC-7Y films by both increasing the volume of conductor present and adding material with a lower resistivity. The results of these tests are presented in Table 4.18.

With the exception of the 3 layer films in test No. 4, all final firing after the desired number of layers had been printed was done under standard firing sequence No. 1. The sheet resistances decreased as expected in most cases for multiple layers (e.g. ~50% for two layers, 66% for 3 layers, etc.), although in some cases (e.g. test No. 1, layers 3, 4 and 5) the decreases were far less than expected. This is most likely due to a severe film cracking problem which occurred in all 3+ layer films (except for test 4) and even some 2 layer films (test No. 4). The cracking in turn resulted in poor film adhesion, almost exclusively along the bus bar where most of the cracking occurred. Cracking occurred whether films were simply dried only between layers

Table 4.18 Dual Composition Multi-Layer Fired Solar Cell Front Contact Properties Fabricated with Inks SC-7Y (bottom layer only) and SC-6Y

Test No.	Layer No.	Ink No. and Age	Intermediate Heat Treat. Preceeding the Layer	Line Defin.	No. of Samples	Sheet Resist. (mΩ/sq)	Initial Adhesion
1	1	SC-7A 28 days	-	A	5	139.5 ± 8.9	excellent
	2	SC-6F 3 days	Batch drying only at 65°C for 30 mins.	A	5	59.2 ± 6.4	excellent
	3	SC-6F 3 days	Batch drying only at 65°C for 30 mins.	B	5	47.1 ± 7.3	poor on bus bar,[a] excellent elsewhere
	4	SC-6F 3 days	Batch drying only at 65°C for 30 mins.	B	5	41.6 ± 2.0	poor on bus bar,[a] excellent elsewhere
	5	SC-6F 3 days	Batch drying only at 65°C for 30 mins.	B	6	41.0 ± 4.8	poor
2	2	SC-7B 16 days (bottom) / SC-6F 19 days (top)	- / Batch drying only at 65°C for 30 mins.	A/B	4	38.6 ± 1.4	excellent
	4	SC-6F 19 days (layers 3+4)	Batch drying only at 65°C for 30 mins.	B	7	17.8 ± 1.4	poor on bus bar,[b] excellent elsewhere
3	1	SC-7B 18 days	-	B	2	79.9 ± 6.8	excellent
	2	SC-6F 21 days	Std. firing sequence #1	A/B	1	28.5	fair on bus bar, excellent elsewhere
	3	SC-6F 21 days	Std. firing sequence #1	B	8	19.7 ± 1.5	poor on bus bar,[b] excellent elsewhere
4	1	SC-7B 24 days	-	A	2	77.9 ± 3.4	excellent
	2	SC-6F 29 days	Batch drying only at 65°C for 30 mins.	A	9	45.3 ± 3.4	poor on bus bar,[b] excellent elsewhere
	3[c]	SC-6F 29 days	Batch drying only at 65°C for 30 mins.	A	5	32.5 ± 2.0	good on bus bar, excellent elsewhere

(a) Cracks were visible with the naked eye in the films after final heat treatment.

(b) Cracks were visible under 40X magnification in the films after final heat treatment.

(c) Final heat treatment was a modified version of std. firing sequence no. 1 where the firing cycle was approximately 3X as long.

and then fired, dried between all layers and fired after every other layer or dried and fired after each layer. Refiring alone was eliminated as the problem source when excellent adhering two layer films were refired with no sign of cracking or detrimental effects on adhesion.

This left the probable cause of the cracking as stresses built up during the excessive organic removal which takes place in multi-layer films. Since silver is very ductile, one possible solution was to relieve the stresses by firing the films very slowly. This was attempted in test No. 4 for the 3 layer films. The result was greatly improved, although not excellent, adhesion compared to 2 layer films fabricated at the same time with the same ink and fired using std. firing sequence No. 1. In both cases, drying was still the only heat treatment between intermediate layers. This new slower firing sequence, which had a maximum temperature of 297°C and total firing cycle of 3 hours (compared to 292°C and 70 minutes for standard firing sequence No. 1) was considered to be very promising for multi-layer films, but further studies were not carried out with ink SC-7Y. The sheet resistances for single layer films needed to be minimized, without sacrificing adhesion, before thicker films were fabricated by multi-layer printing and firing.

4.5.4 Bismuth Oxide Content Optimization

In order to minimize the sheet resistance of the excellent adhering SC-7Y films, three inks were formulated to find the minimum amount of bismuth oxide which would promote long term film adhesion. The inks

were prepared by mixing benzene solutions of silver neodecanoate and bismuth 2-ethylhexanoate with 10 w/o BCA and 20 w/o NDA (relative to the amount of silver neodecanoate), and affecting solvent exchange on the rotavapor. Inks SC-8Y, SC-9Y and SC-10Y were formulated such that upon printing and firing, the fired films would be of theoretical metallic compositions 95 w/o Ag-5 w/o Bi, 97 w/o Ag-3 w/o Bi and 99 w/o Ag-1 w/o Bi, respectively. The thermograms for these three inks are in the Appendix. All three inks were printed on HF cleaned solar cells and fired under standard firing sequence No. 1. Both single and double layer films were fabricated with the intermediate between layer heat treatment consisting of batch drying for 30 minutes at 65°C. The results for the bismuth oxide content optimization study are presented in Table 4.19.

The most important result is that long term single layer adhesion was obtained in the silver films with an addition of only 1 w/o Bi. Although the adhesion was initially excellent for both 1w/o Bi and 0w/o Bi films(SC-1Y), the adhesion began to degrade in the pure silver films within 20 days. The adhesion in the 1w/o Bi films remained excellent for at least 50 days, which was the duration of the long term adhesion test (there was no reason to suspect that the adhesion would begin to degrade). The two layer adhesion was not 100% excellent for any of the films containing Bi_2O_3. Although no cracking was visible, the lack of complete adhesion may still have been due to stresses building up in the films, due to considerable organic removal. When these results are combined with the SC-7Y results for multi-layer films (Table 4.18), it becomes apparent that special processing or other changes will be needed

Table 4.19 Comparison Between Fired Solar Cell Front Contacts Fabricated from Inks SC-8Y (5 w/o Bi), SC-9Y (3 w/o Bi), SC-10Y (1 w/o Bi) and SC-1Y (0 w/o Bi)

Ink #	# of Layers	# of Samples	Sheet Resist. (mΩ/sq)	Resistivity (μΩ-cm)	Line Defin.	Initial Adhesion
SC-8A	1	14	57.8 ± 4.1		A	excellent
SC-8A	2	3	32.3 ± 0.9		A	poor for ½ of bus bar. excellent elsewhere
SC-9C	1	16	40.1 ± 3.9	3.11	A	excellent
SC-9C	2	3	24.6 ± 0.8		A/B	excellent, except for small piece of bus bar which didn't adhere.
SC-10B	1	9	37.5 ± 1.1	2.30	A/B	excellent (a)
SC-10B	2	1	21.1		B	poor for ½ of bus bar. excellent elsewhere
SC-1B	1	8	26.2 ± 3.9	1.99	B	excellent (b)
SC-1B	2	6	20.2 ± 1.6		B	excellent

(a) Long term adhesion for 50+ days.

(b) Adhesion begins to degrade within 30 days.

to produce high quality multi-layer films.

The other result of consequence in Table 4.19 is the decreases in single and double layer sheet resistances and the resistivities as the theoretical Bi content in the fired films was decreased from 5 to 0 w/o. All of the reductions were statistically significant.

4.5.5 Microstructural Studies

The extensive long term adhesion results obtained during this research clearly prove that bismuth, assumed to be present as bismuth oxide, is effective as an adhesion promoter in silver MOD films on silicon solar cells. In an attempt to better understand the mechanisms at work, several bismuth oxide containing films were removed from their solar cells using mercury vapor leaching, and an examination made of the exposed interface between the former film and solar cell. The SC-8A films were used for this purpose due to their higher bismuth oxide content, which should cause a magnification of the mechanisms at work in the SC-10Y films. Unfortunately, SEM and EDAX analysis of the interfaces revealed only the silicon surface. However, EDAX analysis also did not detect bismuth in films containing a known bismuth content. It can therefore be concluded that EDAX analysis is not a viable detection method for small amounts of bismuth in MOD films. There was some minor evidence that the silicon surface had been altered in texture and appearance, but these changes could not be qualified without further studies. Lacking a more sensitive and extensive evaluation of the interface, there are no experimental clues to guide the development of a theoretical model for adhesion.

Topographical studies were conducted on films of varying bismuth contents. All films were fired using standard firing sequence No. 1. Figure 4.3 shows some of the results for 1 layer films made from inks SC-1Y (0% Bi), SC-10Y (1% Bi), SC-9Y (3% Bi) and SC-8Y (5% Bi). One obvious effect of the bismuth addition was to decrease the overall porosity and the size of the remaining pores in the films. With bismuth present, a stronger and more uniform bond develops between the silver films and the substrate, which leads to shrinkage in the z direction only during sintering. The microstructures of films made from inks SC-10Y (1% Bi) and SC-8Y (5% Bi) were very similar, so further microstructural studies concentrated on SC-10Y films because of their equivalent adhesion and lower sheet resistance. Figure 4.4 shows a comparison of 2 layer films made from inks SC-1Y and SC-10Y, and the reduced porosity with 1% Bi addition is even more evident. The 1 and 2 layer films with 1 % Bi addition had very similar topography (Figures 4.3b and 4.4b), whereas the layer pure silver films (Figure 4.4a) had much higher porosity than the 1 layer (Figure 4.3a). The bismuth addition definitely provides better bonding to the silicon which prevents extensive shrinking in the x and y directions during sintering.

4.6 Additional Studies with Ink SC-10Y

4.6.1 Fired Film Properties

Additional studies with single and multi-layer films made from ink SC-10Y were conducted after the encouraging long term adhesion results were obtained. The thermogram and important properties of this ink are shown on Fig. 4.5. All films were printed on the same lot (346-208) of

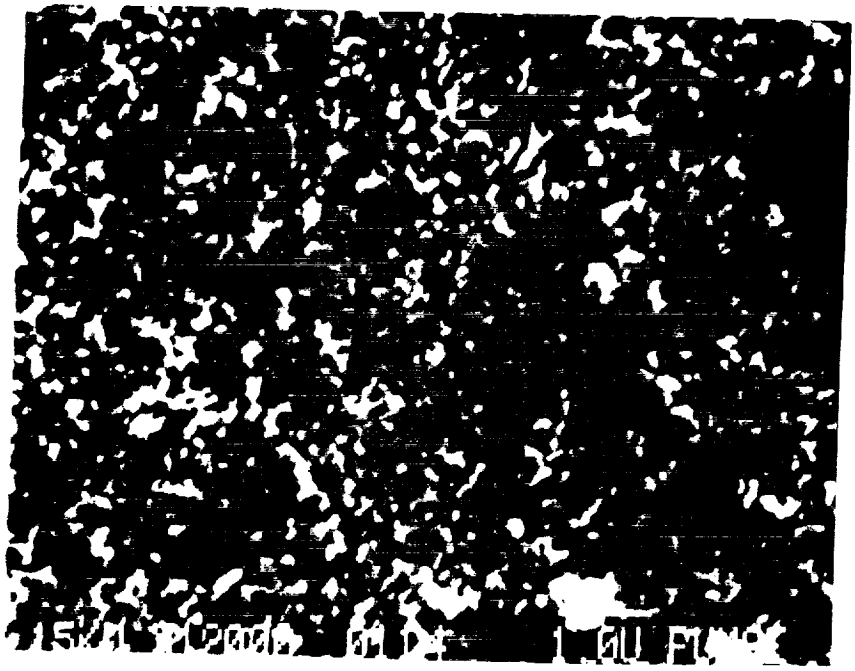
(a) 0% Bi

(b) [illegible]

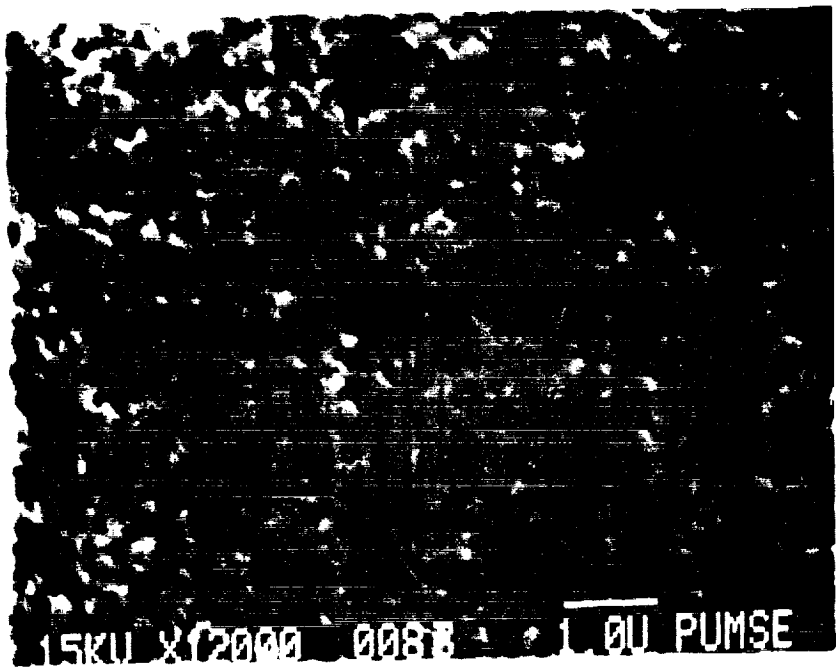
(c) 3% Bi

(d) 5% Bi

Figure 4.3 Microstructure of 1 Layer Silver Films with Varying Bismuth Content (12,000X).



(a) 0% Bi



(b) 1% Bi

Figure 4.4 Microstructure of 2 Layer Silver Films with 0 and 1% Bismuth Addition (12,000X).

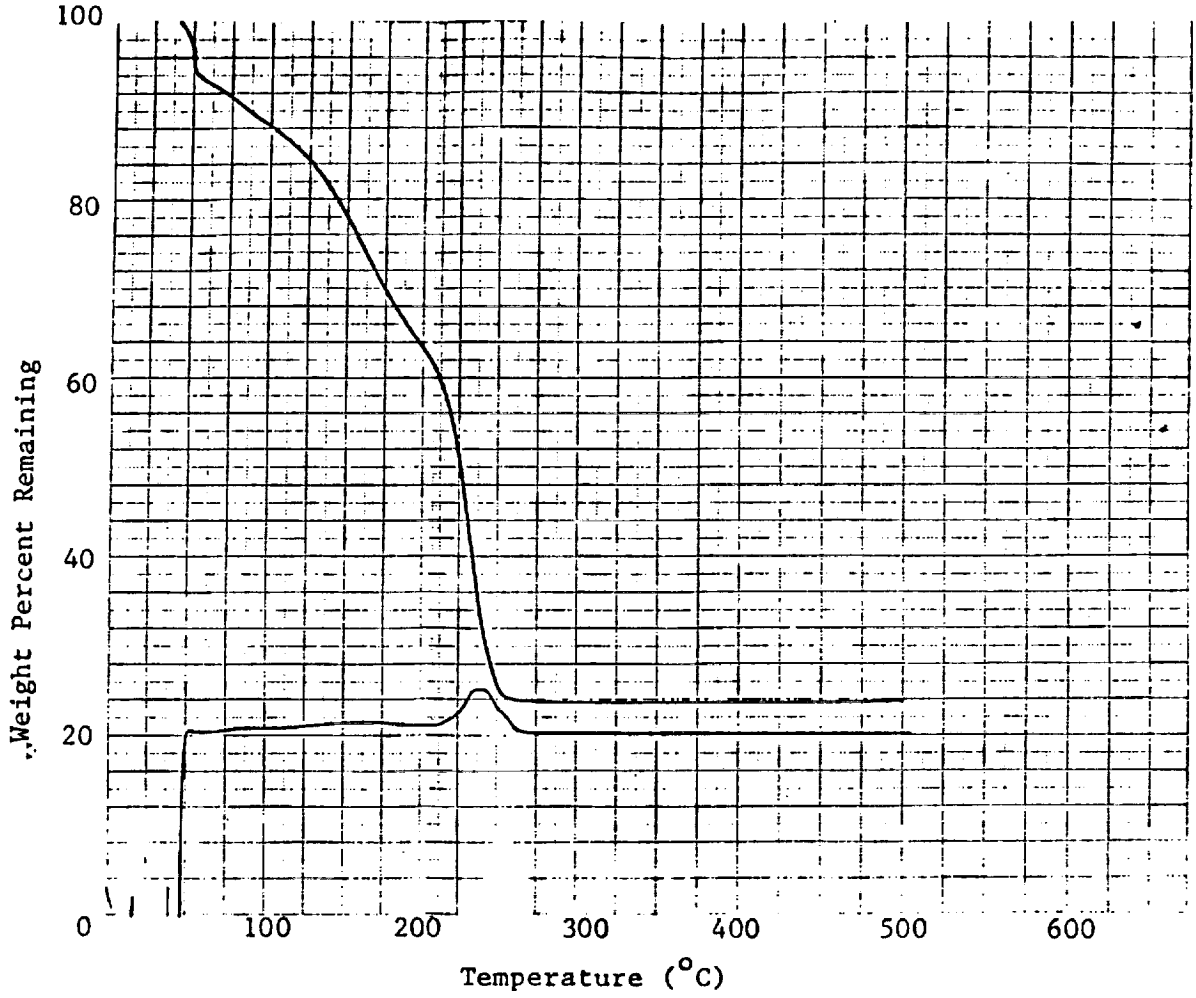


Figure 4.5 Thermogram of ink SC-10 at 10°C/minute

Important Properties

Theor. Fired Film Composition: 99 w/o Ag - 1 w/o Bi

T_D: 257°C

Inorganic Content: 23.6 w/o

solar cells which were cleaned in HF prior to printing. Some of the films were fired using standard firing sequency No. 1, while others were fired using a cycle that was 3 times as long.

Some fired film properties for films made from ink SC-10Y are presented in Table 4.20. The most important, but unexpected, result was the excellent solder leach resistance and solderability of the two SC-10B films which were tested. Fluxing was done using a 15:1 dilution of Alpha 611 flux, which was suitably mild for fluxing the MOD films made from ink SC-10Y, whereas this concentration of flux attacked the Ag/Pt films (see Section 4.4.2). The solder pot temperature was held at 203 ^{o}C ± 12^{o}C and the films were dipped once for 10 seconds. Unfluxed SC-10B films showed no leaching but only 20% solder acceptance, while the fluxed SC-10B films showed 100% solder leach resistance and solder acceptance. One of the anticipated drawbacks to films fabricated with ink SC-10Y was a lack of solder leach resistance, since there was no platinum in the films. These results suggest that the bismuth oxide promotes solder leach resistance as well as long term adhesion, and that platinum will not be needed in the final ink. This makes ink SC-10Y an even more viable candidate for photovoltaic metallization. In addition, it will be easier to keep the film sheet resistance low if platinum is not needed.

The other important results for films made from ink SC-10Y were those for the multi-layer films produced in test Nos. 5-9 in Table 4.20. These films were fired using a much slower firing cycle (similar to that used in test No. 4 for the 3 layer films in Table 4.18) than that employed under standard firing sequence No. 1. Not only did the films

Table 4.20 Properties of Films Fabricated from Ink SC-10Y.

Test No.	Ink No.	No. of Layers	Line Defin.	No. of Samples	Sheet Resist. (mΩ/sq)	Initial Adhesion	Solderability[a] % Solder Accept.	Solderability[a] % Solder Leach Resist.
1	SC-10B (2 days)	1	A/B	9	37.5 ± 1.1	excellent	100	100
2	SC-10B (2 days)	2	B	1	21.1	excellent except for poor on ½ of bus bar	100	100
3	SC-10B[b] (28 days)	1	B	6	41.6 ± 1.2	not checked	-	-
4	SC-10B[b] (28 days)	2	B	4	24.3 ± 0.7	not checked	-	-
5[c]	SC-10C	1	A	4	56.6 ± 5.3	excellent	-	-
6	SC-10C	2	A	4	29.7 ± 2.2	excellent	-	-
7	SC-10C	3	B	4	19.9 ± 1.1	excellent	-	-
8	SC-10C	4	B/C	4	15.0 ± 0.6	excellent	-	-
9	SC-10C	5	B/C	4	13.6 ± 0.8	excellent	-	-

(a) Films were successfully fluxed in a 15:1 methanol dilution of Alpha 611 flux prior to solder dipping.

(b) Films sent to JPL for photovoltaic evaluation. For this reason they were not adhesion tested.

(c) Tests 5-9 involved slow firing as opposed to std. firing sequence No. 1. A drying step of 65°C for 30 mins. was conducted only between multiple layers.

not crack, including those with 5 layers, but the adhesion remained excellent and the 5 layer sheet resistance was nearly 80% less than that for single layer films. (This is the theoretical decrease in sheet resistance expected when the thickness is increased by a factor of five.) The slower firing sequence either provides annealing of the ductile silver films thereby relieving the stresses which had previously caused cracking, or it allows for removal of the gaseous decomposition products at a rate slow enough to prevent film cracking. The one negative quality to these multi-layer films was their lack of acceptable line definition for 4 and 5 layer films. This was a result of ink rheology, which can be corrected by using slightly different ink rheologies for the upper layers. These results were very promising, since the 5 layer sheet resistance was the lowest obtained for any films evaluated during this study.

4.6.2 Photovoltaic Evaluation

Single and double layer films fabricated with ink SC-10B (28 days) were sent to JPL for photovoltaic evaluation. According to JPL, the as-received solar cells had high shunt resistances, which were decreased considerably after grinding the edges. After edge grinding, all cells were evaluated both prior to and following a forming gas heat treatment at 400°C for ~30 minutes. This treatment is typically done on conventional, sintered silver contacts and was used in an attempt to enhance the performance of cells fabricated with the MOD silver contacts. Some of the important results from the JPL evaluation are summarized in Table 4.21. The efficiency values can be expected to increase by ~ 4% after

Table 4.21 Results from JPL's Photovoltaic Evaluation of MOD Silver Metallized Solar Cells Compared to Those of a Typical JPL Standard Cell.

Cell Description	V_{oc} (mv)	I_{sc} (mA)	Efficiency (%)	Fill Factor	Series Resist. (ohms)	Shunt Resist. (ohms)
JPL Standard[a]	573.0	123.2	13.3	0.752	0.275	81.5
Single Layer MOD Silver[b]	529.8	72.6	5.6	0.582	1.430	299.1
Single Layer MOD Silver[c]	530.4	72.6	6.1	0.633	1.171	99.4
Single Layer MOD Silver[c,d]	518.4	71.9	4.4	0.474	1.714	341.0
Two Layer MOD Silver[b]	520.5	58.0	2.6	0.350	3.783	18.4
Two Layer MOD Silver[c]	522.6	66.8	3.5	0.401	2.658	49.8
Two Layer MOD Silver[c,d]	515.2	66.2	4.1	0.484	1.645	385.2

(a) JPL Standard Cell with anti-reflective coating. Cells metallized with MOD silver do not have AR coating.

(b) As received from Purdue.

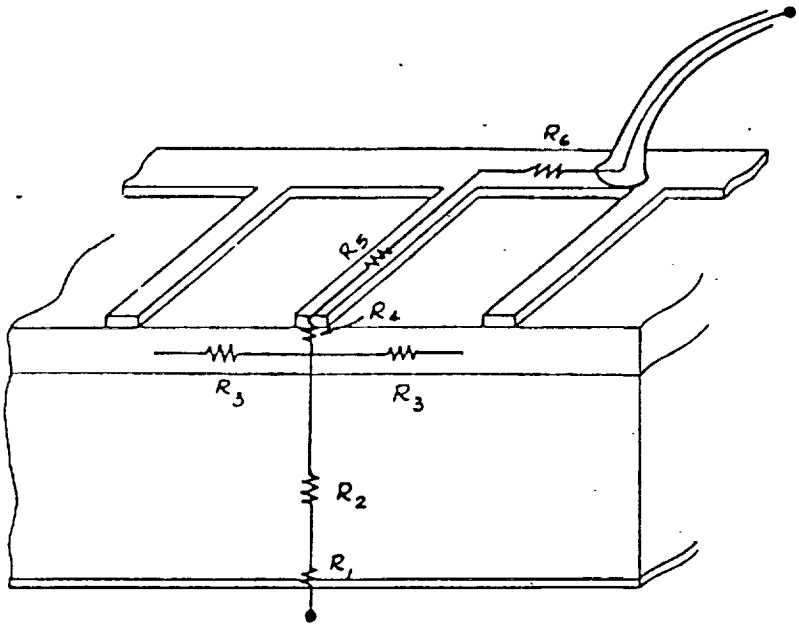
(c) After edge grinding to remove contamination.

(d) After treatment in forming gas to 400°C at 10°C/min for 30 minutes.

an anti-reflective coating is applied.

The most important result is the high series resistance of the MOD metallized cells compared to the standard JPL cell. The overall series resistance is a combination of six resistances as shown in Figure 4.6. Of special concern for the present project are the three resistances directly related to the front contact, namely, the series resistances in the fingers (R_5) and the bus bar (R_6), and the contact resistance (R_4) between the top metallization and solar cell surface. The series resistances R_5 and R_6 within the contact grid itself can be lowered by fabricating as thick and dense a film as possible. The 2 layer films in Table 4.21 had sheet resistances half those of the single layer films, which means that resistances R_5 and R_6 were half that of the single layer films, but the series resistance of the 2 layer films was twice that of the single layer films. This result is possibly due to an increase in R_4 for the two layer films. The contact resistance is directly related to adhesion, and all of the films had excellent adhesion, but the Scotch tape test is a threshold test. R_4 could have increased for the 2 layer films without causing a degradation in measured adhesion. Of the other three resistances in Figure 4.6, R_2 and R_3 are properties of the bulk silicon and would not be expected to change, which leaves only changes in R_1, the back contact resistance, as the other possibility to explain the results.

Qualitative experiments were conducted to investigate the possibility of changes in the back contact resistance during processing of the MOD conductors on the top surface. The back electrode consists of a thin Ti layer (sometimes Ti/Pd is used) covered with a thick silver



$$R_s = \sum_{i=1}^{6} R_i$$

R_1 = back contact R_4 = front contact

R_2 = bulk R_5 = grid lines

R_3 = diffused layer R_6 = bus lines

Figure 4.6 The Six Factors Contributing to the Overall Solar Cell Series Resistance.

film. Several as received cells were etched with dilute HNO_3 to remove the silver layer, and the Ti layer was found to have a low sheet resistance. Other cells were HF cleaned and fired using standard firing sequence No. 1, and then subjected to similar etching and resistance testing. Some of these cells still had a low resistance Ti layer, but for others the resistance was higher by a factor of 100 or more. Further experiments demonstrated that the HF cleaning was the primary source of the problem. Leaving cells from lots 346-206, 346-207 or 246-213 in the dilute HF for a few minues caused a complete loss of adhesion of the back electrode. The adhesion was stil excellent as measured by the Scotch tape test after the standard 10 second HF dip was used, but there were bubbles under the silver indicating some attack of the Ti layer had occurred. This result means that the resistance of the Ti layer would be extremely sensitive to the time in the HF etch, and variations of a few seconds could produce large changes. This variable increase in resistance of the Ti layer, and hence an increase in R_1, can explain the results in Table 4.21 which showed an increase in series resistance for 2 layer films when a decrease should have been observed. If the back contacts have to have a Ti layer, then the processing of the MOD films will have to be changed.

5. SPECIFICATIONS FOR INK FORMULATION

All of the chemicals and reagents used for formulating ink SC-10Y are listed in Table 5.1. Synthesize silver neodecanoate following the procedure given in Section 3.1.2, an store the white powder in a dark bottle with a tight fitting lid. Synthesize bismuth 2-ethylhexanoate

Table 5.1 Chemicals and Reagents for Formulating Ink SC-10Y.

Name	Formula	Source	Grade	Cost
Busmuth nitrate	$Bi(NO_3)_3 \cdot 5H_2O$	Mallinckrodt	Analytical Reagent	8.89/4 oz.
Nitric acid	HNO_3 (70%)	Fisher Scientific	Reagent A.C.S.	9.26/7 lb.
2-ethylhexanoic acid	$C_7H_{15}COOH$ (99%)	Aldrich	Reagent	7.85/1 kg.
Benzene	C_6H_6	Mallinckrodt	Spectr AR	4.40/Pt.
Neodecanoic acid	$C_9H_{19}COOH$ (95.2%)	Exxon	Prime	gift
Methanol	CH_3OH	Fisher Scientific	Spectroanalyzed Certified A.C.S.	3.33/qt.
Ammonium hydroxide	NH_4OH (58%)	Mallinckrodt	Analytical Reagent	5.57/4 lb.
Silver nitrate	$AgNO_3$ (99.9+%)	Alfa	A.C.S.	225.00/500 g
Butyl carbitol acetate	$C_{10}H_{20}O_4$	Fisher Scientific	Purified	50.90/4 liter

following the procedure given in Section 3.1.4, and store the benzene solution in a dark bottle with a tight fitting lid. Ink SC-10Y contains 30 w/o silver, and the amounts of the other ingredients are determined by the amount of silver neodecanoate used. The formulation procedure for 5 grams of ink (larger batches are scaled by weight) is as follows:

NOTE: Ag = silver

Bi = bismuth

AGND = silver neodecanoate

BI2EH = bismuth 2-ethylhexanoate

Bi_2O_3 = bismuth oxide

NDA = neodecanoic acid

BCA = butyl carbitol acetate

1. (30% Ag) X (5 g ink) = (1.5 g Ag) X $(\frac{100\ g\ AGND}{38.68\ g\ Ag})$ = 3.878 g AGND

2. Since AGND is a white power it is necessary to dissolve it in benzene so that a homogeneous ink formulation is achieved. It was determined that 2.63 g of benzene is required to dissolve each gram of AGND. Therefore, 10.199 g of benzene is used to dissolve 3.878 g of AGND.

3. The BI2EH in benzene soltuion is assayed by TGA to determine X, the number of grams of Bi_2O_3, produced per 100 grams of solution. The amount of Bi2EH solution needed in the ink which will produce fired films of composition 99% Ag/1% Bi is calculated as follows:

$$(3.878\ g\ AGND)\ X\ (\frac{38.68\ g\ Ag}{100\ g\ AGND})\ X\ (\frac{1\ g\ Bi}{99\ g\ Ag})\ X\ (\frac{100\ g\ BI2EH\ soln}{X\ g\ Bi_2O_3})X$$

$$\left(\frac{465.96 \text{ g } Bi_2O_3}{417.96 \text{ g Bi}}\right) = \frac{1.689}{X} \text{ g BI2EH solution.}$$

4. The amounts of BCA and NDA screening agents relative to the amount of AGND in the ink are calculated as follows:

$$\text{Amt. BCA} = (10.0\%) \text{ X } (3.878 \text{ g AGND}) = 0.3878 \text{ g}$$

and

$$\text{Amt. NDA} = (20.0\%) \text{ X } (3.878 \text{ g AGND}) = 0.7756 \text{ g}$$

5. The various ingredient materials are combined and thoroughly mixed and the solution transferred to the rotavapor. Upon application of a vacuum of 12-14 torr and 30-40^{o}C, the homogeneous solution undergoes solvent exchange (the majority of the benzene is evaporate in favor of the screen agents) and a smooth, homogeneous paste suitable for screen printing results.

Specifications cannot be written on the processing of the MOD inks. The screen printing parameters were not optimized, and the optimum firing parameters are uncertain due to the possible degredation of the back contact during standard firing sequence No. 1, as discussed in Section 4.6.2.

6. DATA FOR SAMICS EVALUATION

All items on Format A - Process Description were addressed, and a disucssion of how the various values were obtained is included. There is still a considerable uncertainty in the optimum firing sequence for the MOD silver films, but the data were calculated based on the use of standard firing Sequence No. 1.

SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

FORMAT A — PROCESS DESCRIPTION

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Dr. / Pasadena, Calif. 91103

A-1 Process [Referent]

Note: Names given in brackets [ ] are the names of process attributes requested by the SAMIS computer program.

A-2 [Descriptive. Name] of Process: Screen Printed MOD Silver Metallization

PART 1 – PRODUCT DESCRIPTION

A-3 [Product. Referent]: AGCOND

A-4 Descriptive Name [Product. Name]: Silver Conductor on Silicon Solar Cell

A-5 Unit Of Measure [Product. Units]: 5 CM Cells

PART 2 – PROCESS CHARACTERISTICS

A-6	[Output. Rate] (Not Thruput)	5.5	Units (given on line A-5) Per Operating Minute
A-7	[Inprocess. Inventory. Time]	64.4	Calendar Minutes (Used only to compute in-process inventory)
A-8	[Duty. Cycle]	0.93	Operating Minutes Per Minute
A-8a	[Number. Of. Shifts. Per. Day]	3	Shifts
A-8b	[Personnel. Integerization. Override. Switch]	On	(Off or On)

PART 3 – EQUIPMENT COST FACTORS (Machine Description)

A-9	Component [Referent]	Printer	Kiln	
A-9a	Component [Descriptive. Name]	Screen Printer with Auto Loading	Belt Furnace with Auto Deloading	
A-10	Base Year For Equipment Prices [Price. Year]	1985	1985	
A-11	[Purchase. Cost. Vs. Quantity. Bought. Table] (Number Of and $ Per Component)	58,000	47,000	
A-12	Anticipated [Useful. Life] (Years)	5	5	
A-13	[Salvage. Value] ($ Per Component)	4,000	4,000	
A-14	[Removal. And. Installation. Cost] ($/Component)	1,000	1,000	

Note: The SAMIS computer program also prompts for the [Payment. Float. Interval], the [Inflation. Rate. Table], the [Equipment. Tax. Depreciation. Method], and the [Equipment. Book. Depreciation. Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

A-15 Process Referent (From Front Side Line A-1) MODAG

PART 4 – DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)

[Facility. Or. Personnel Requirement]

A-16 Catalog Number (Expense Item Referent)	A-18 Amount Required Per Machine (Per Shift) [Amount. Per. Machine]	A-19 Units	A-17 Requirement Description or Name
A2096D	100	Sq. Ft./M	Floor Space, Production
B3752D	1.0	Person/M	Operator-Production Machine

PART 5 – DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)

[Byproduct] and [Utility. Or. Commodity Requirement]

A-20 Catalog Number (Expense Item Referent)	A-22 Amount Required Per Machine Per Minute [Amount. Per. Cycle]	A-23 Units	A-21 Requirement Description or Name
C1032B	0.216	kWh/Mm	Electricity
C2032D	46	Cu. Ft./Mm	Compressed Air
	0.00709	$/Mm	Silver Ink
D1D	0.002116	Cu. Ft./Mm	Fumes, Ventilation Required
E1578D	0.0006	Screen/Mm	Screen, SS 200 Mesh
E1624D	0.0006	Squeegee/Mm	Squeegees
EG4D	0.000044	Gal./Mm	Toluene

PART 6 – INTRA-INDUSTRY PRODUCT(S) REQUIRED

A-24 [Required. Product] (Reference)	A-28 [Yield] * (%)	A-26 [Ideal. Ratio] ** Of Units Out/Units In	A-27 Units Of A-26***	A-25 Product Name
SI Wafer	90	1.0	Cells/Wafer	Metallized Cell

PREPARED BY

DATE

*100% minus percentage of required product lost in this process.

**Assume 100% yield here.

***Examples: Modules/Cell or Cells/Wafer.

Explanation of Data in Format A

PART 1 - MODAG PRODUCT DESCRIPTION

The process for metallo-organic decomposition (MOD) silver metallization of silicon photovoltaic cells involves screen printing of a MOD ink onto the silicon cells followed by drying and firing. A cell size of 5 cm X 5 cm (or circular 5 cm diameter) was assumed. An automatic process with magazine loading and deloading is specified.

PART 2 - MODAG PROCESS CHARACTERISTICS

A-6 Output Rate = 5.5 cells/min.

The output rate was determined by the belt furnace selected and the cycle time required. The furnace has a heated length of 2.5 m and an overall length of 2.75 m, and the belt is 32 cm wide. The process requires a 1 hour firing cycle so the belt speed must be 275/60 = 4.58 cm/min. With 6 cells across the belt this gives an output rate of 4.58 X 6/5 = 5.5 cells/min.

A-7 Inprocess Inventory Time = 64.4 min.

The cells move a total of 1.2 m in traversing the screen printer. For a 5 cm cell moving at the rate of 5.5 cells/min. the time in the screen printer will be 4.4 min. This added to the firing time of 60 min. gives the inprocess time. Note that the time the cells spend in the magazines before auto laoding to the screen printer or after auto deloading from the belt furnace was not

included in the total inprocess inventory time becuase this could vary from minutes to many hours depending on the delivery schedules for blanks and finished cells.

A-8 Duty Cycle = 0.93

A down time of 5% is a conservative estimate for an automated screen printer. The belt furnace will be shut down for cleaning once a month for one shift. Assuming 1 hour for cooling and 1 hour for temperature stabilization after cleaning gives a total down time of 10 hours per month. For 3 shifts, 5 days a week this is approximately 2% down time.

A-8a Number of Shifts Per Day = 3

Arbitrary assumption.

A-8b Personnel Integerization Override Switch = On

An operator must be in attendance at all times.

PART 3 - MODAG EQUIPMENT COST FACTORS

A-9a Component

The printer specified is a Model CP645 from Presco Division/AMI, North Branch, NJ. The belt furnace is a custom made unit from BTU Engineering Corp., N. Billerica, MA.

A-11 Purchase Cost

These numbers were given over the telephone by sales engineers

at Presco and BTU. The basic price of the printer is $24,000, the magazine loader is $26,000, and the unit to put the single row of parts emerging from the printer into rows of up to 10 across is $8,000, for a total printer cost of $58,000. The custom belt furnace is estimated to cost $21,000 and the magazine deloader is $26,000 for a total of $47,000.

A-12 Anticipated Useful Life (years) = 5

Arbitrary assumption.

A-13 Salvage Value ($/Component) = $4,000

Arbitrary assumption.

A-14 Cost of Removal and Installation = $1,000

Arbitrary assumption.

PART 4 - MODAG DIRECT REQUIREMENTS PER MACHINE

Floor Space

Magaine Loader (4' X 4')	16
Printer (4' X 4')	16
Belt Furnace (26' X 2')	52
Magazine Deloader (4' X 4')	16
	---
	100 ft.^{2}

Operator

One operator per shift per machine is required.

PART 5 - MODAG DIRECT REQUIREMENTS PER MACHINE PER MINUTE

Electricity

The printer requires 2.2 kW, the loader and deloader 0.88 kW each and the belt furnace 9.0 kW, for a total of 12.96 kW, or 12.96/60 = 0.216 kWh/Mm.

Compressed Air

The printer requires 10 ft./min., the magazine loader and deloader 8 $ft.^3$/min. each, and the belt furnace 20 $ft.^3$/min, for a total of 46 $ft.^3$/min.

Silver Ink SC-10Y

It was assumed that the grid pattern was 6 mil lines, 2" long with 0.15" spacing and that there were two bus bars 20 mil wide and 2" long. Assuming a printed film thickness of 1 mil this gives 0.00394 cm^3 of ink per cell. With a specific gravity of 1, thic volume gives 1.181×10^{-3} g Ag and 1.193×10^{-5} g Bi per cell. Using the cost data given in Table 5.1 and the synthesis yield data given in Sections 3.1.2 and 3.1.5 gives a chemical cost per cell of 6.444×10^{-4} dollars. Assuming a labor cost equal to the materials cost gives an ink cost of $1.28 \times 10^{-}$ dollars per cell, and with an output rate of 5.5 cells per minute a cost of 0.00709 dollars per machine minute.

Fumes, Ventilation Required

With 3.94×10^{-3} g of ink per cell there will be $0.70 \times 3.94 \times 10^{-3} = 2.76 \times 10^{-3}$ g of organic matter per cel (the ink contains 30 w/o Ag). If it assumed that the organic matter is $C_{10}H_{22}$, then 2.26×10^{-3} g corresponds to 1.942×10^{-5} moles. Each mole of $C_{10}H_{22}$ combusted produces 10 moles of CO_2 and 11 moles of H_2O, so $21 \times 1.942 \times 10^{-5} = 4.079 \times 10^{-4}$ moles of gas will be produced per cell. Using the ideal gas law (PV = nRT) at standard pressure and temperature gies 9.979×10^{-3} ℓ or 3.536×10^{-4} ft.^{3} of fumes per cell. At a production rate of 6 cells/minute this gives 0.002116 ft. fumes per machine minute.

Screens and Squeegees

It was assumed that the screen and squeegee would be replaced after 10,000 prints. At a production rate of 6 cells/min. this gives 0.0006 screens and squeegees per machine minute.

Toluene

The toluene is used for cleaning screns, and it was assumed that the screen would be cleaned once an hour using 10 ml toluene. A rate of 10 ml/hr corresponds to 0.000044 gal/min.

PART 6 - MODAG INTRA-INDUSTRY PRODUCT REQUIRED

A-28 Yield (%) = 90

Arbitrary estimate.

APPENDIX

Thermograms of Metallo-Organic Compounds and Inks

A1. Silver monomethyl succinate

A2. Silver 2-ehtylbutyrate

A3. Silver 2-ethylhexanoate

A4. Silver neopentanoate

A5. Solid silver neodecanoate

A6. Platinum amine -2ethylhexanoate in benzene

A7. Diglycine platinum (II)

A8. Platinum 2,4-pentanedionate

A9. Platinum-bis-dimethylglyoxime

A10. Platinum 2-ethylhexanoate in benzene

A11. Boron-bis-n-propoxy-2-ethylbutyrate

A12. Boron-n-propoxy-diacetate

A13. Ethoxy-silicon-tri-2-ethylhexanoate

A14. Bismuth 2-ethylhexanoate in benzene

A15. Cr-2-ethylhexanoate solid

A16. Chromium 2,4-pentanedionate

A17. Ni-2-ethylhexanoate

A18. CO-2-ethylhexanoate in mineral spirits

A19. Neodecanoic Acid

A20. Butyl Carbitol Acetate

A21. Ink SC-1Y

A22. Ink SC-2Y

A23. Ink SC-3Y

A24. Ink SC-4Y

A25. Ink SC-5Y

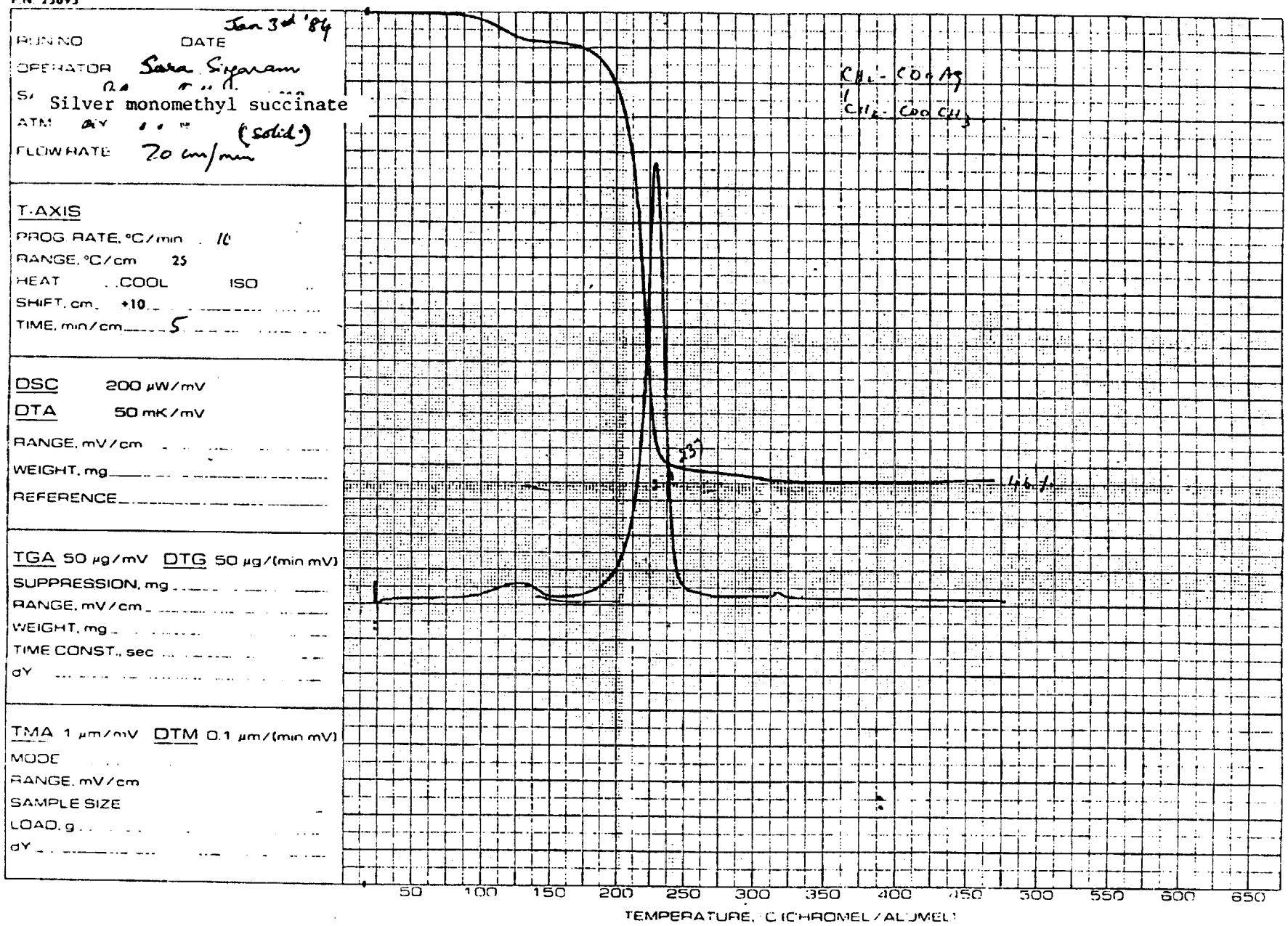
A26. Ink SC-6Y

A27. Ink SC-7Y

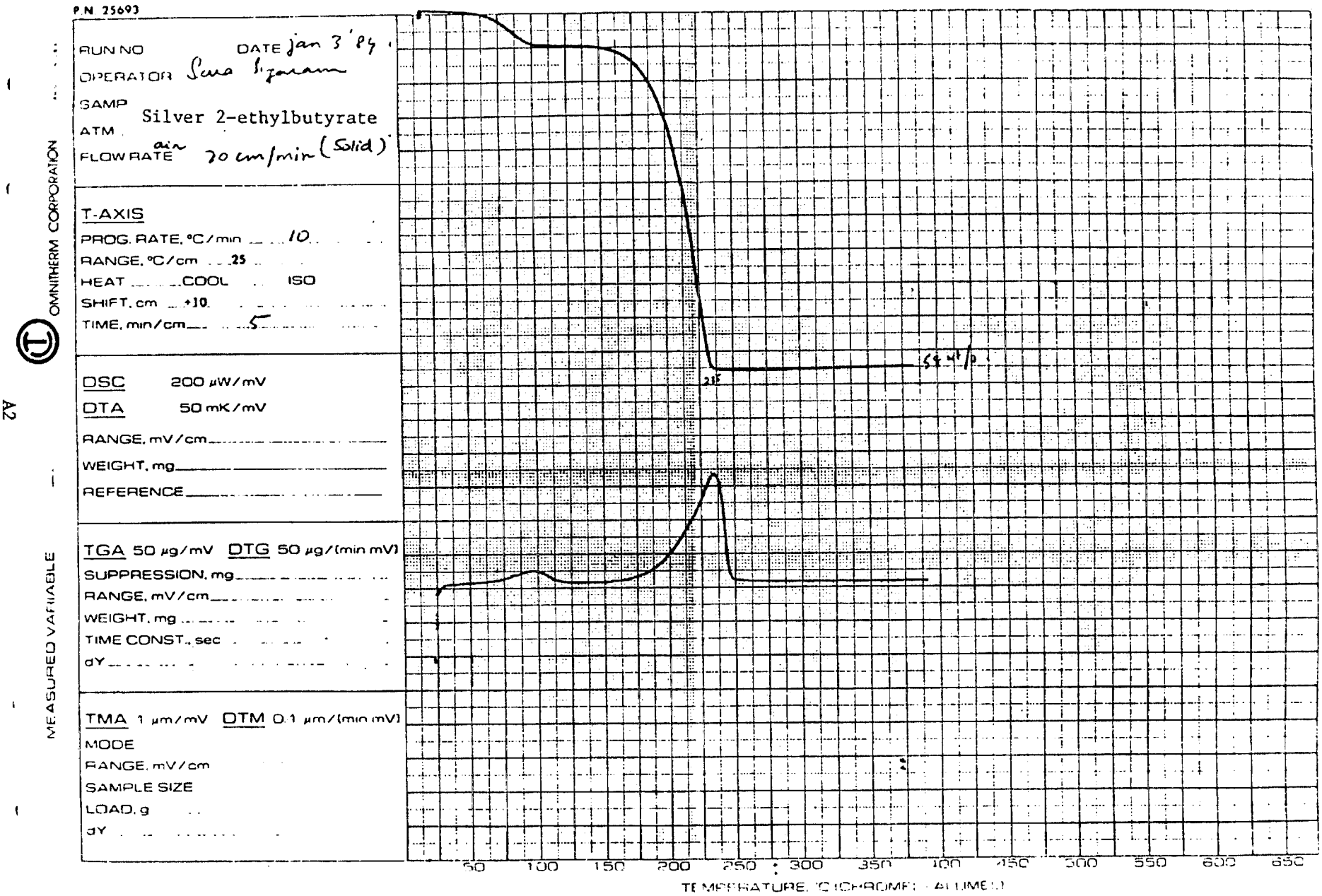
A28. Ink SC-8Y

A29. Ink SC-9Y

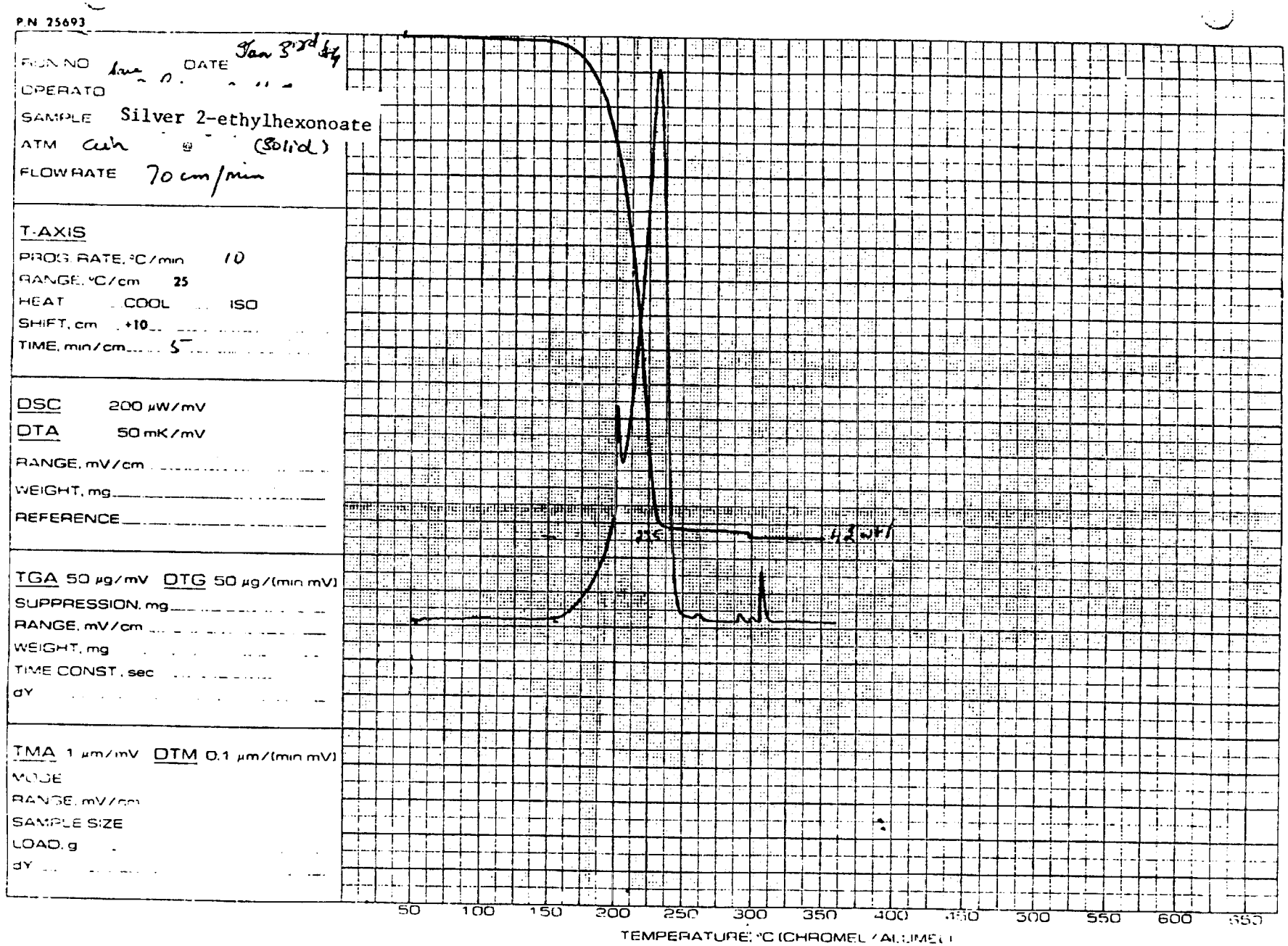
A30. Ink SC-10Y



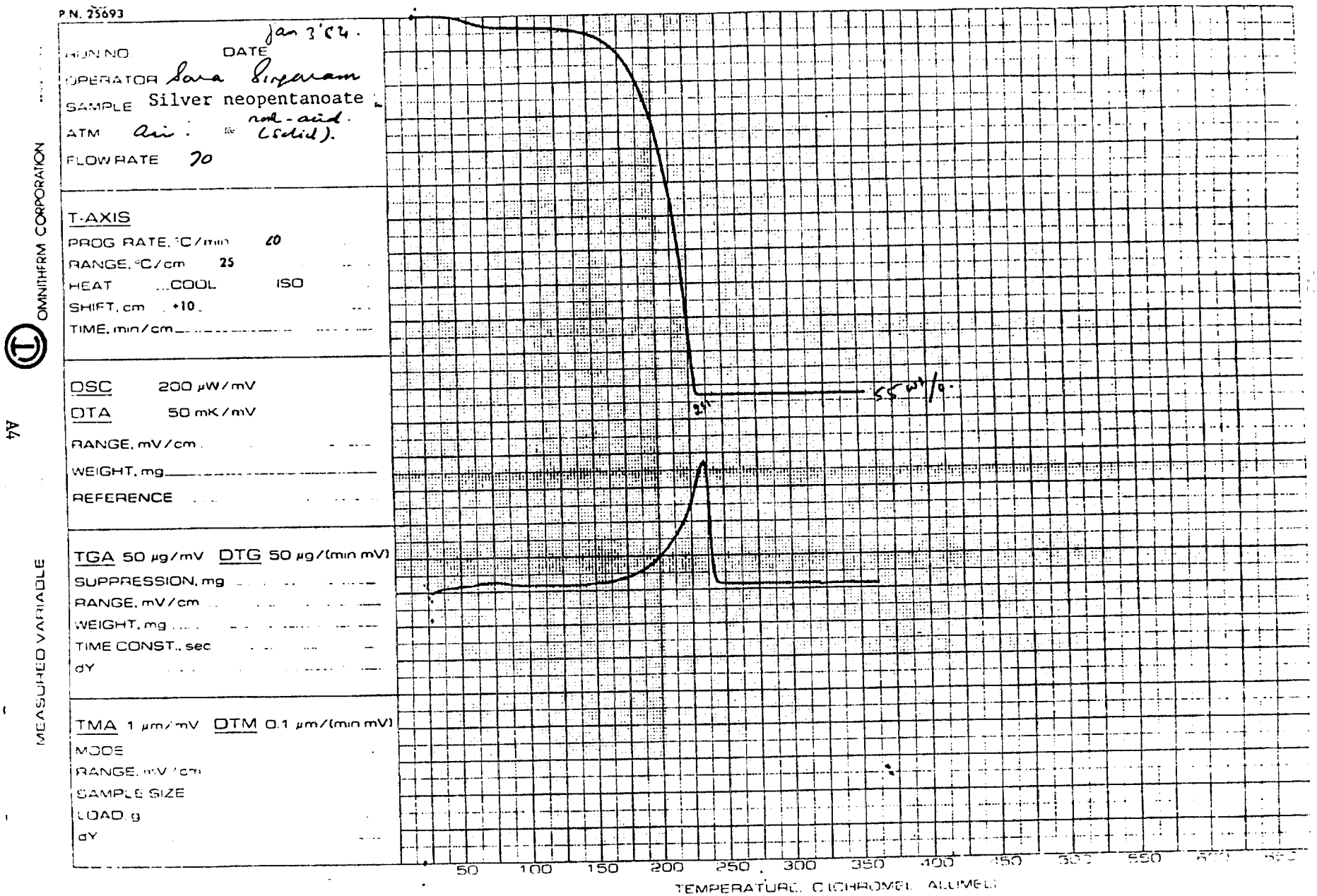
Thermogram of Silver Monomethyl Succinate.



Thermogram of Silver 2-ehtylbutyrate.



Thermogram of Silver 2-ethylhexanoate.



Thermogram of Silver Neopentanoate.

A5

OMNITHERM CORPORATION

RUN NO. DATE 1/5/84

OPERATOR

SAMPLE Solid Silver Neodecanoate

ATM Air @

FLOW RATE 70 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, sec/cm

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 µg/mV DTG 50 µg/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

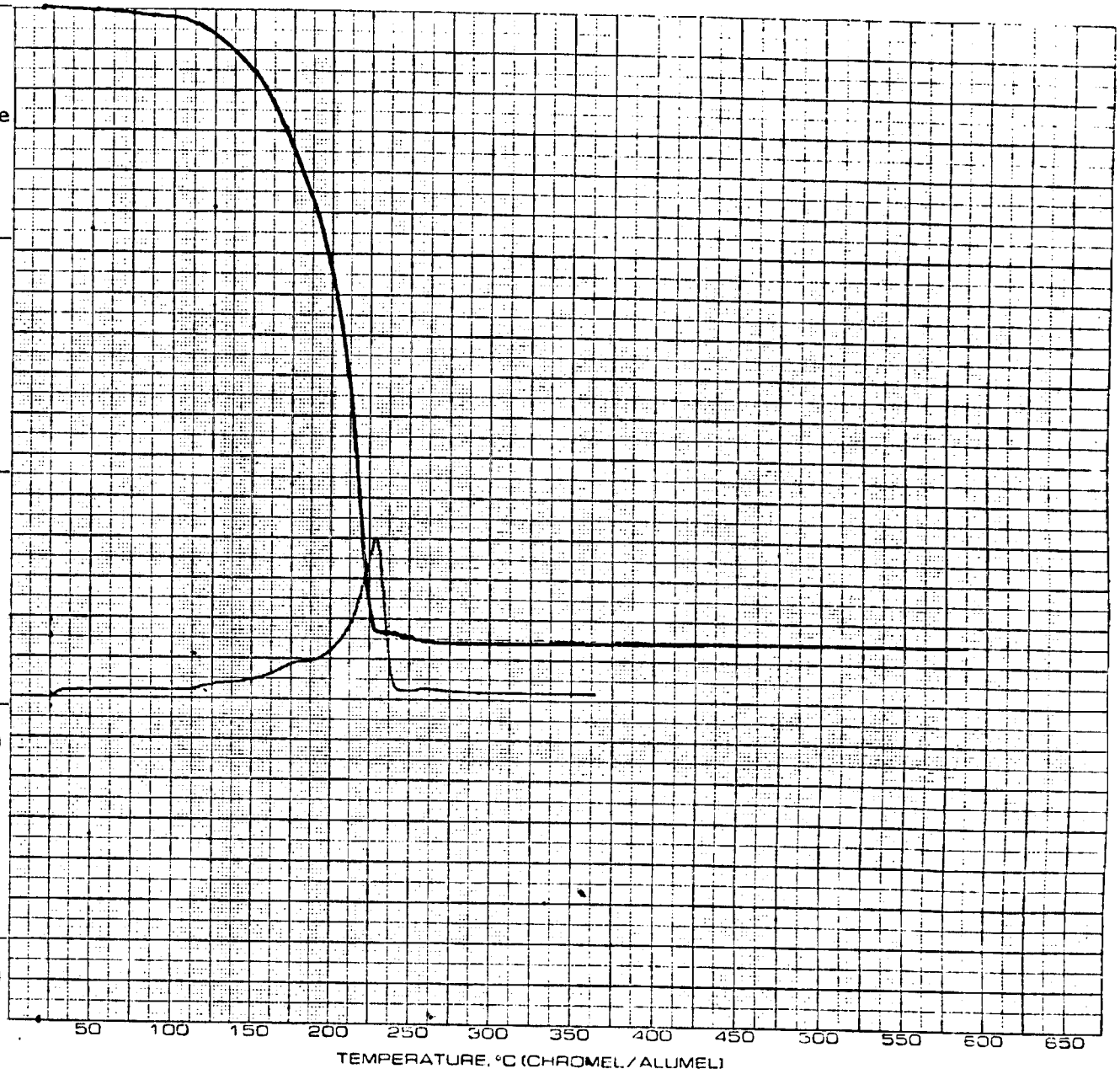
WEIGHT, mg

TIME CONST., sec

TMA mV DTM 0.1 µm/(min mV)

mV/cm

SIZE



DATE 3/30/84

OPERATOR

SAMPLE Platinum amine 2-ethylhexanoate in benzene

ATM Air

FLOW RATE 70 cc/min.

T-AXIS

TYPE 3 RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME min/cm

DSC 200 uW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 31 [illegible]/mV DTG 50 µg/(min mV)

Y1 DEPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONSTANT, sec

[illegible] mV DTM 0.1 µm/(min mV)

10 wt% Pt

100 200 300 400 500 600 700 800 900 1000 1100

TEMPERATURE, °C

A6

RUN NO. DATE 4/23/84

OPERATOR

SAMPLE Diglycine Platinum(II)

ATM Air @

FLOW RATE 70 cc/min.

T-AXIS

PROG RATE, °C/min. 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, min/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

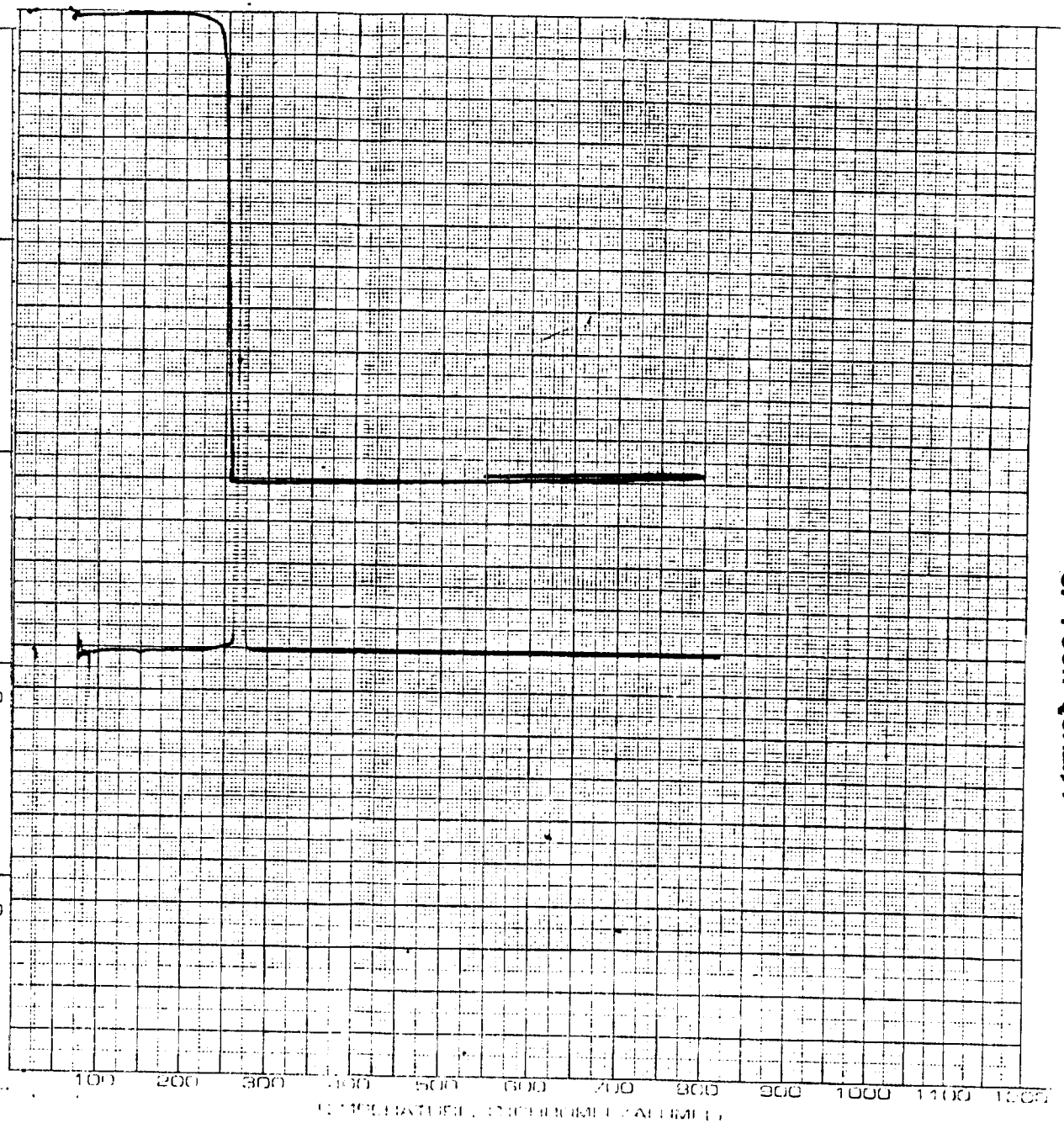
SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA DTM 0.1 μm/(min mV)



OMNITHERM CORPORATION

DATE 3/30/84

OPERATOR

SAMPLE Platinum 2,4-pentanedionate

ATM Air

FLOW RATE 70 cc/min

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, min/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

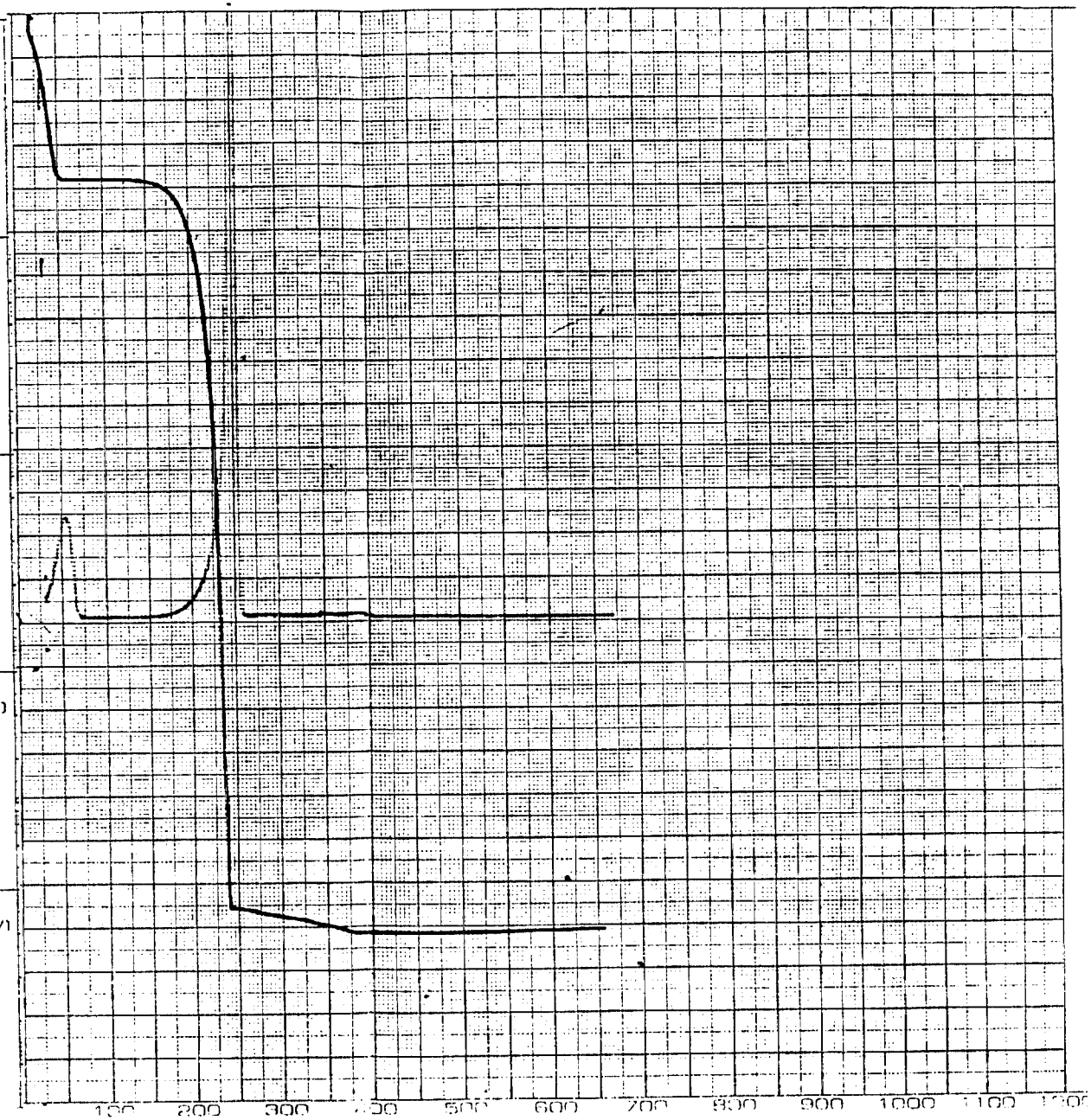
SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

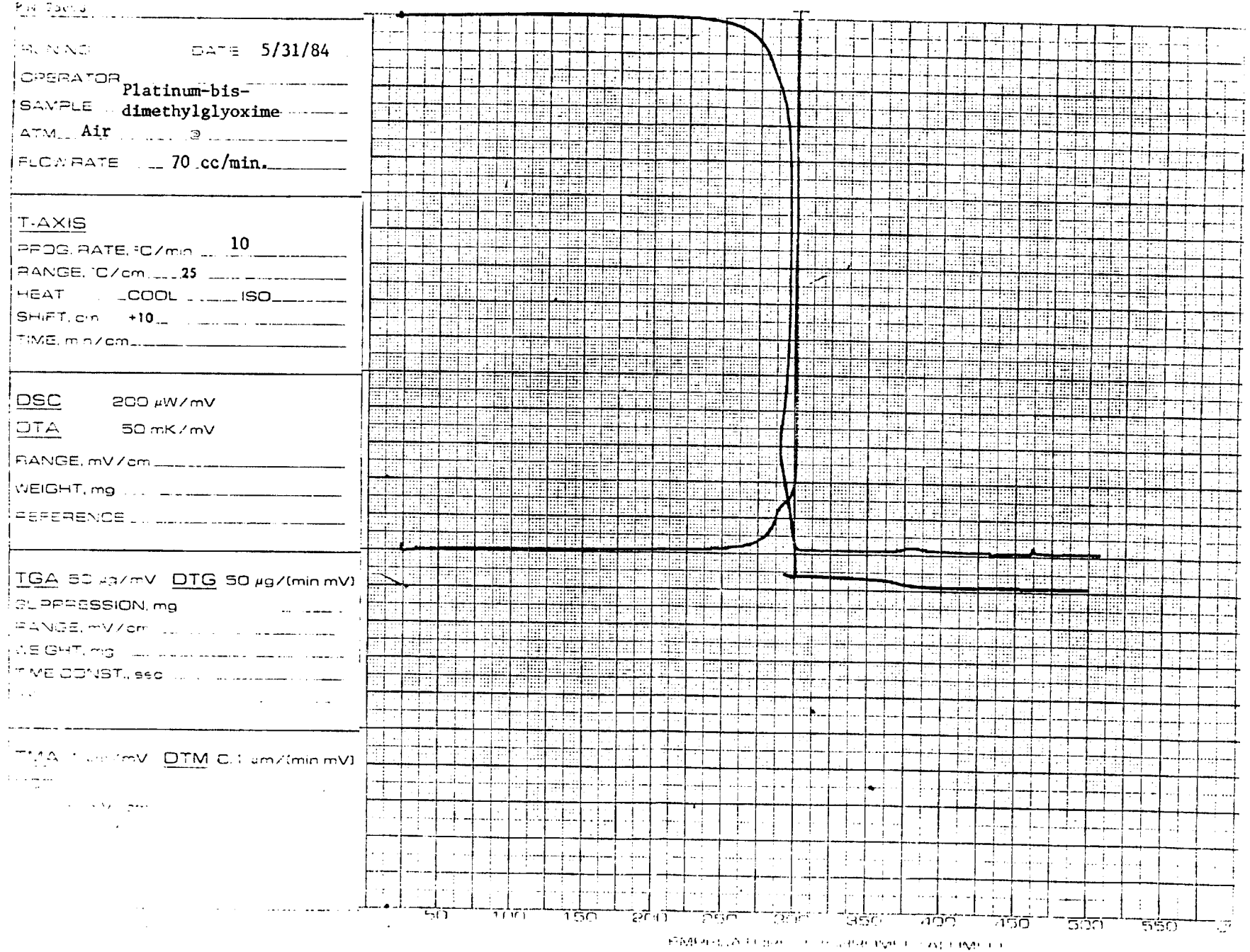
TMA mm/mV DTM 0.1 μm/(min mV)



TEMPERATURE - THERMOELECTRIC ALUMEL

OMNITHERM CORPORATION

A8



OMNITHERM CORPORATION

A9

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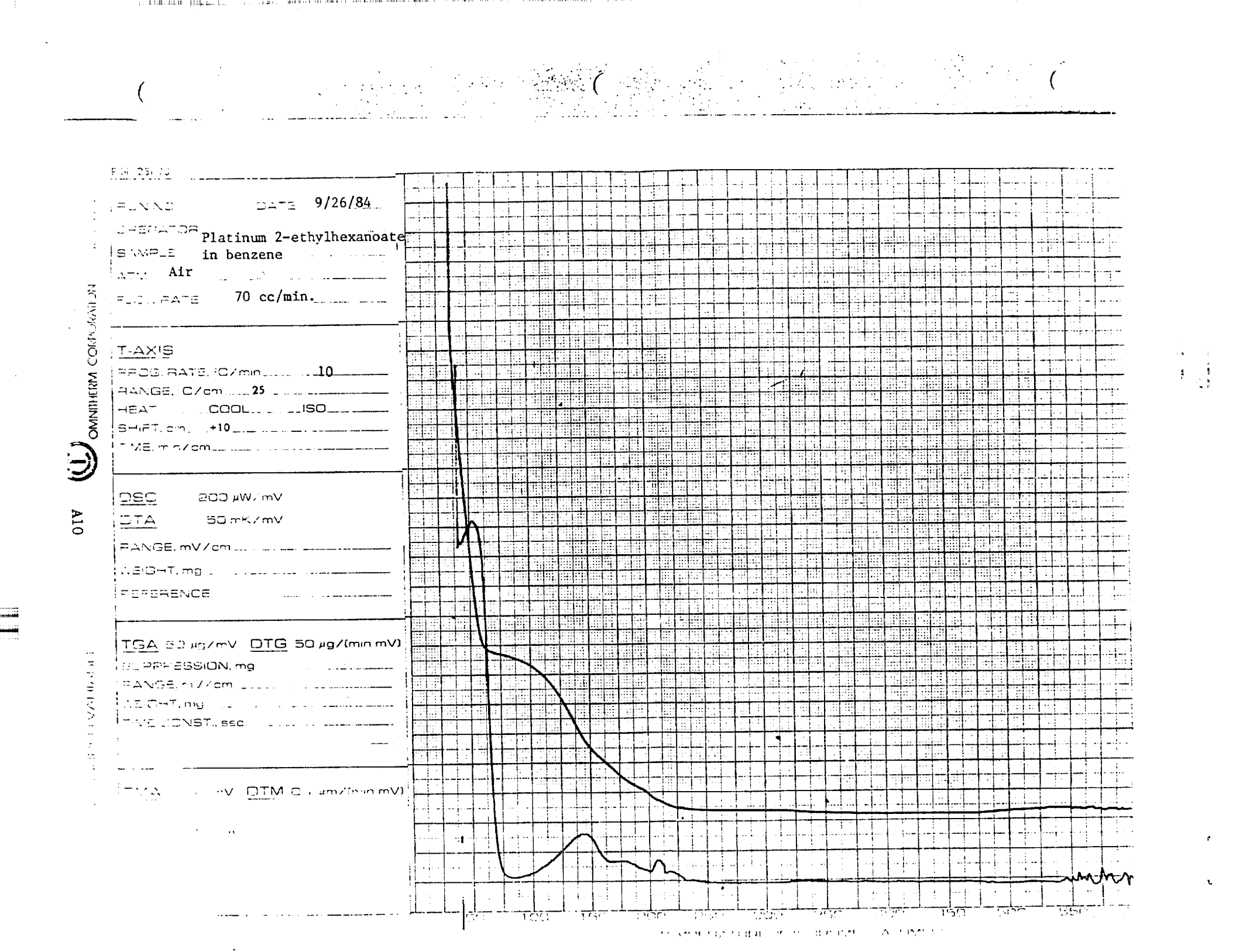

FUNNO
DATE 9/26/84
OPERATOR
SAMPLE Platinum 2-ethylhexanoate in benzene
ATM Air
FLOW RATE 70 cc/min.
T-AXIS
PROG. RATE, °C/min 10
RANGE, °C/cm 25
HEAT COOL ISO
SHIFT, cm +10
TIME, min/cm
DSC 200 μW/mV
DTA 50 mK/mV
RANGE, mV/cm
WEIGHT, mg
REFERENCE
TGA 50 μg/mV DTG 50 μg/(min mV)
SUPPRESSION, mg
RANGE, %/cm
WEIGHT, mg
TIME CONST., sec
DTMA mV DTM 0.1 μm/(min mV)
OMNITHERM CORPORATION
A10

ORIGINAL PAGE IS
OF POOR QUALITY

P.N. 25693

RUN NO. DATE 10/25/83

OPERATOR

SAMPLE Boron-n-propoxy-diacetate

ATM Air

FLOW RATE 95 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 mg/mV DTG 50 μg/(min mV)

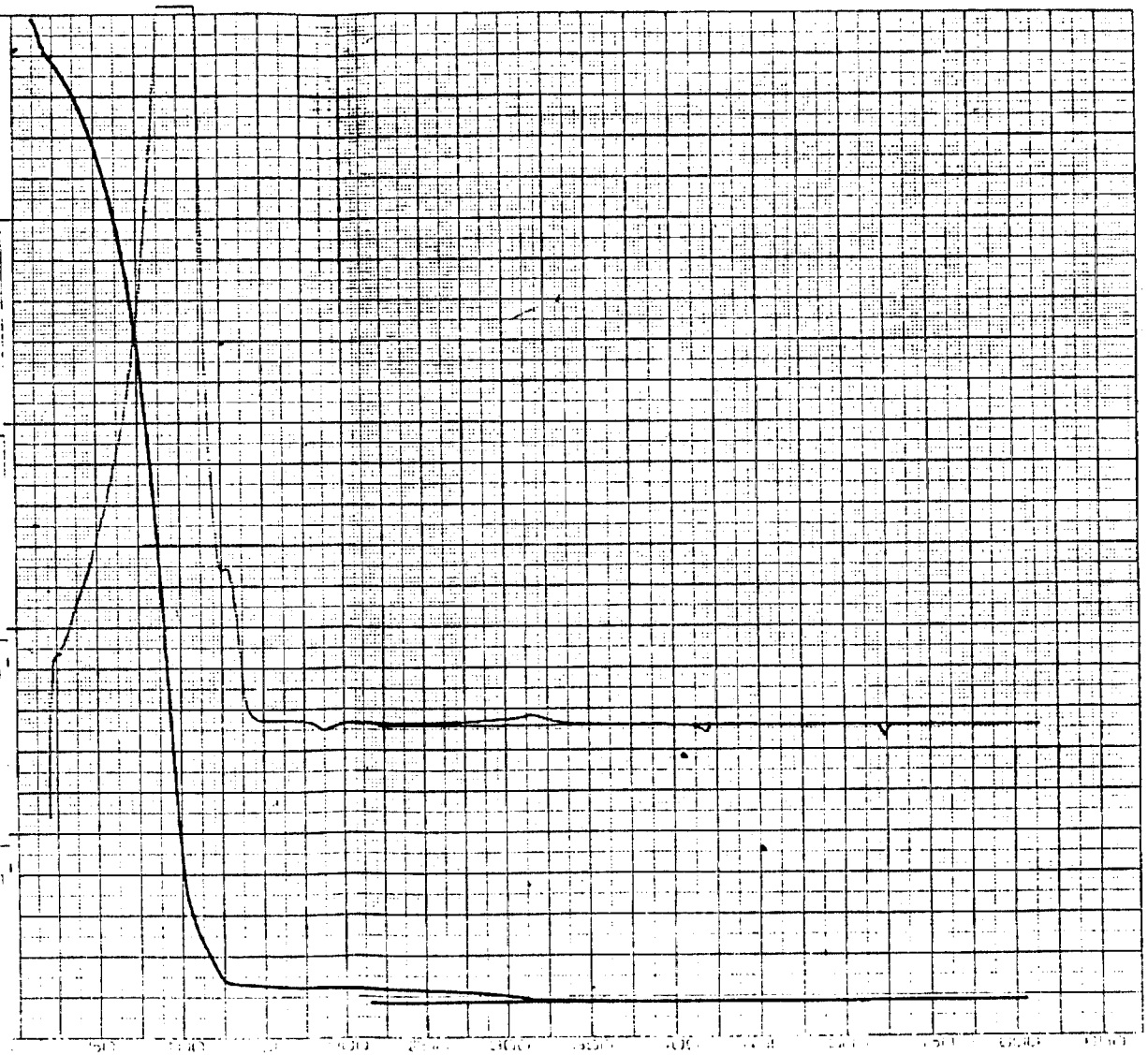
SUPPRESSION, mg

RANGE, mg/cm

WEIGHT, mg

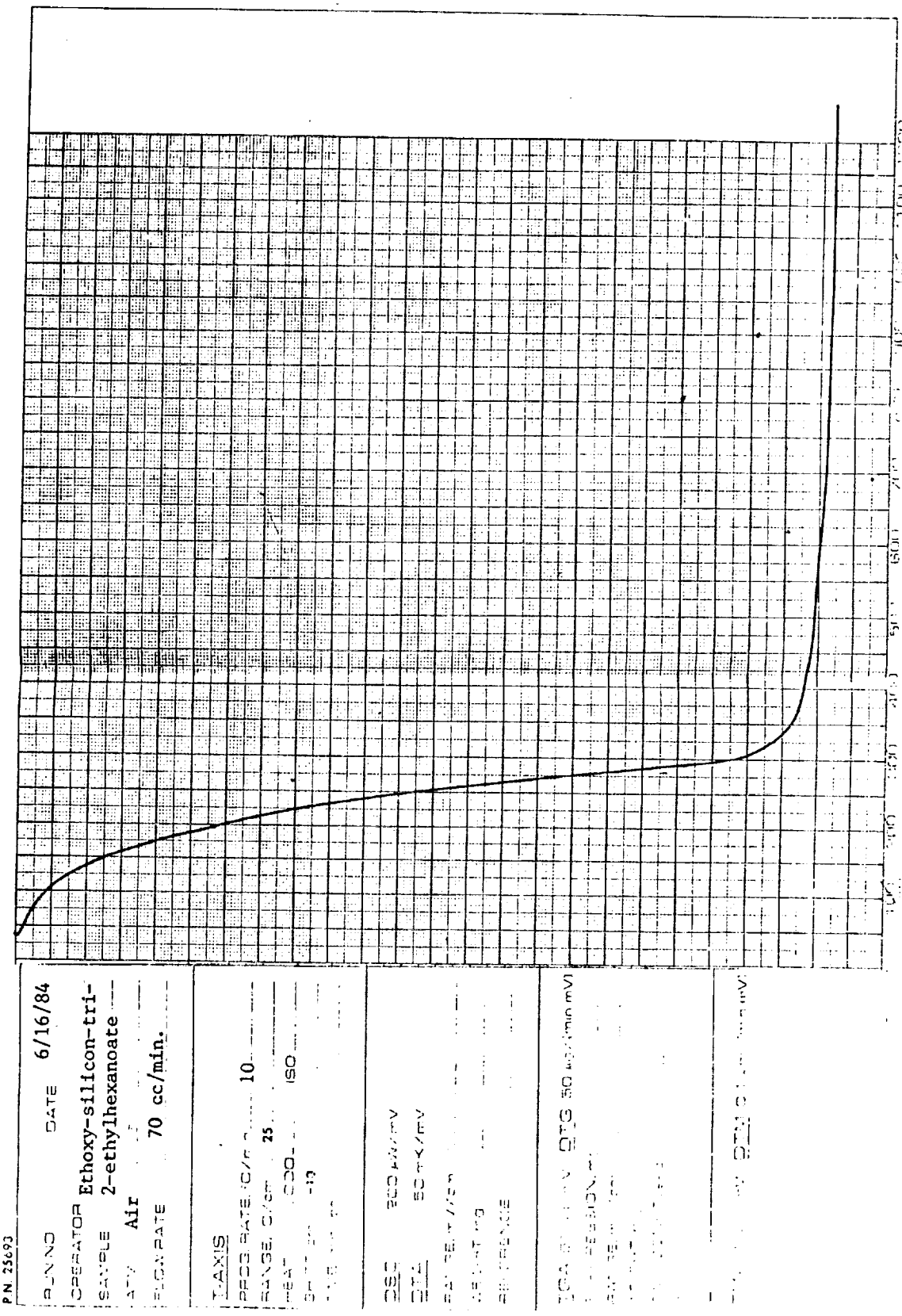
TIME CONST., sec

DTM



OMNITHERM CORPORATION

A12



DATE 10/4/84

Bismuth 2-ethylhexanoate
in benzene

Air

70 cc/min.

TAKE

PROG. RATE, °C/min. 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, min/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

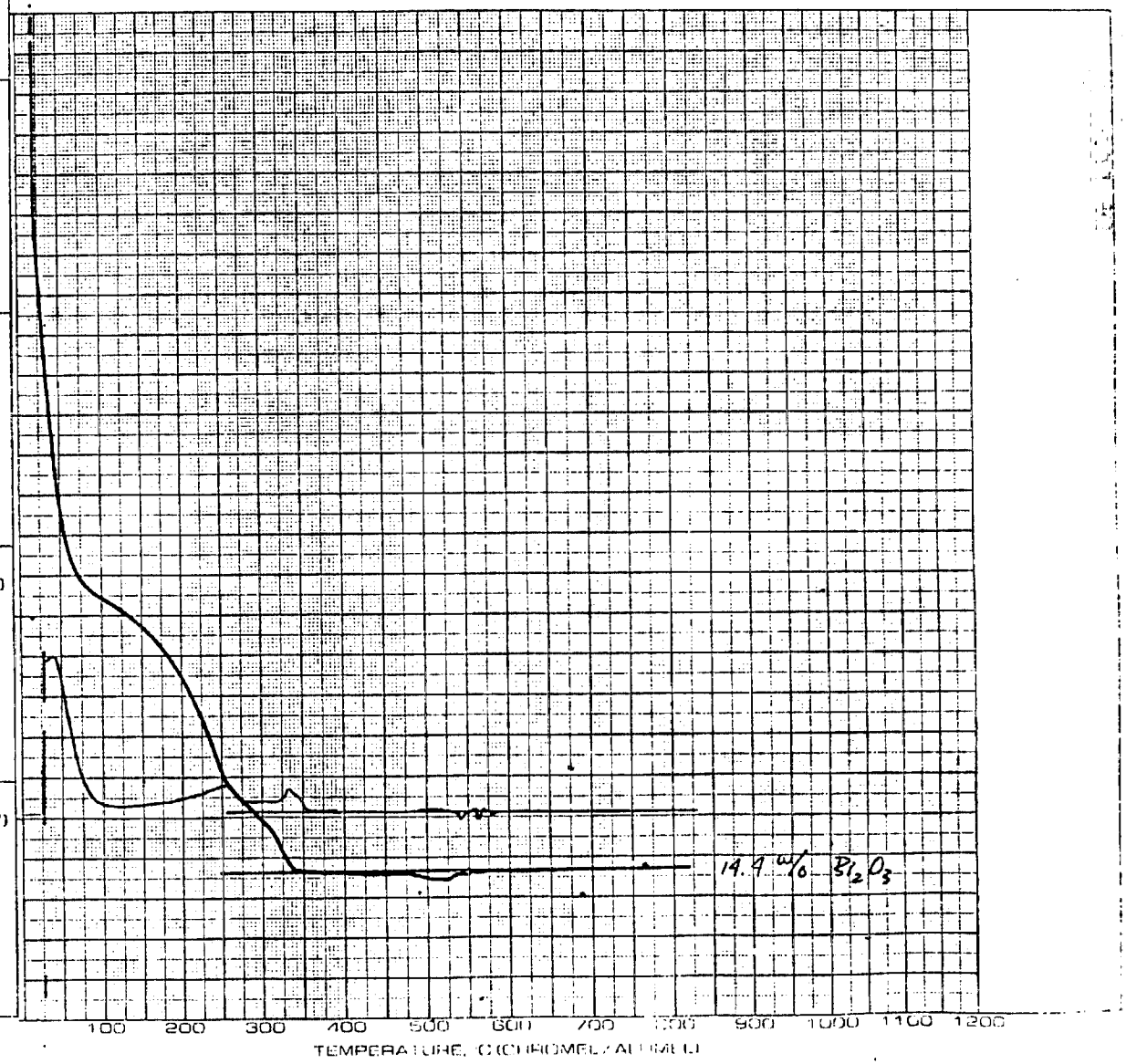
SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA mV DTM 0.1 μm/(min mV)



A14

P.N. 25693

OMNITHERM CORPORATION

A15

RUN NO. _____ DATE 3/5/85

OPERATOR Sara Sizemore

SAMPLE Cr-2-ethyl Resorcinate Std

ATM air @ _____

FLOW RATE 70 cc/min

T-AXIS

PROG. RATE, °C/min 10.

RANGE, °C/cm 25 50

HEAT _____ COOL _____ ISO _____

SHIFT, cm +10

TIME, min/cm _____

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm _____

WEIGHT, mg _____

REFERENCE _____

TGA 50 µg/mV **DTG** 50 µg/(min mV)

SUPPRESSION, mg _____

RANGE, mV/cm _____

WEIGHT, mg _____

TIME CONST., sec _____

dY _____

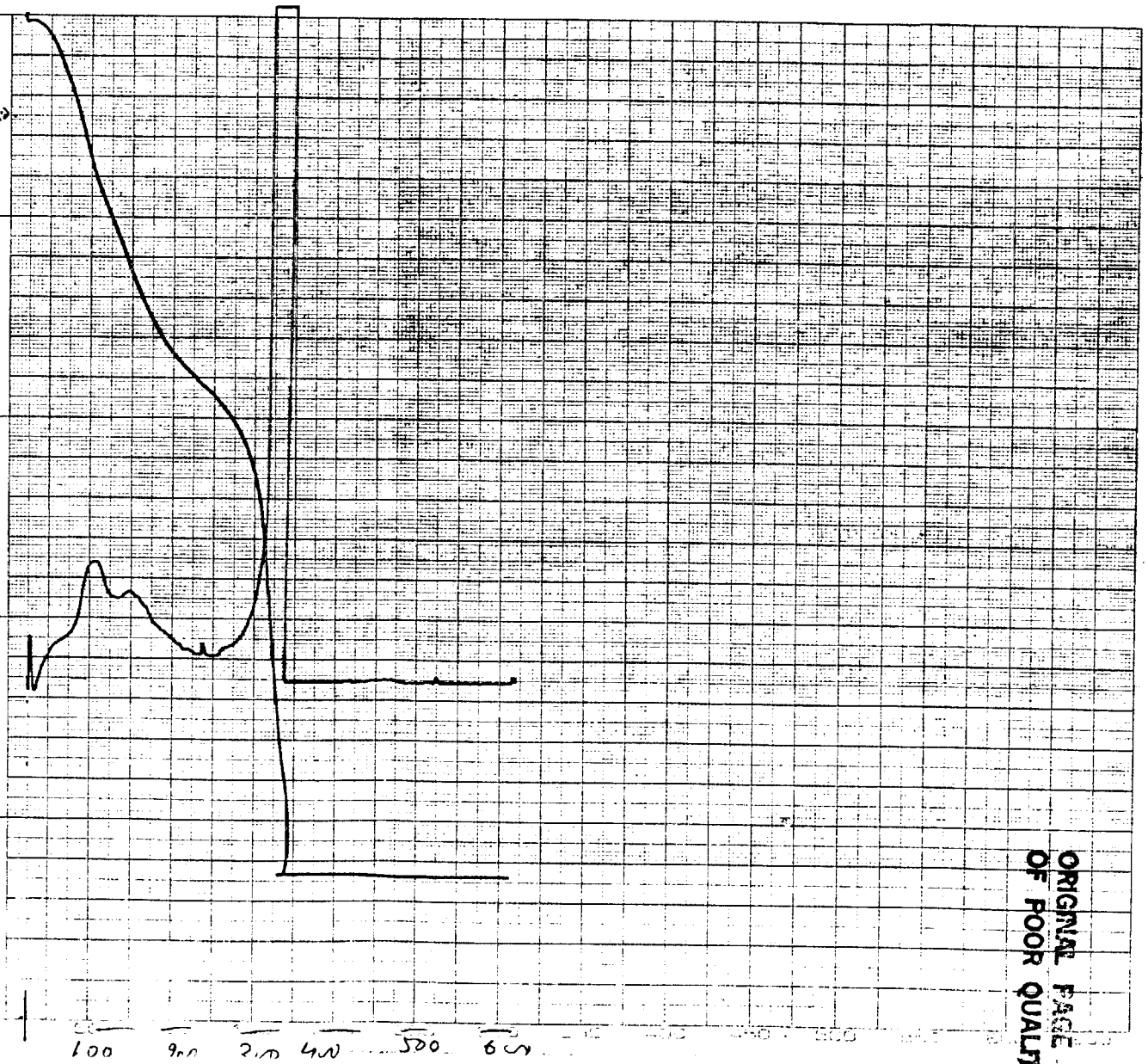
TMA 1 µm/mV **DTM** 0.1 µm/(min mV)

MODE _____

RANGE, mV/cm _____

SAMPLE SIZE _____

TYPE _____



P.N. 25693

RUN NO. _____ DATE 3/10/85

OPERATOR Sara

SAMPLE Chromium 2,4-Pentanedionate

ATM air @

FLOW RATE 70 cc/min

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT _____ COOL _____ ISO _____

SHIFT, cm +10

TIME, min/cm _____

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm _____

WEIGHT, mg _____

REFERENCE _____

TGA 50 µg/mV **DTG** 50 µg/(min mV)

SUPPRESSION, mg _____

RANGE, mV/cm _____

WEIGHT, mg _____

TIME CONST., sec _____

dY _____

TMA 1 µm/mV **DTM** 0.1 µm/(min mV)

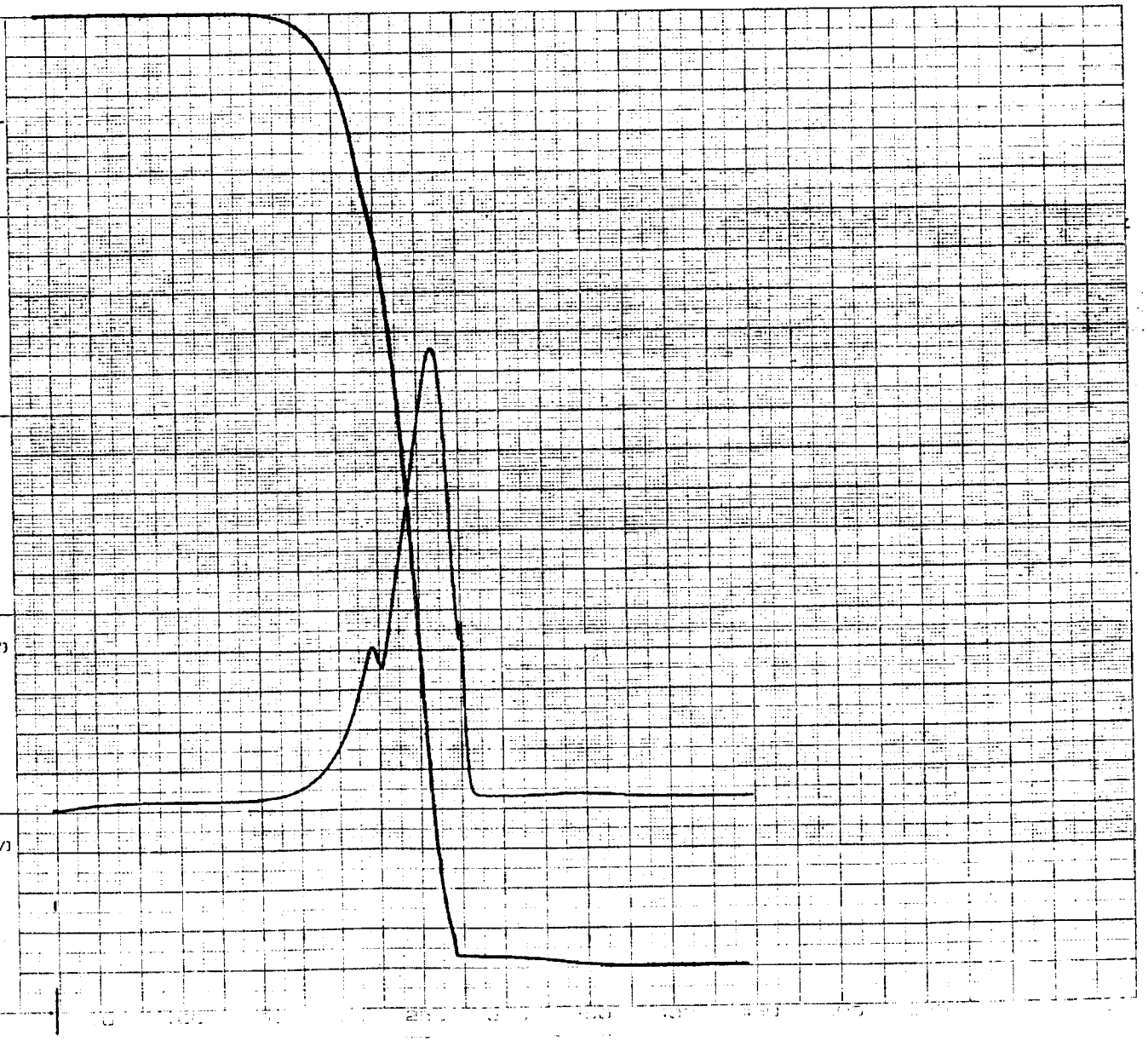
MODE _____

RANGE, mV/cm _____

SAMPLE SIZE _____

LOAD, g _____

dY _____



OMNITHERM CORPORATION

A16

MEASURED VARIABLE

P.N. 25693

RUN NO. _____ DATE 3/29/85

OPERATOR Sowe Sivaram

SAMPLE Ni-2-ethyl hexanoate in benzene

ATM air @ _____

FLOW RATE 70 cc/min

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT _____ COOL _____ ISO _____

SHIFT, cm +10

TIME, min/cm _____

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm _____

WEIGHT, mg _____

REFERENCE _____

TGA 50 μg/mV DTG 50 μg/(min mV)

SUPPRESSION, mg _____

RANGE, mV/cm _____

WEIGHT, mg _____

TIME CONST., sec _____

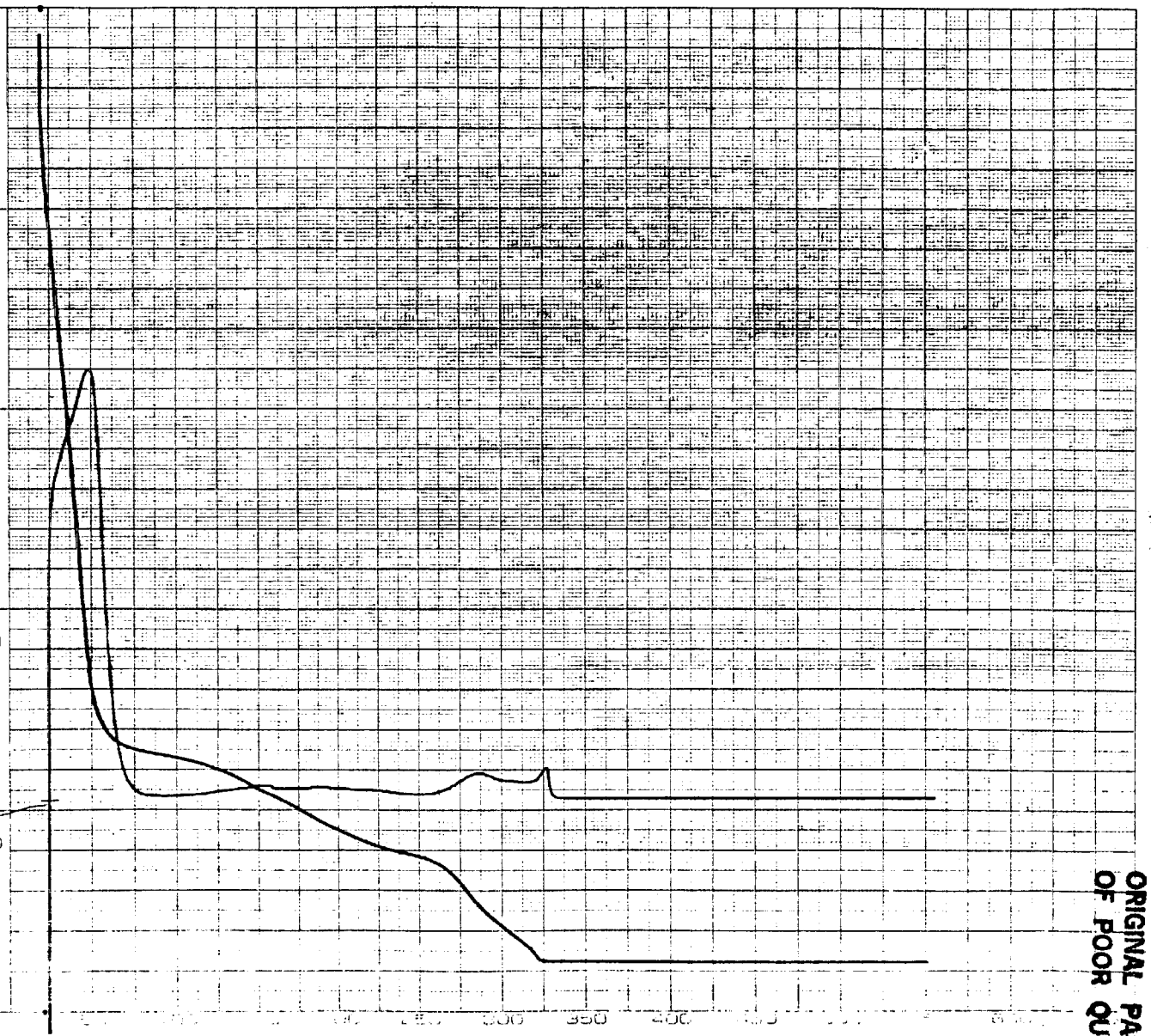
dY _____

TMA 1 μm/mV DTM 0.1 μm/(min mV)

MODE _____

RANGE, mV/cm _____

SAMPLE SIZE _____



OMNITHERM CORPORATION

A17

MEASURED VARIABLE

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P.N. 25693

RUN NO. _____ DATE 3/22 PS

OPERATOR Sara

SAMPLE Co-2 ethylhexanoate in mineralspirits

ATM air @ _____

FLOW RATE 2 cc/min

T-AXIS

PROG. RATE, °C/min 10°

RANGE, °C/cm 25

HEAT _____ COOL _____ ISO _____

SHIFT, cm ±10

TIME, min/cm _____

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm _____

WEIGHT, mg _____

REFERENCE _____

TGA 50 µg/mV DTG 50 µg/(min mV)

SUPPRESSION, mg _____

RANGE, mV/cm _____

WEIGHT, mg _____

TIME CONST., sec _____

dY _____

TMA 1 µm/mV DTM 0.1 µm/(min mV)

MODE _____

RANGE, mV/cm _____

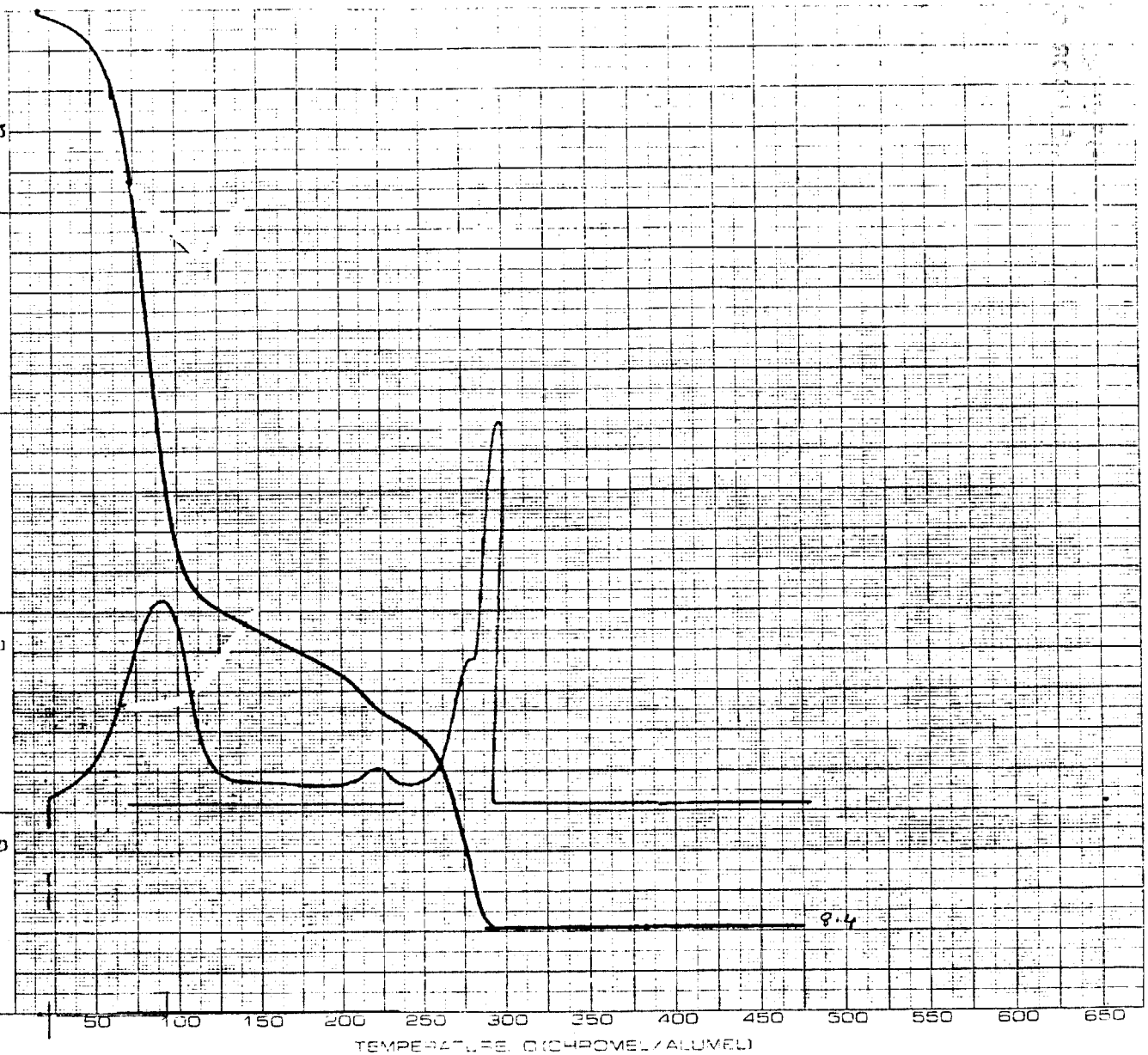
SAMPLE SIZE _____

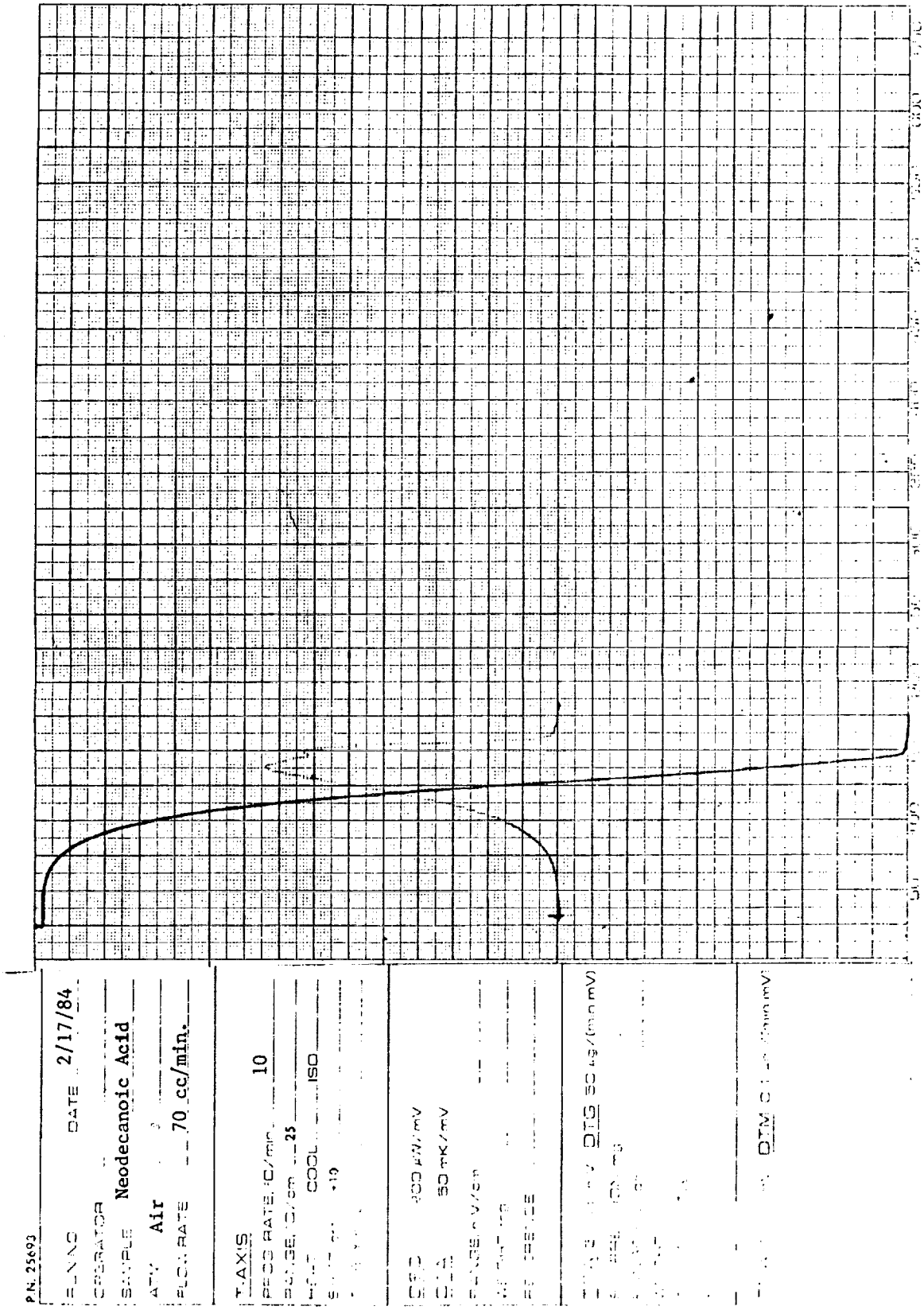
LOAD, g _____

dY _____

OMNITHERM CORPORATION

MEASURED VARIABLE A18





P.N. 23693

RUN NO. DATE 2/15/84

OPERATOR

SAMPLE Butyl Carbitol_Acetate

ATM Air

FLOW RATE 70 cc/min

T-AXIS

PROG RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

DSC 400 μW/mV

DTA 50 mK/mV

RANGE mV/cm

WT SHIT (mg)

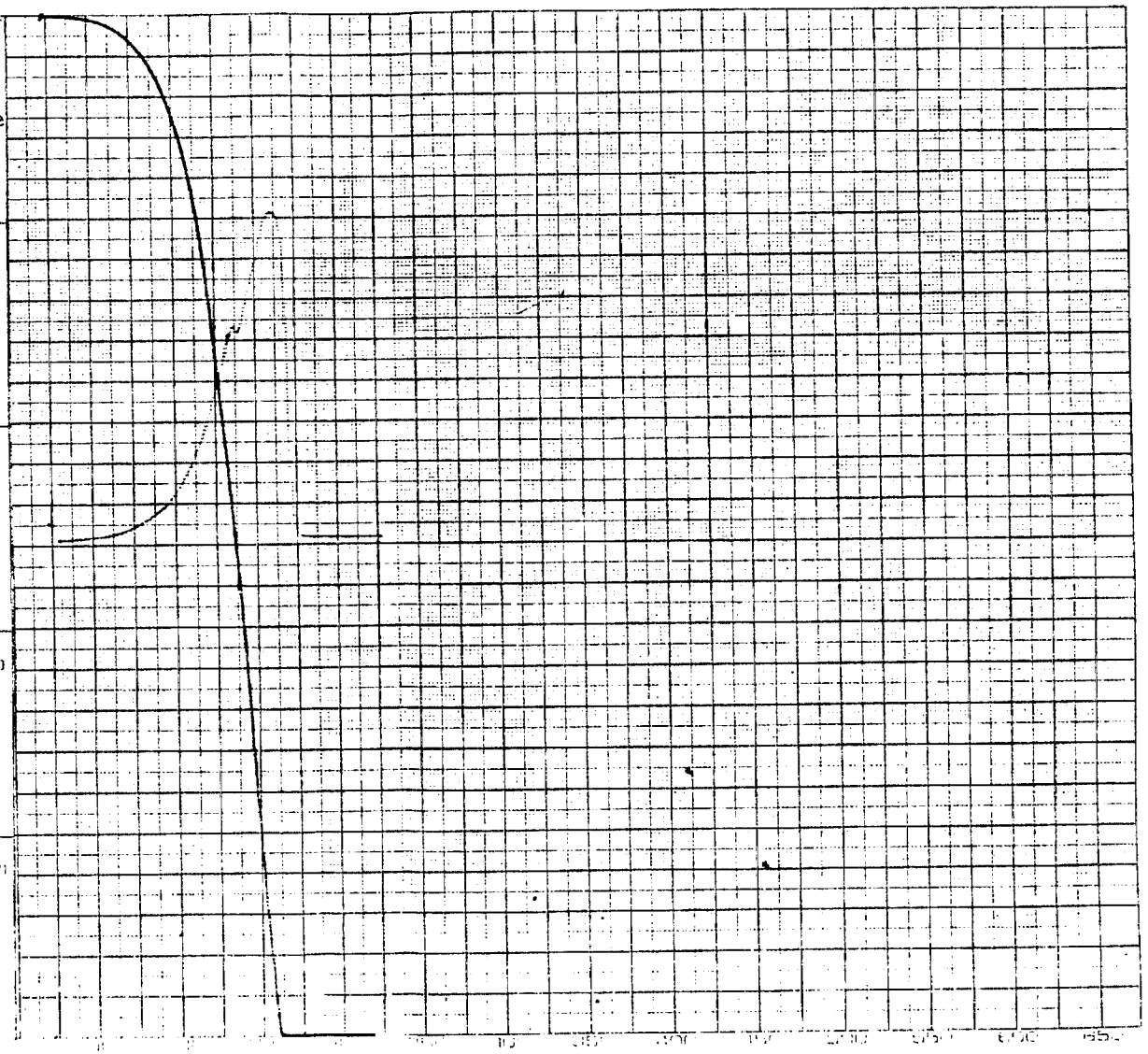
REFERENCE

TG 2.5 mV DTG 50 μg/(min mV)

POSITION, mg

RANGE mV/cm

T1 mV DTM 0.1 mg/(min mV)



A20

DATE 4/4/85

Ink SC-1Y

Air

70 cc/min.

AXIS

10

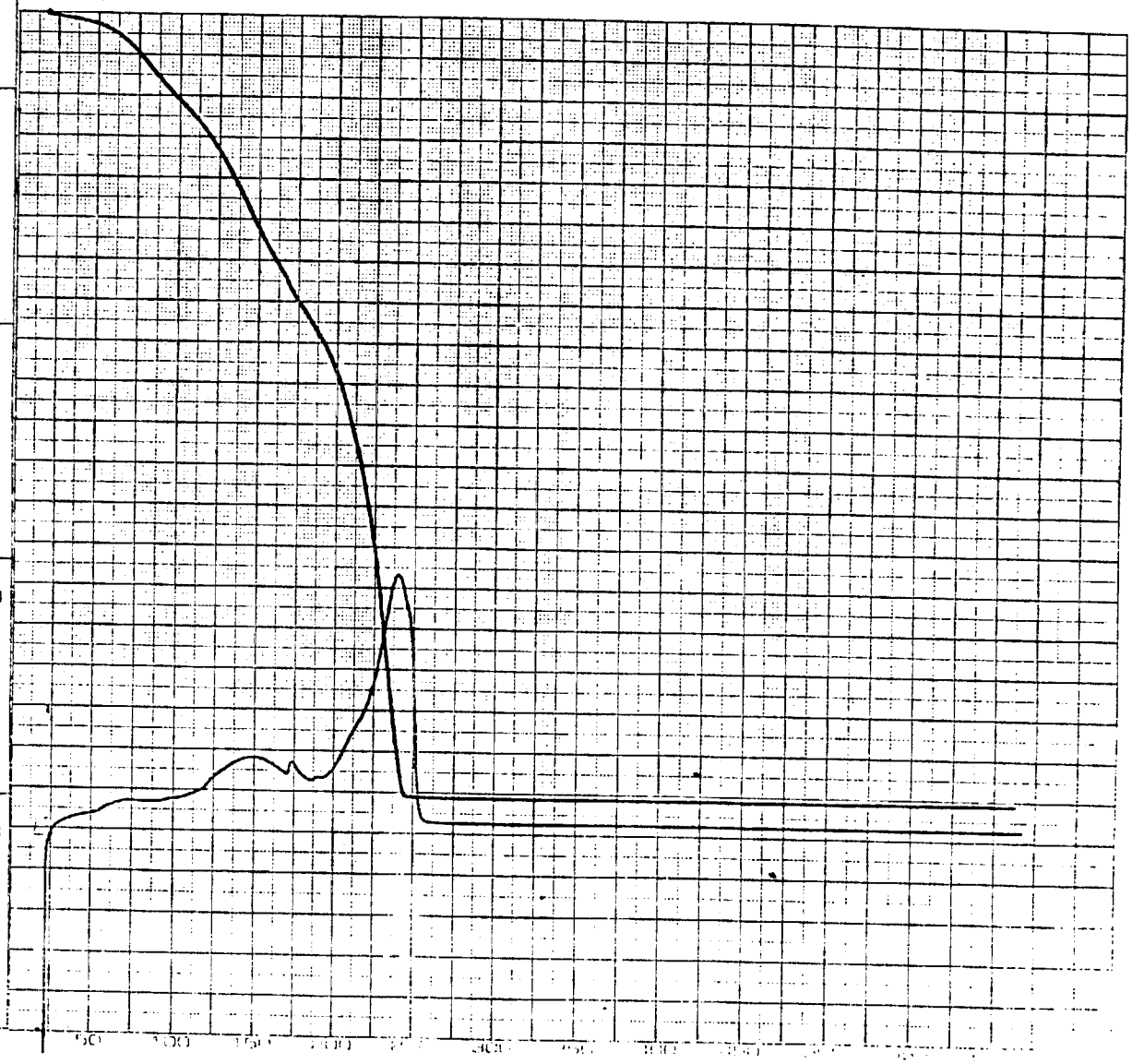
25

COOL ISO

+10

SC 200 μW/mV

TA 50 mK/mV



DATE 2/3/84

Ink SC-2Y

Air

70 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

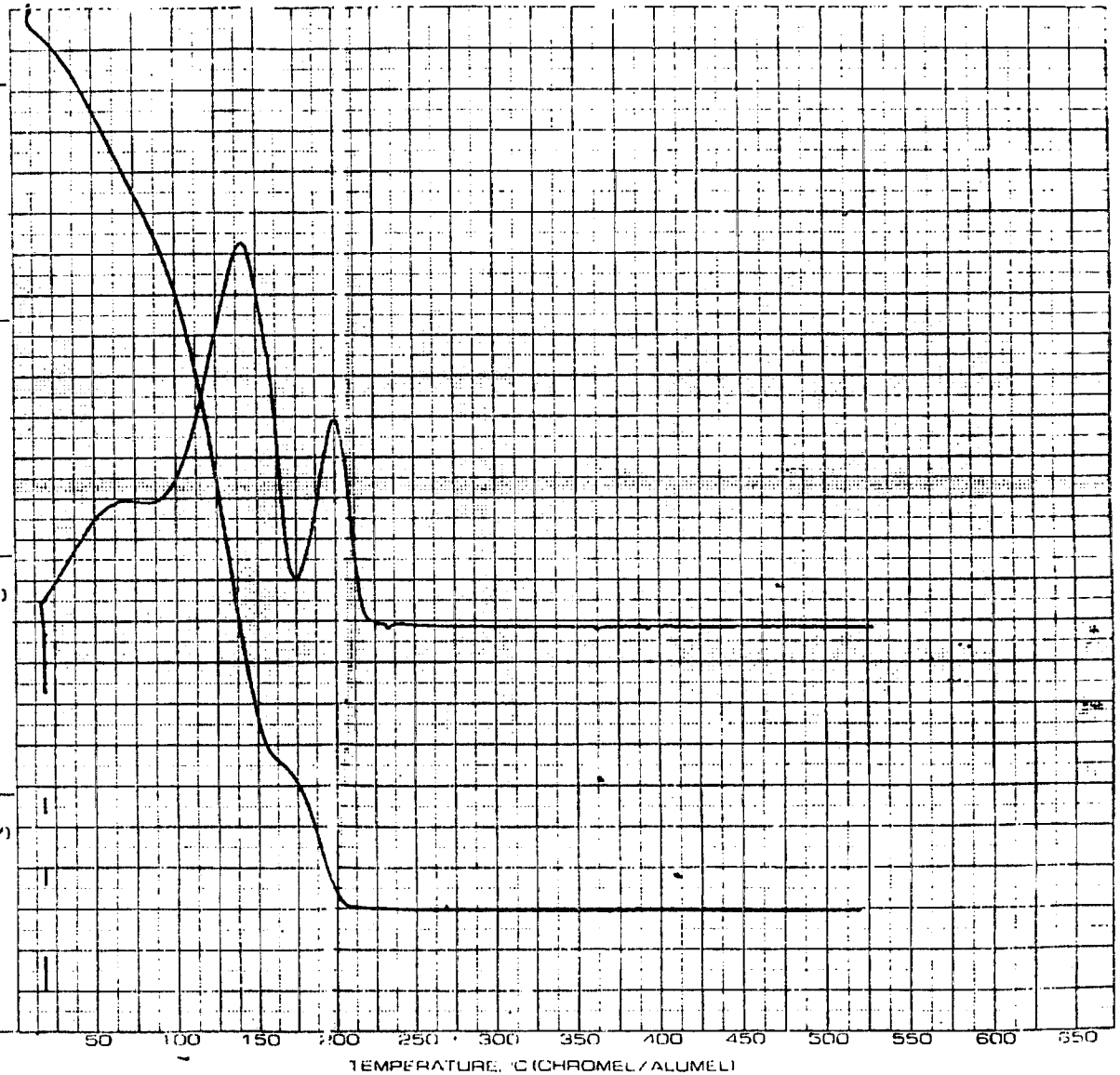
SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA DTM



OMNITHERM CORPORATION

A22

DATE 2/3/84

SAMPLE Ink SC-3Y

ATM Air @

FLOW RATE 70 cc/min.

T-AXIS

PROG. RATE, °C/min. 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME cm/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

SUPPRESSION, mg

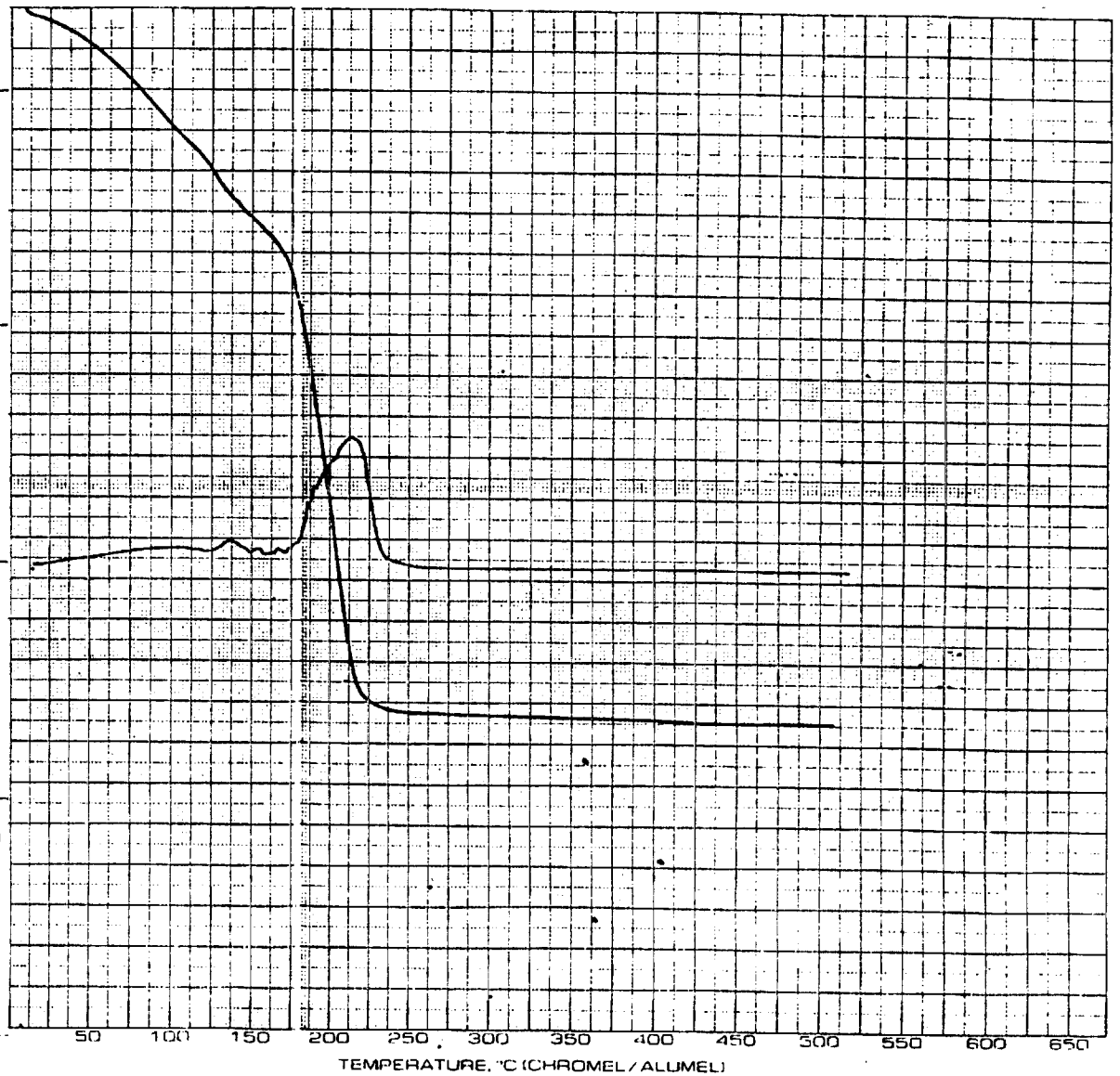
RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA DTM 0.1 μm/(min mV)

mV/cm



OMNITHERM CORPORATION

A23

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DATE 4/4/84

OPERATOR

SAMPLE Ink SC-4Y

ATM Air

FLOW RATE 70 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 µg/mV DTG 50 µg/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

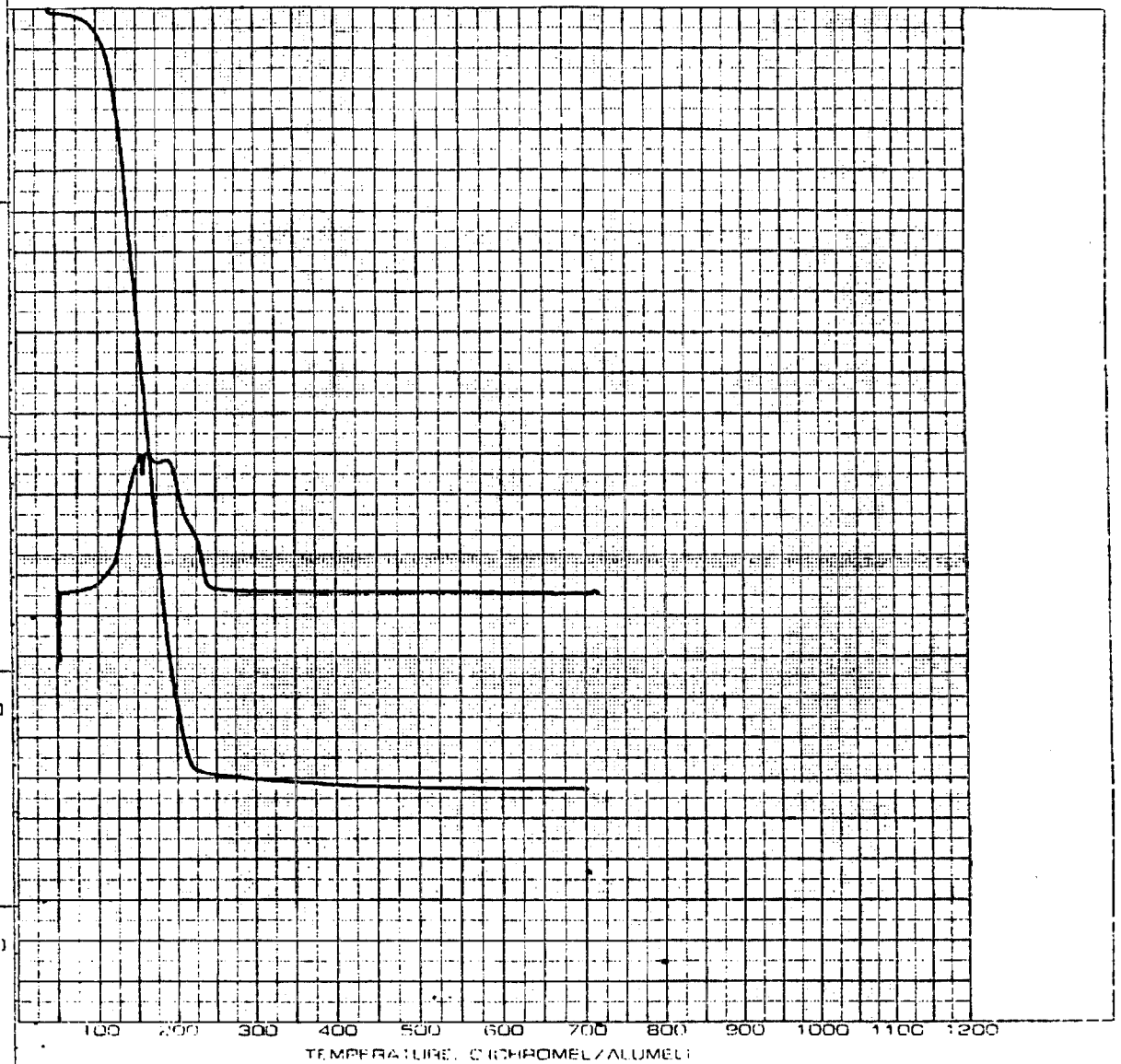
WEIGHT, mg

TIME CONST., sec

TMA DTM 0.1 µm/(min mV)

mV/cm

SIZE



OMNITHERM CORPORATION

A24

DATE 5/7/84

SAMPLE Ink SC-5Y

ATM Air

FLOW RATE 70.cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

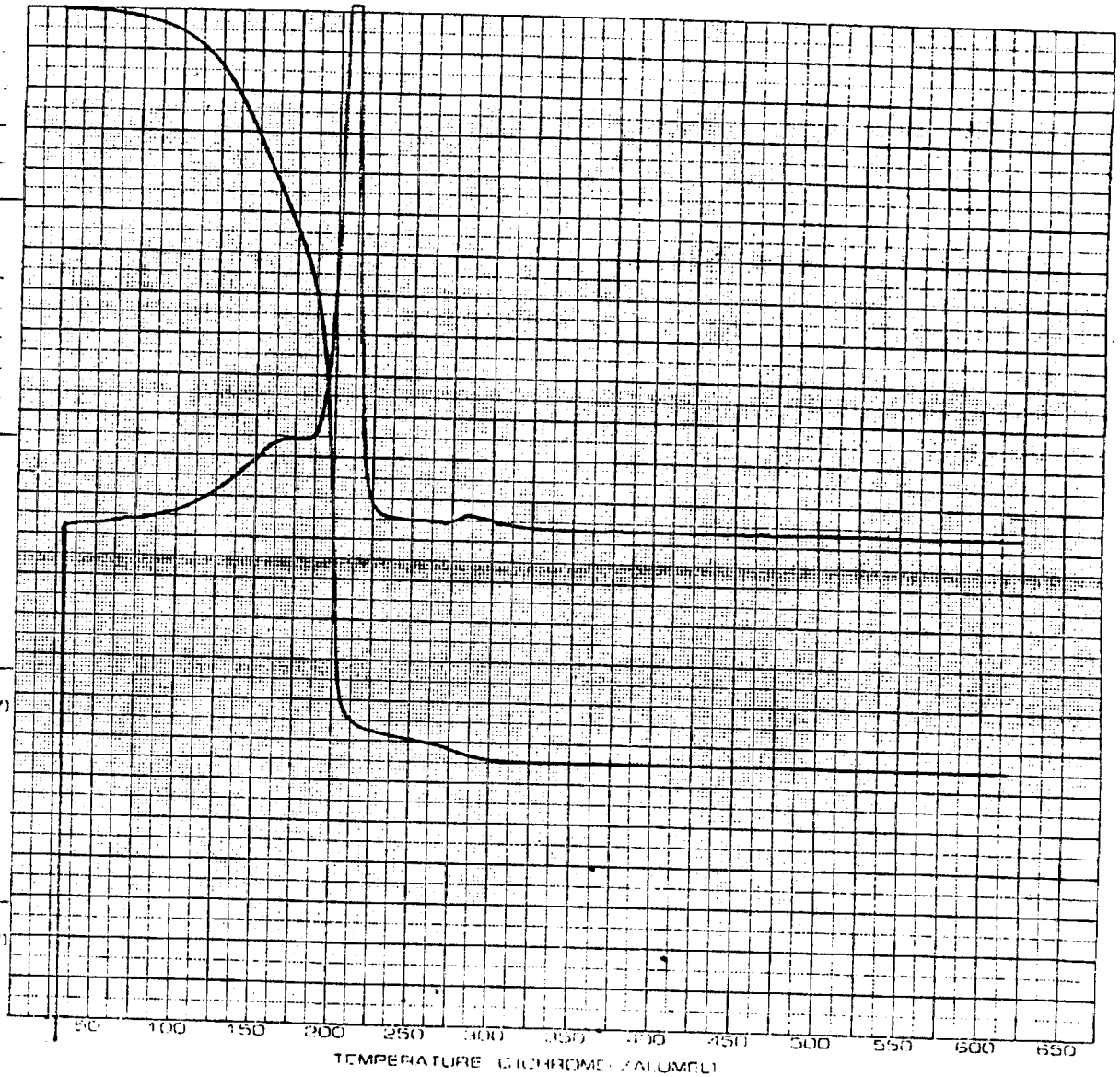
SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

DTMA DTM



OMNITHERM CORPORATION

A25

DATE 9/27/84

Ink SC-6Y

Air

70 cc/min.

TGA

10

25

COOL ISO

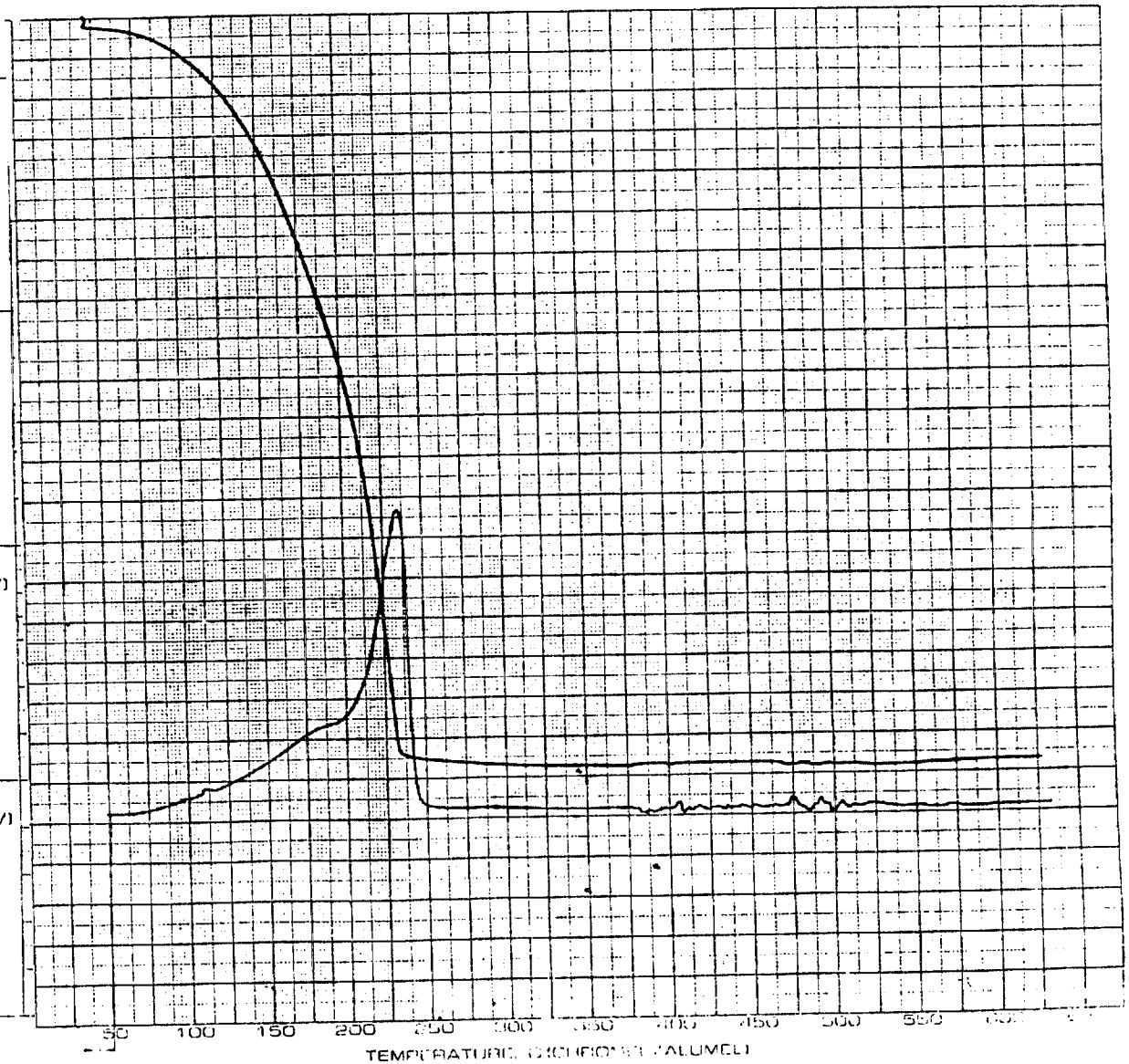
+10

DSC 200 μW/mV

DTA 50 mK/mV

DTG 50 μg/(min mV)

DTM 0.1 mg/(min mV)



A26

DATE 10/15/84

Ink SC-7Y

Air

RATE 70 cc/min.

TAKS

RATE, °C/min. 10

RANGE, °C/cm 25

COOL ISO

cm +10

cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

EXPOSSION, mg

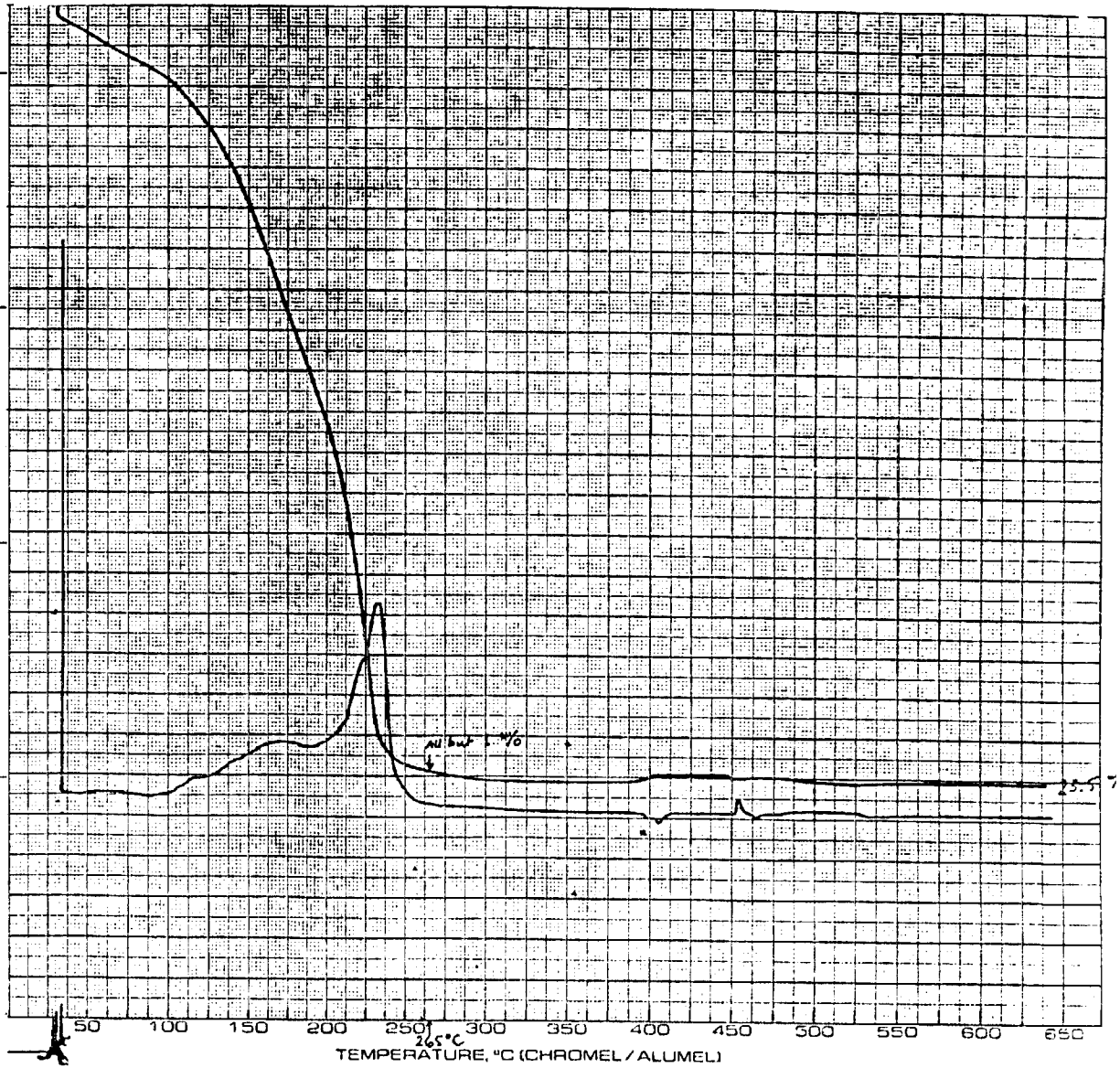
RANGE, mV/cm

WEIGHT, mg

TIME CONSTANT, sec

TMA mV DTM μm/(min mV)

mV/cm



A27

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DATE 4/18/85

SAMPLE Ink SC-8Y

Air

FLOW RATE 80 cc/min

TEMP

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME cm/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

SUPPRESSION, mg

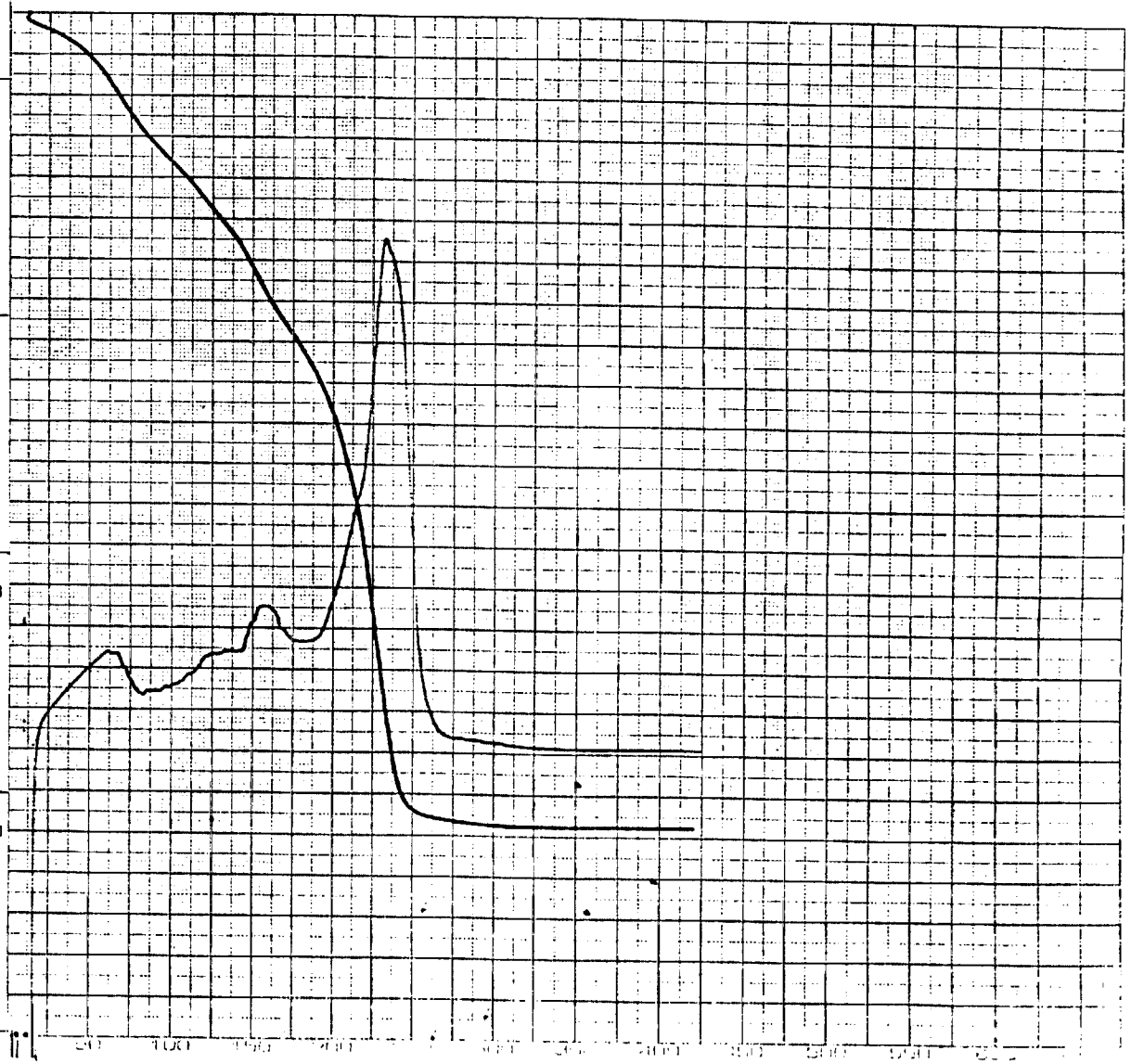
RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA mV/mV DTM 0.1 μm/(min mV)

mV/cm



DATE 12/12/84

SAMPLE Ink SC-9Y

ATM Air

FLOW RATE 70 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, min/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

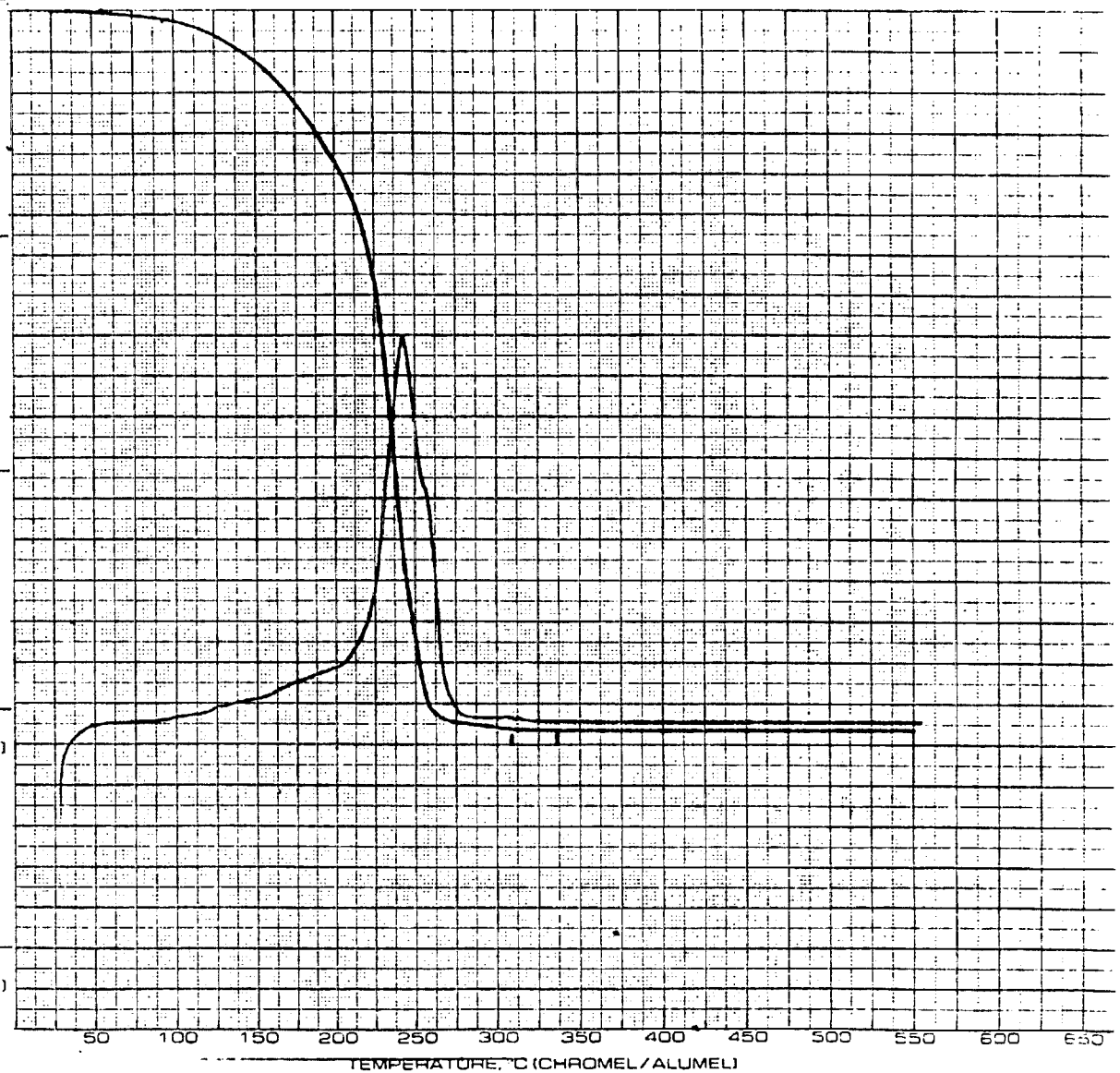
WEIGHT, mg

TIME CONST., sec

TMA DTM 0.1 μm/(min mV)

RANGE, mV/cm

PROBE SIZE



OMNITHERM CORPORATION

A29

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DATE 3/28/85

SAMPLE Ink SC-10Y

ATM Air

GAS RATE 70 cc/min.

T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SET PT. cm +10

TIME min/cm

DSC 200 μW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)

SUPPRESSION, mg

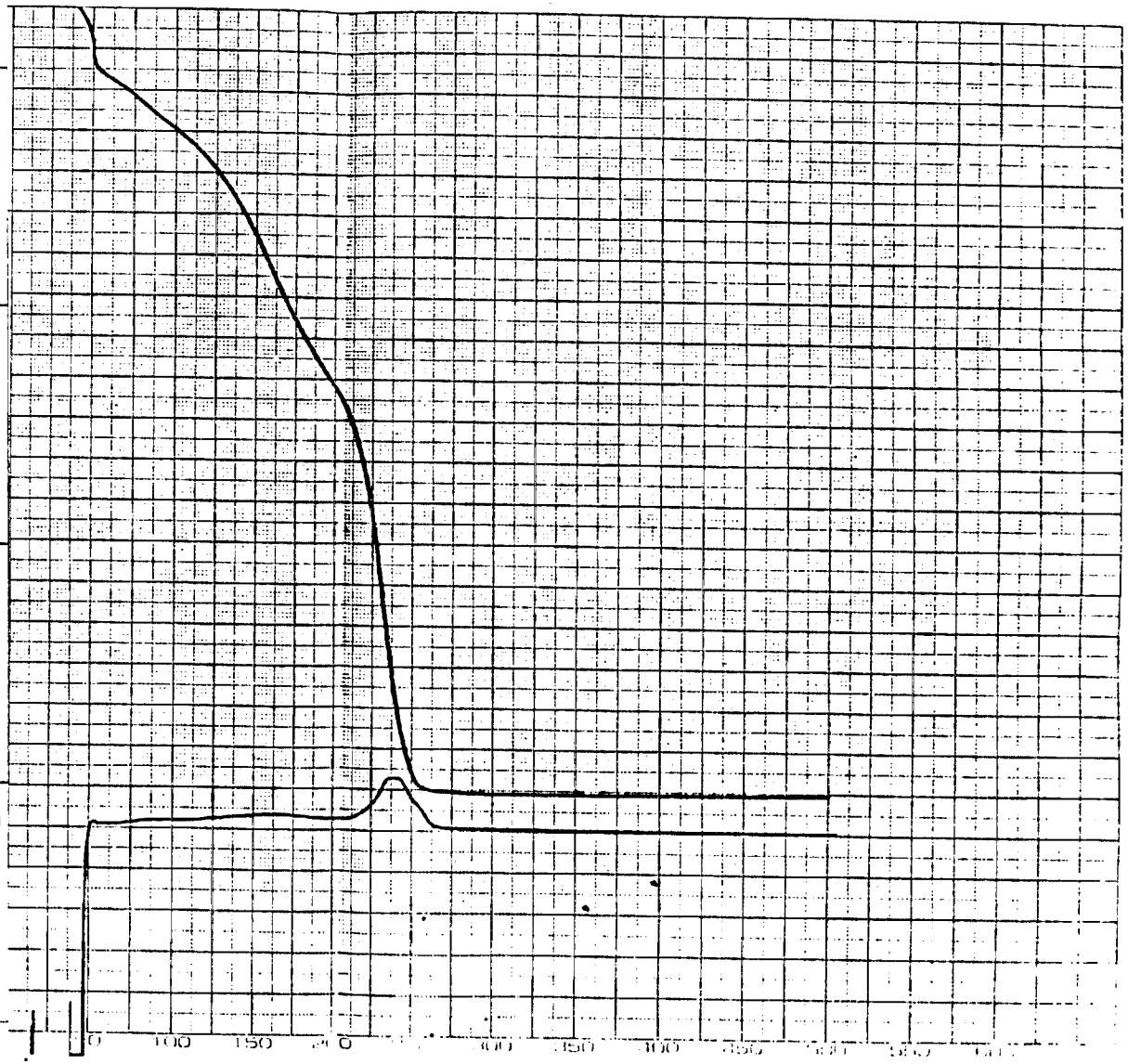
RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

TMA DTM 0.1 μm/(min mV)

mV/cm



A30

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