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MOD SILVER METALLIZATION: SCREEN PRINTING AND INK-JET PRINTING

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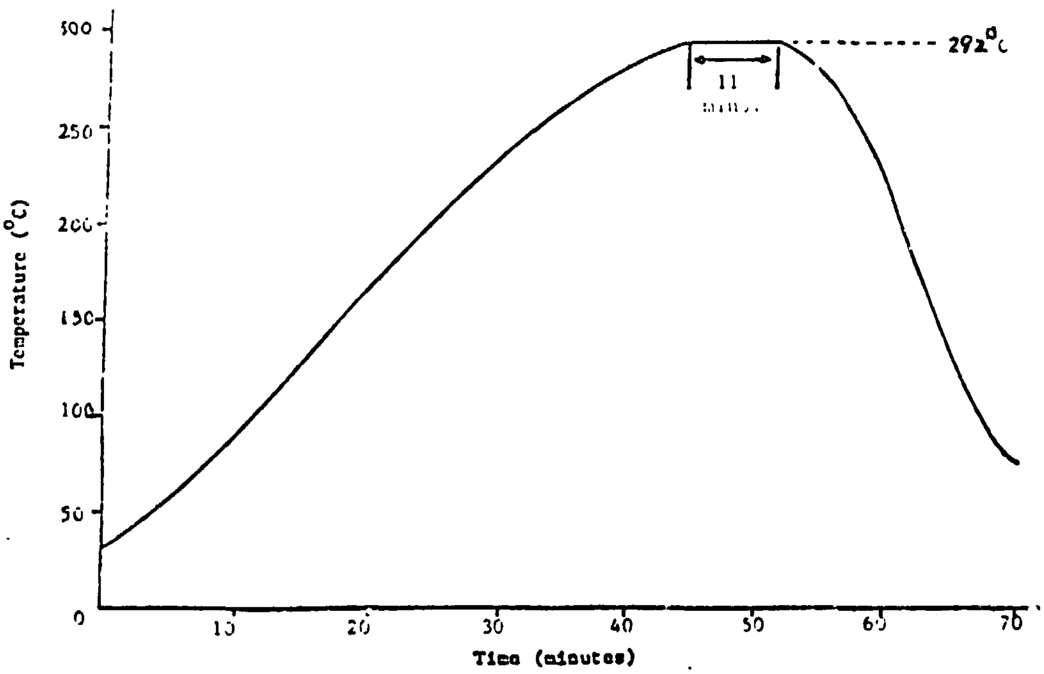
Experimental Variables

1. Ink Chemistry
2. Deposition Parameters
3. Time-Temperature Processing

Time-Temperature Profile for Standard Firing Sequence No. 1



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Ink Chemistry

1. Silver Compound
   Ag Neodecanoate
2. Adhesion Agent
3. Solder Leach Resistant Agent
4. Solvent(s)
   a. Screen Printing
      Low Boiling - Benzene
      High Boiling - Neodecanoic
      Acid: Butyl Carbitol
      Acetate (2:1)
   b. Ink Jet Printing
      Low Boiling

Properties of Metallo-Organic Base Metal Oxide Binder Compounds and Those of Silver Inks Formulated with Them.

Binder Compound	T_D (°C)	w/o Product	T_D for 97/3 Ink (°C)	Comments
Bismuth 2-ethylhexanoate in benzene	340	14.4	310	Smooth ink decomposition with all but 1 w/o decomposed by 270°C.
Chromium (II) 2,4-pentanedionate solid	270[(a)]	4.2	318	Definite 2-stage ink decomposition occurs at 232°C.
Nickel 2-ethylhexanoate in benzene	323	5.0	292	All but 3.6 w/o decomposed by 232°C. Possible 2-stage decompositing occurring.
Cobalt 2-ethylhexanoate in benzene	292	8.4	283	2-stage ink decomposition occurs at 243°C and 283°C, although its not as severe as in Ag/Cr ink.

(a) Except for 1 w/o, which decomposed by 365°C.

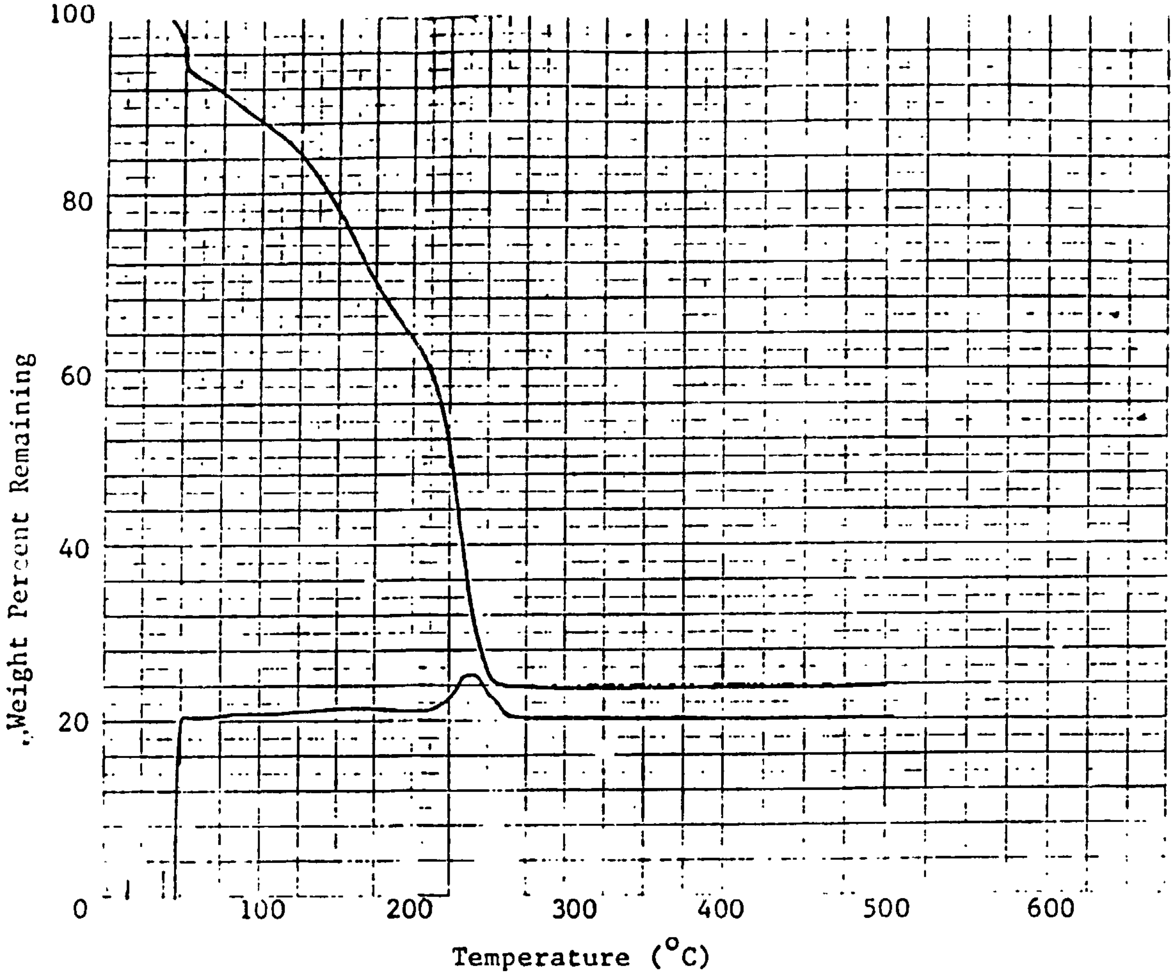
Fired Front Contact Properties of Inks with Four Different Compounds Added for Potential Adhesion Promotion.

Ink	Fired Film Appearance	Line Defin.	Sheet Resistance ($m\Omega/sq \pm \sigma$) # of Films	Initial Value	Value After 60 sec. Spike at 800°C	Initial Adhesion
Ag/Bi (SPC3-3A)	silver with copperish tint	A	16	40.1 ± 3.9	24.9 ± 1.5	excellent
Ag/Cr	dark silver/ grey	A/B	7	89.0 ± 3.8	51.2	good to excellent
Ag/Ni	dark with purple tint	A	9	157.7 ± 7.5	91.3	excellent
Ag/Co	dark with greenish yellow tint	A	9	>860	98.3	fair to good

Firing Study Results for Bismuth Oxide Content Optimization

Ink[(a)] Chemistry	# of Layers	Line Defin.	Sheet Resist. (mΩ/sq)	Initial Adhesion
95% Ag 5% Bi	1	A	57.9	Excellent
95% Ag 5% Bi	2	A	32.3	One half of bus bar poor. Excellent elsewhere.
97% Ag 3% Bi	1	A	40.3	Excellent
97% Ag 3% Bi	2	A/B	24.6	Excellent, small piece of bus bar removed.
99% Ag 1% Bi	1	A/B	38.8	Excellent
99% Ag 1% Bi	2	B	21.1	One half of bus bar poor. Excellent elsewhere.

(a) Based on expected theoretical fired film composition which is not verified analytically.



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

<u>Important Properties</u>

Theor. Fired Film Composition: 99 wt.% Ag - 1 wt.% Bi

T_D: 257°C

Inorganic Content: 23.6 wt. %

Fired Film Thickness Values and Resistivity Calculated Values.

Film I.D.	Average Film Thickness (μm) Bus Bar	Finger	Overall Average	Sheet Resist. (μΩ/sq)	Resistivity (μΩ-cm)
1 Layer Pure Silver	1.08	0.62	7.6×10^{-5}	2.62×10^{4}	1.99
1 Layer 1 w/o Bi	0.75	0.53	5.9×10^{-5}	3.88×10^{4}	2.30
1 Layer 3 w/o Bi	1.21	0.58	7.7×10^{-5}	4.03×10^{4}	3.11

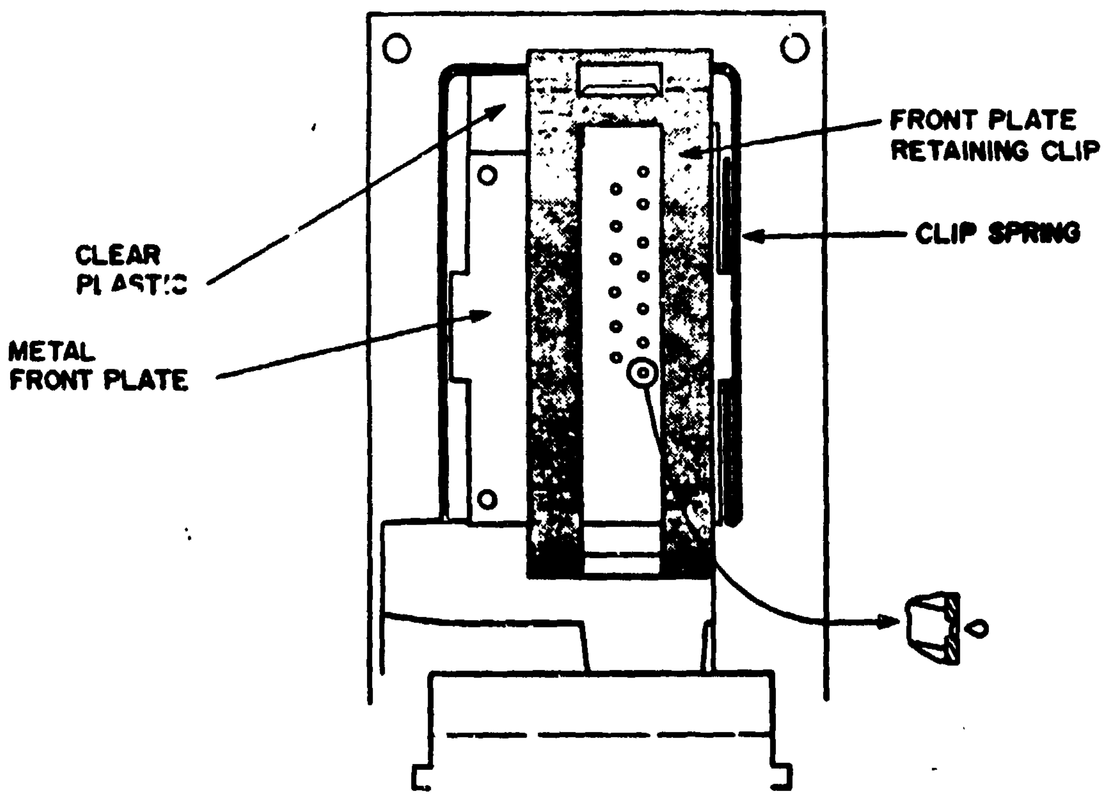
Summary of the Effects of 60 Second Thermal Spiking.

Bismuth Content (wt. %)	Spiking Temp. (°C)	Initial Sheet Resist. (mΩ/sq)	Final Sheet Resist. (mΩ/sq)	Δ Sheet Resist. (mΩ/sq)	Adhesion Effects	Photovoltaic Response Improvement
5	600	57.8	27.1	30.7	Good before spiking. Excellent after spiking.	Slight Negative
5	700	61.0	26.9	34.1	Same as Above	Very Positive
5	750	59.2	27.1	32.1	Same as Above	Very Positive
5	800	53.6	25.7	27.9	Same as Above	Very Positive
3	600	41.4	27.5	13.9	Excellent Before & After Spiking.	None
3	700	39.6	26.0	13.6	Same as Above	Slight Negative
3	750	37.7	26.5	11.2	Same as Above	Positive
3	800	37.3	24.9	12.4	Same as Above	Positive
1	600	37.4	26.1	11.3	Excellent Before & After Spikinkg.	Slight Positive
1	700	37.8	24.2	13.6	Same as Above	Positive
1	750	38.0	27.9	10.1	Same as Above	Very Positive
1	800	36.4	28.6	7.8	Same as Above	Very Positive

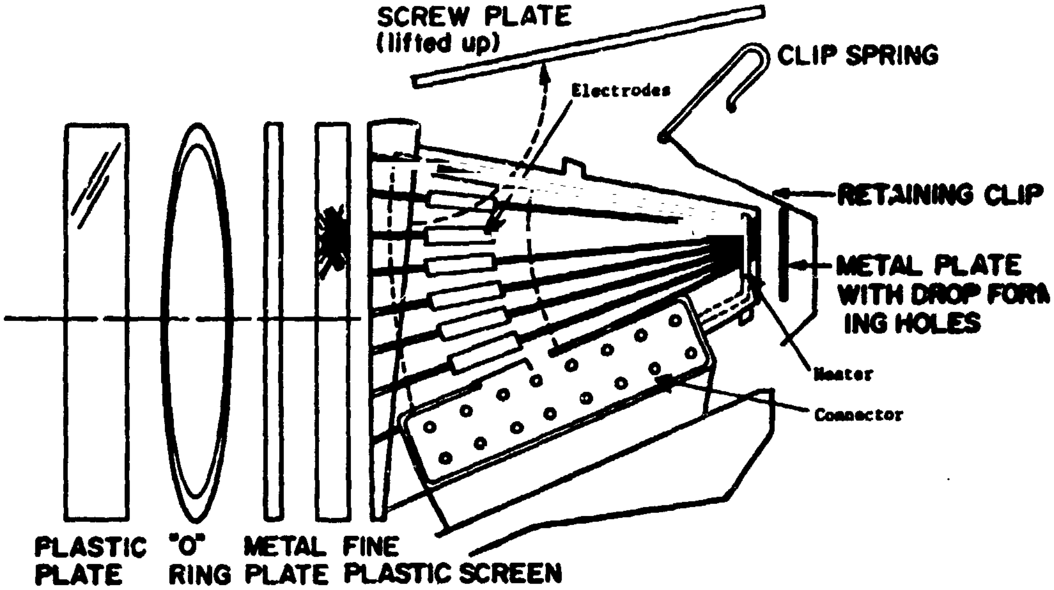
Photovoltaic Evaluation of MOD Silver (1 w/o Bi) Metallized Solar Cells Without AR Coating.

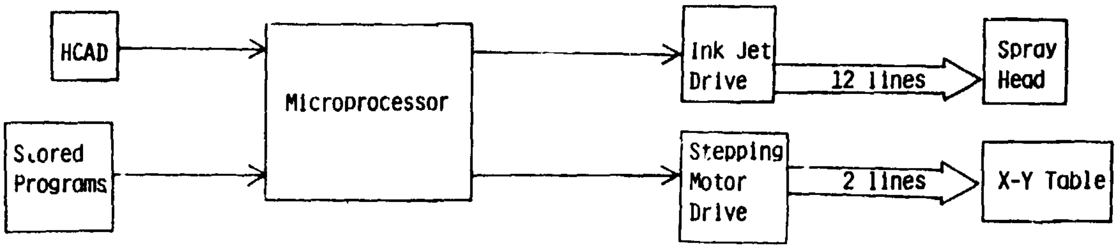
Cell Description	V_{oc} (mv)	I_{sc} (mA)	Efficiency (%)	Fill Factor	Series Resist. (ohms)	Shunt Resist. (ohms)	Sheet Resist. (mΩ/sq)
Single Layer MOD Silver	530.4	72.6	6.1	0.633	1.171	99.4	39
Two Layer MOD Silver	522.6	66.8	3.5	0.401	2.658	49.8	21

Nozzle Assembly (Front View)

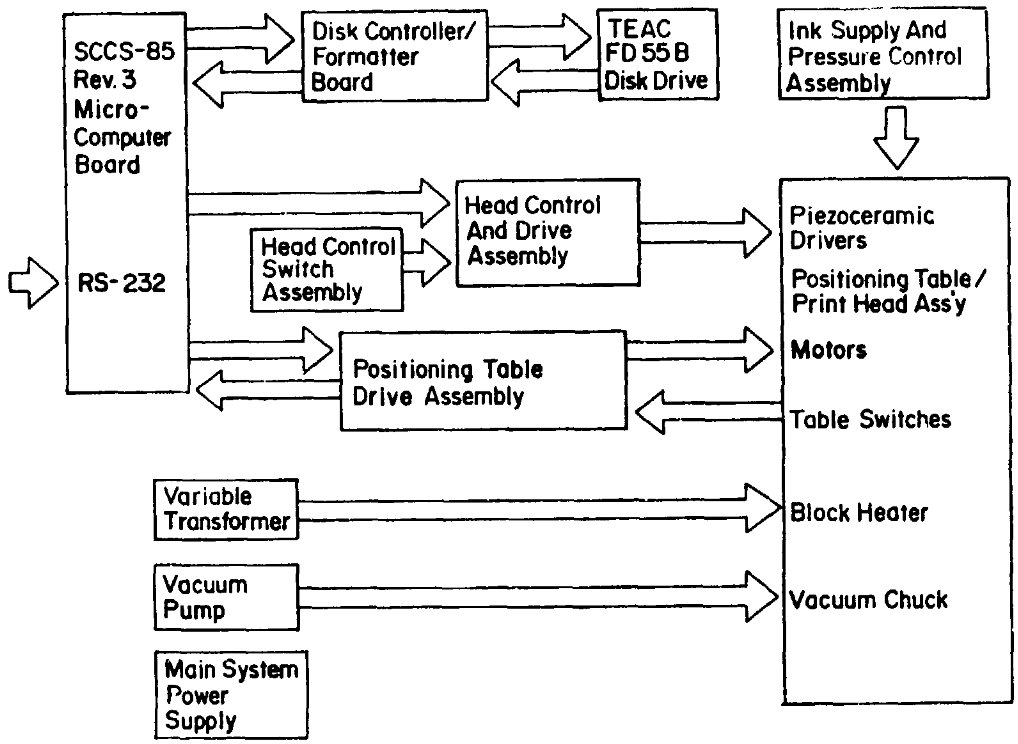


Nozzle Assembly (Side View)





Ink-Jet Printing System



Ink Requirements

1. No Particulates
2. Low Viscosity
3. High Surface Tension
4. High Inorganic Content
5. Non Clogging
6. Stable

Ink-Jet Printing Studies

<u>Ink Parameters</u>

1. viscosity
2. surface tension
3. metal content
4. solvent vapor pressure

<u>Printer Parameters</u>

1. pulse voltage
2. pulse frequency
3. ink pressure
4. nozzle diameter
5. nozzle-substrate separation

<u>Substrate Parameters</u>

1. velocity
2. temperature

<u>Firing Parameters</u>

1. heating rate
2. maximum temperature
3. time at maximum temperature

Solvents Evaluated for Ink-Jet Printing

Solvent	B.P. (^{0}C)	Comments
xylene	137	Poor line definition for thick prints.
toluene	111	Poor line definition for very thick prints
cyclohexane	80.7	Voids in prints
benzene	80	Good prints
hexane	69	Clogging
tetrahydrofuran	66	Clogging

Theory

w - dry film width

t - dry film thickness

$$tw = C \left(\frac{f}{s}\right) \upsilon$$

C - constant for a given ink and printer

f - drop frequency

s - substrate speed

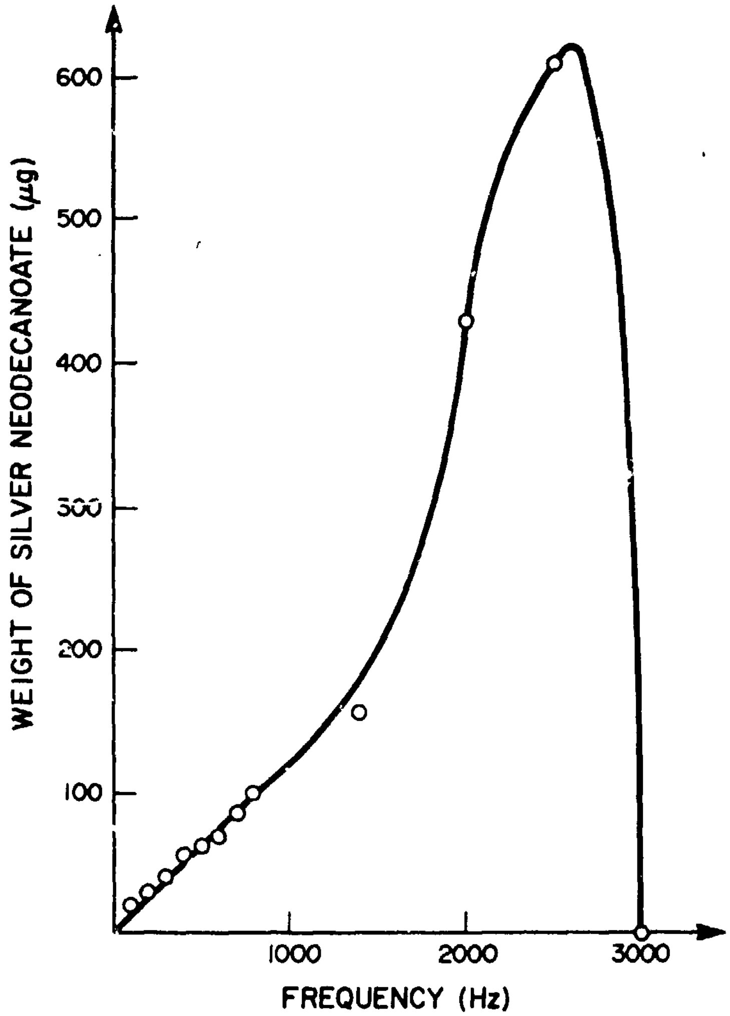
υ - velocity of ink in nozzle

$\upsilon = \upsilon(\eta, \gamma, V)$ for a given printer

η - ink viscosity

γ - ink surface tension

V - input voltage



Summary

1. Screen printed MOD Ag films with low porosity and excellent adhesion can be formed on Si below 300°C.

2. The photovoltaic response is promising, but the contact resistance must be reduced.

3. Excellent line definition can be achieved with ink jet printed MOD inks.