N85-32428

MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

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Approach

1. Identify and characterize suitable metallo-organic (MO) compounds.

2. Develop generic synthesis procedures for the MO compounds.

3. Develop generic fabrication procedures for screen printing inks.

4. Optimize processing parameters for top surface cell metallization.

5. Model the interrelationships between ink chemistry and processing, and film properties and cell performance.

Ag Neodecanoate Synthesis and Characterization

Reaction:

$$R_2 - \underset{R_3}{\overset{R_1}{C}} - COOH + NH_4OH \xrightarrow[25^oC]{H_2O} R_2 - \underset{R_3}{\overset{R_1}{C}} - COONH_4 + H_2O$$

$$R_2 - \underset{R_3}{\overset{R_1}{C}} - COONH_4 + AgNO_3 \xrightarrow[25^oC]{H_2O} R_2 - \underset{R_3}{\overset{R_1}{C}} - COOAg + NH_4OH$$

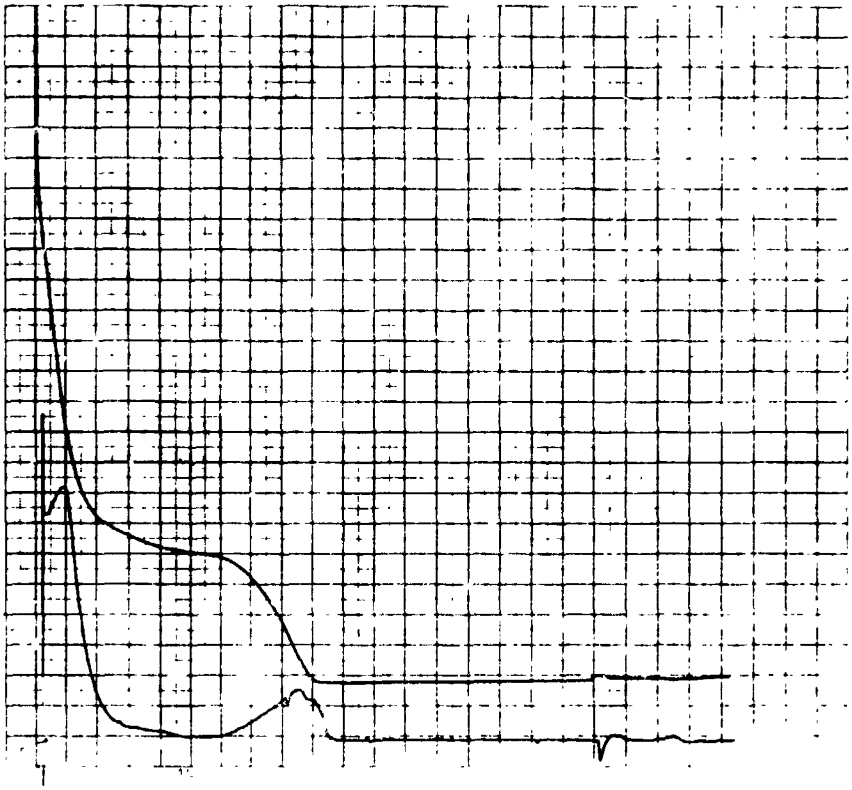
$R_1 + R_2 + R_3 = C_8H_{19}$

w/o Silver: 38.7

Form: white solid

Solubility: aromatic solvents

Thermogram of Ag Neodecanoate in Benzene



Platinum (II) 2-ethylhexanoate Synthesis and Characterization

Reaction:

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

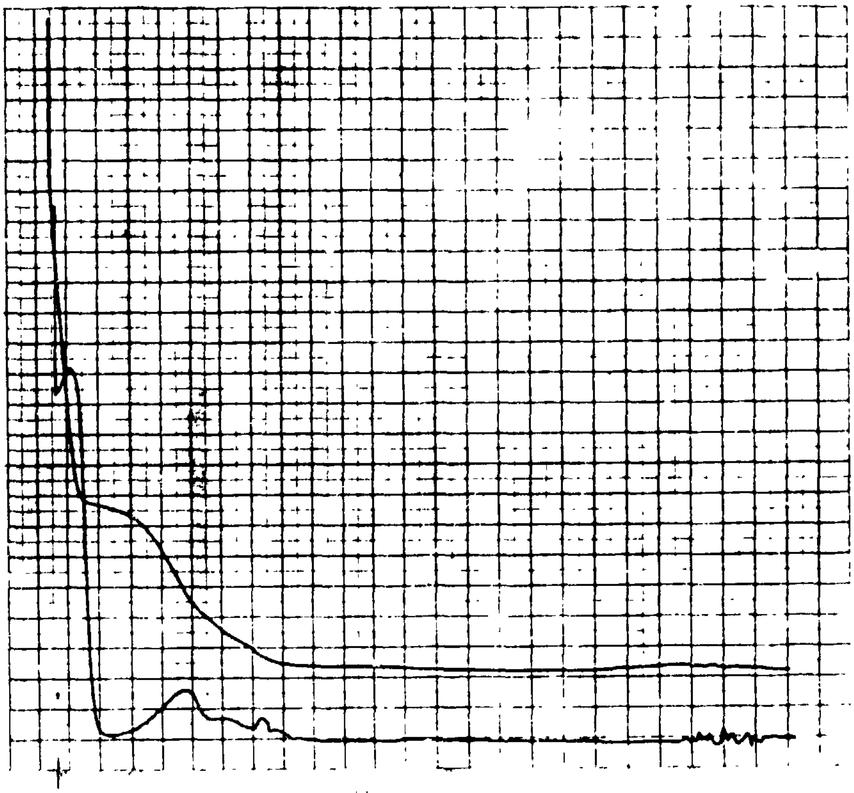
$$K_2PtCl_4 + 2C_7H_{15}COO^-(C_2H_5)_3NH^+ \xrightarrow[50^0]{H_2O} Pt(C_7H_{15}COO)_2 + 2KCl + 2(C_2H_5)_3NHCl$$

w/o Platinum: 41

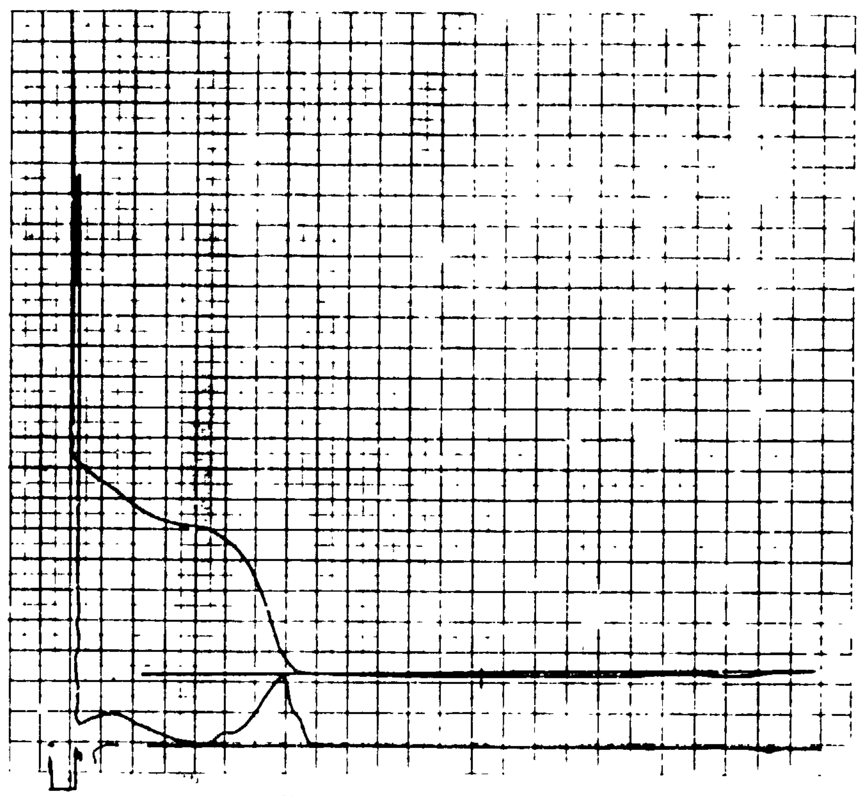
Form: black oil

Solubility: aromatic solvents

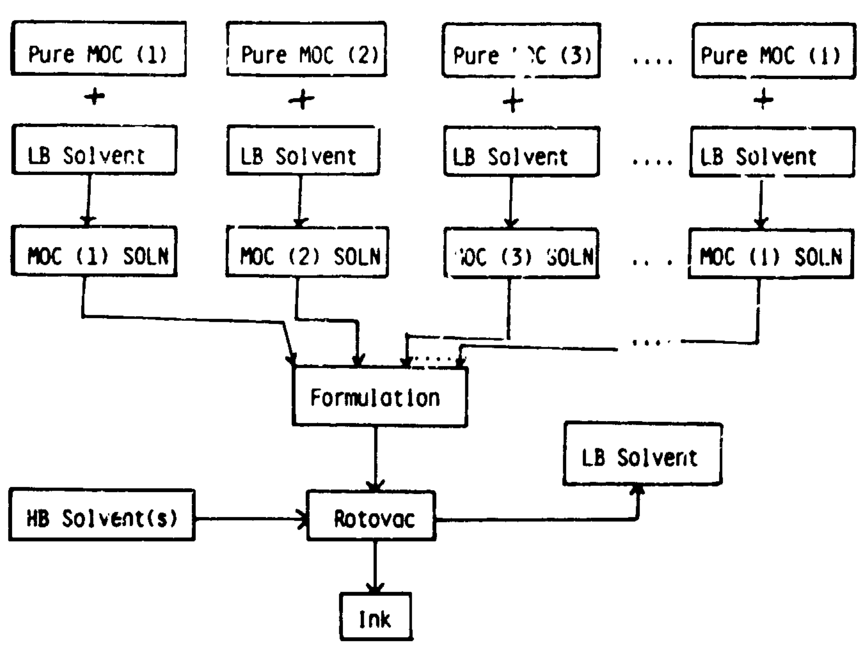
Thermogram of Pt 2-ethylhexanoate in Benzene



Thermogram of Ag Neodecanoate Plus 2-ethylhexanoate in Benzene



Screen-Printing Ink Fabrication



Critical Steps in Ink Fabrication

Metallo-organic compounds
1. Selection
2. Purity

Low Boiling Solvent
1. Selection
2. Purity

High Boiling Solvent(s)
1. Selection
2. Purity
3. Amount

Rotovac
1. Time
2. Temperature
3. Pressure

Low Boiling Solvents Evaluated

	B.P.(°C)	Comments
xylene	137	incomplete solvent exchange dark films
toluene	111	incomplete solvent exchange dark films
benzene	80	near complete solvent exchange silver films
tetrahydrofuran	66	near complete solvent exchange silver films

High-Boiling Solvents Evaluated

	B.P.(°C)
α- terpineol	217-218
butyl carbitol acetate	236-249
phenyl ether	259
dodecane	215-217
neodecanoic acid	250-257
triglyme	216
decalin	186-195

Ink SPC1-YZ

1. Dissolve x grams of Ag neodecanoate in benzene to give approximately 11 w/o Ag in solution.

2. Add Pt 2-ethylhexanoate in benzene to give fired composition 96 w/o Ag - 4 w/o Pt.

3. Add 0.13x grams of butyl carbitol acetate and 0.26x grams of neodecanoic acid.

4. Mix in the rotovac for 15 minutes at room temperature and pressure.

5. Solvent exchange in the rotovac for 1 hour at 40°C under water pump vacuum.

6. The smooth, black ink screen prints well and produces 24.5 w/o Ag + Pt when fired to 285°C or higher.

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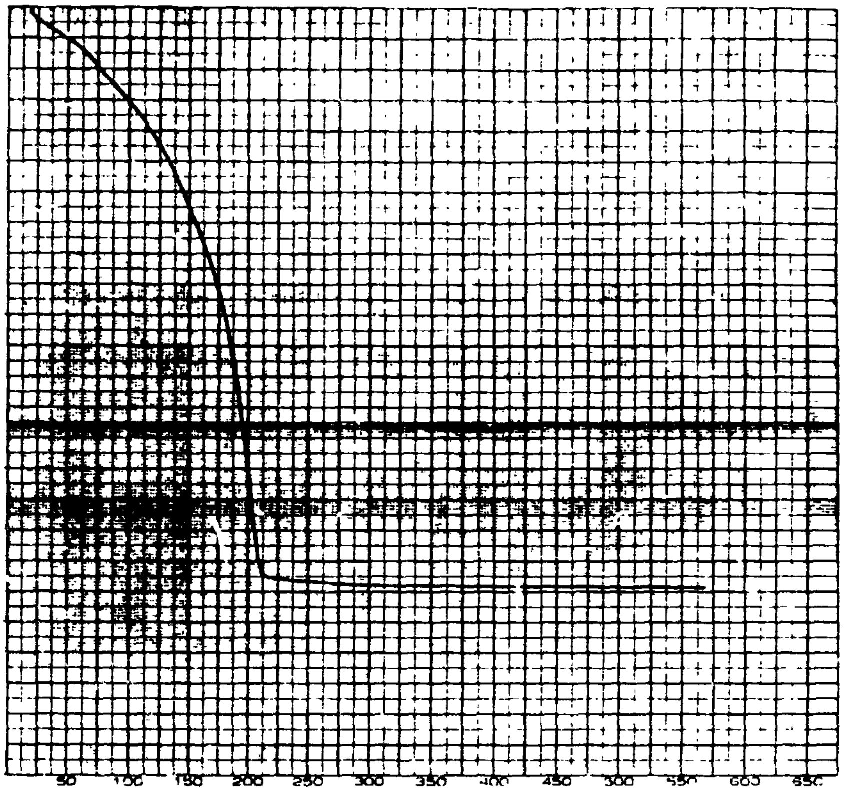
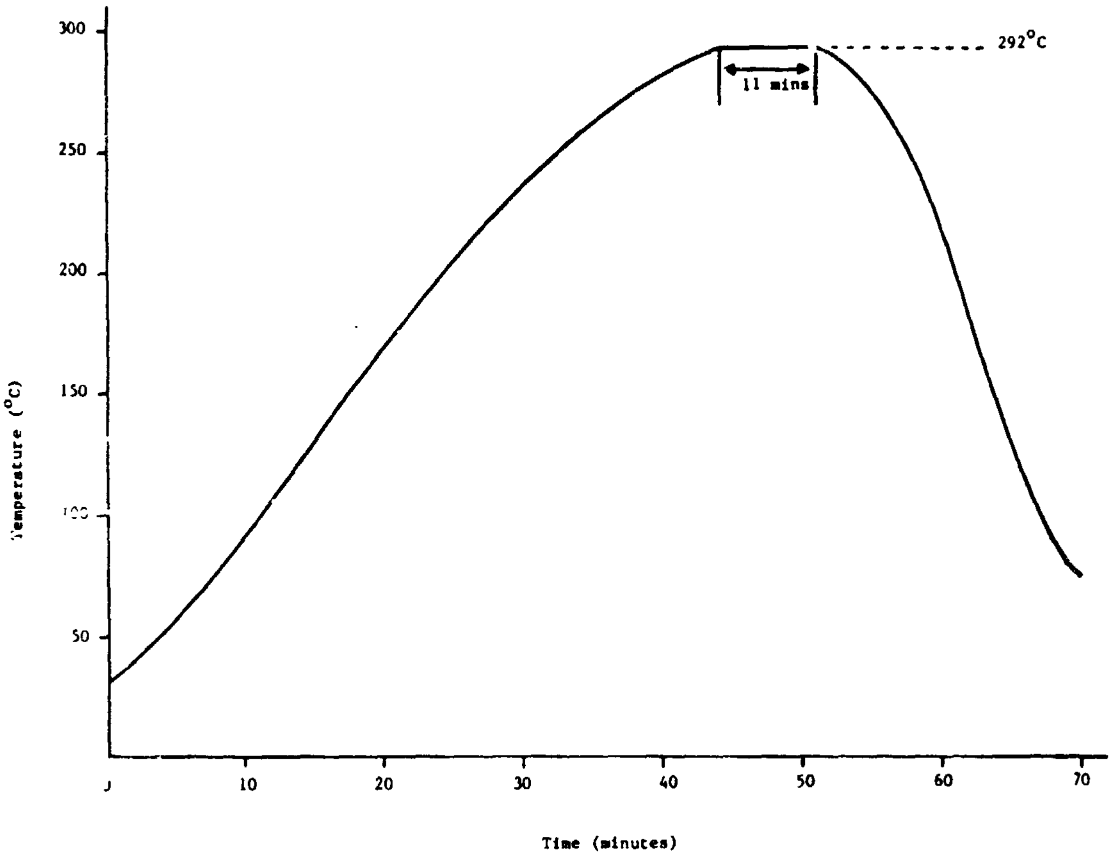
Thermogram of Ag-Pt Ink SPC1-1A



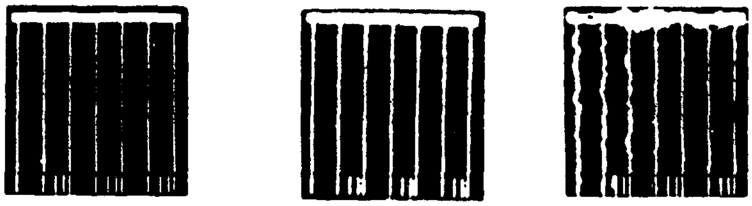
Standard Firing Sequence No. 1 Profile



Film Characteristics Evaluated

1. Appearance
2. Sheet Resistance (Density)
3. Line Definition
4. Adehsion

Rating System for Reporting Line Definition of Fired Films Using the JPL Pattern



A. Excellent B. Acceptable C. Unacceptable

Firing Study Results for Ink SPC1-YZ

Test#	Ink#	Firing Sequence Temp (°C)	Time (min)	Type of Furnace	Substrate*	Surface Appearance	Line Defin.	Sheet Resist. (mΩ/sq)	Adhesion
1	SPC1-1A Age-3.5 hr R.H.=42%	65 200 325	30 30 20	1	Al_2O_3 (d)	whitish silver	B	56	excellent (poor on connecting bar)
2	SPC1-1C Age-19 days R.H.=54%	65 200 325	30 30 30	1	cells (d),(i) (batch 172-2)	whitish silver	B(A for narrow lines)	40	poor to fair
3	SPC1-1A Age-3.5 hr R.H.=42%	65 200 325	30 30 20	1	cells (a),(d) (batch 172-2)	whitish silver	A	45	zero
4	SPC1-1A (b) Age-3.5 hr R.H.=42%	65 200 325	30 30 20	1	Al_2O_3 (d)	whitish silver	B	26	poor
5	SPC1-1B Age-16 day R.H.=52%	65 200 325	30 (c) 30 30	1	Al_2O_3 (d)	whitish silver	A	62	zero
6	SPC1-1D Age-25 day R.H.=54%	65 200 325	30 30 30	1	Al_2O_3	whitish silver	B	80	good on narrow lines, poor on connecting bar
7	SPC1-1D Age-25 day R.H.=54%	Std. Firing Sequence #1 (e)		4	Al_2O_3	whitish silver	B(A for connecting bar)	72	excellent
8	SPC1-1E Age-27 day R.H.=unknown	Std. Firing Sequence #1		4	cells (i) (batch 341-177)	whitish silver	A	58	good to excellent on narrow lines, fair to poor on wide connecting bar
9	SPC1-2A Age-2 hr R.H.=50%	65 200 325	30 30 30	1	cells (i) (batch 341-177)	whitish silver	B	87	poor (zero)
10	SPC1-2A Age-2 hr R.H.=50%	Std. Firing Sequence #1		4	cells (i) (batch 341-177)	whitish silver	B	54	excellent
11	SPC1-2A Age-2 hr R.H.=50%	2nd layer printed and the firing sequence of Test 10 repeated		4	cells (i) (batch 341-177)	whitish silver	B	23	poor to fair

Test#	Ink#	Firing Sequence Temp (°C) Time (min) Type of Furnace	Substrate*	Surface Appearance	Line Defin.	Sheet Resist. (mΩ/sq)	Adhesion
12[f]	SPC1-2B Age-8 day R.H.=48%	Std. firing sequence #1	cells[i] (batch 341-177)	whitish silver	C	47	excellent
13	SPC1-2B Age-8day R.H.=48%	Std. Firing Sequence #1	cells[i] (batch 341-177)	whitish silver	B	56	excellent
14	SPC1-2A Age-8 day R.H.=48%	Second layer printed and the firing sequence of test #2 was repeated	cells[i] (batch 341-177)	whitish silver	B	24	excellent
15	SPC1-2B Age-8 day R.H.=48%	Same as test #3 except batch drying step (30 mins at 65°C) is skipped after 2nd layer is printed	cells[i] (batch 341-177)	whitish silver	B	24	excellent
16	SPC1-2C Age-15 day R.H.=54%	Std. Firing Sequence #1	cells[d],[i] (batch 341-177)	whitish silver	B	51	excellent
17	SPC1-2C Age-15 day R.H.=54%	Std. Firing Sequence #1	cells [i] (batch 341-177)	whitish silver	B	53	excellent
18	SPC1-2C Age-15 day R.H.=54%	Second layer printed and the firing sequence of test #6 was repeated	cells[i] (batch 341-177)	whitish silver	B	26	excellent
19	SPC1-2C Age-15 day R.H.=54%	Third layer printed and fired. Unfortunately, firing was insufficient due to mechanical failure).	cells[i] (batch 341-177)	whitish silver	C[g]	16	fair to poor
20	SPC1-2E Age-28 days R.H.=54%	2 layers printed with only a drying step between layers of 30 mins at 70°C. Once 2nd layer was printed the Std. Firing Sequence #1 was used.	cells[i] (batch 341-177)	whitish silver	B	29	excellent
21	SPC1-2E Age=28 days R.H.=54%	Std. Firing Sequence #1	cells[i] (batch 341-177)	whitish silver	B	76	excellent
22	SPC1-2D Age-28 day R.H.=54%	Std. Firing Sequence #1	cells[i] (batch 346-193)	whitish silver	B	72	excellent (initially)
23	SPC1-2F Age-53 day R.H.=60%	Std. Firing Sequence #1	cells[i] (batch 346-193)	whitish silver	B	77.8	excellent

Test#	Ink#	Firing Sequence: Temp (°C)	Firing Sequence: Time (min)	Firing Sequence: Type of Furnace	Substrate*	Surface Appearance	Line Defin.	Sheet Resist. (mΩ/sq)	Adhesion
24	SPC1-2F Age-53 day R.H.=60%	Std. Firing Sequence #1			cells[(i)] (batch 346-193)	whitish silver	B	61.4	excellent
25	SPC1-2F Age-53 day R.H.=60%	Std. Firing Sequence #1			cells[(a)] (batch 346-193)	whitish silver	B[(k)]	60.3	excellent
26	SPC1-3A Age-6 hr R.H.=58%	Std. Firing Sequence #1			cells[(i)] (batch 346-193)	whitish silver	A/B[(l)]	62.0	excellent on narrow lines poor on connecting bar
27	SPC1-3A Age-6 hr R.H.=58%	Std. Firing Sequence #1			cells[(a)] (batch 346-193)	whitish silver	A	57.7	excellent
28	SPC1-3A Age-8 hr R.H.=58%	Second layer printed and Std. Firing Sequence #1 repeated			cells[(i)] (batch 346-193)	whitish silver	A/B	22.9	poor
29	SPC1-3A Age-8 hr R.H.=58%	Second layer printed and Std. Firing Sequence #1 repeated			cells[(a)] (batch 346-193)	whitish silver	A/B	23.5	poor
30	SPC1-3A Age-10 hr R.H.=58%	Third layer printed and Std. Firing Sequence #1 repeated			cells[(i)] (batch 346-193)	whitish silver	B	20.0	poor
31	SPC1-3A Age-10 hr R.H.=58%	Third layer printed and Std. Firing Sequence #1 repeated			cells[(a)] (batch 346-193)	whitish silver	A/B	14.9	poor

*Al_2O_3 = AlSiMag 838 substrates

cells = solar cells supplied by JPL.

(a) cells cleaned in hydrofluoric acid prior to printing by HF cleaning procedure.
(b) 2 layers printed. Sequence = print-dry-fire-print-dry-fire.
(c) the length of time at 65°C was varied from 30 minutes to 120 minutes in increments of 30 minutes but no effect on fired film properties was observed.
(d) cells or other substrates printed as-received. No pre-drying step of at least 30 mins. at 65°C was performed.
(e) Standard Firing Sequence #1 as detailed in section 3.2 is as follows:

Temp.	Time	
65	30 --	batch dry
R.T.-263	6.7°/min	belt fire
263-292	4.6°/min	
292	11.3 min	
292-245	7°/min	
245-62	18.3°/min	
62-R.T.	1.1°/min	

(f) two layers printed with no heat treatment between printings.
(g) poor line definition was due to mechanical problems with screen printer which have subsequently been corrected.
(h) see Table 4.4 for detailed results of Test NO. 22.
(i) cells not cleaned prior to printing.
(j) cells cleaned by methanol cleaning procedure.
(k) lines sharper but more thready than above two.
(l) A/B rating means some cells showed A rating and others B rating.

Adhesion vs Time Study With Single-Layer Fired Films of Ink SPC1

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	30,65	Adhesion losses occurring both on connecting bar and 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.

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Brief Adhesion/Time Study with Single Layer Fired Films of Ink SPCI[a] 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[b]	60%	100	
0	HF[c]	60%	100	
0	MeOH[d]	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 [illegible] apparent visual differen[illegible] between this and day 3 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 d[illegible]
18	HF	55.5%	2	
18	MeOH	55.5%	1	

Summary

1. Bright Ag or Ag/Pt films with near theoretical density can be formed on Si below 300°C provided:

   a. the proper MO compounds are selected (Ag neodecanoate and Pt 2-ethylhexanoate work);

   b. the proper low boiling solvent is used in the formulation (benzene or tetrahydrofuran work);

   c. the proper high boiling solvent is used in the ink (a mixture of butyl carbitol acetate and neodecanoic acid works);

   d. the MO compounds are suitably purified;

   e. a low temperature drying step is used (30 minutes at 65°C works; and

   f. a proper firing profile is used (a 70 minute cycle with 11 minutes at 292°C works).

2. Excellent adhesion can be achieved with the proper ink chemistry and processing conditions, but the adhesion begins to degrade after several days.

3. A binding agent will be required to achieve reproducible, long term adhesion.