CHAPTER IV

RESULTS AND DISCUSSION

4.1 Selection of colophonies

The colophonies are either a pure colophony WW or modified type for better resistance and solubility. These materials may be referred to generically as resins and as used herein the term "resin" includes natural resins such as rosin, chemically modified rosin, and synthetic resins. For the good characters, the colophony must have the following characteristics:

1. Softening point must be between 70-150 ^{O}C.
2. The color of this colophony must be colorless to yellow because the preferred solder paste is used in no clean process.
3. The acid value of the colophony must be closed to or higher than the natural rosin because if the colophony has the high acid value it would affect the corrosion, wetting and dewetting properties.
4. The hydrogenated rosin has greater resistance to oxidation than the natural rosin.
5. The hydrogenated rosin is pale to white because most of its double bond has been hydrogenated.
6. The colophony must be easily dispersed in solvents, together with additional activators and gelling agents.

From this rational, KE604 was selected as the best candidate for solder paste flux.

Table 4.1 The comparison of two types of colophonies.

Items	WW ROSIN	KE604
Type	WW	Hydrogenated Rosin
Color	Pale yellow	Colorless
Appearance	Transparent Lump	Transparent Lump
Softening point, ^{O}C	78 minimum	122-132
Acid Value, mgKOH/g	165 minimum	230-245
Price	27 ฿/KG	533.25 ฿/KG

4.2 Selection of solvents

The solvent was selected regarding its ability to dissolve the colophony, its low rate of evaporation at room temperature (but with sufficient rate at preheat temperature), its low flammability and its compatibility with the other flux components, whereas its boiling point should lie below the soldering temperature and more preferably from about 170 ^{O}C to about 215 ^{O}C. From Table 4.2, the most suitable solvent was diethylene glycol diethyl ether.

Table 4.2 The properties of twelve types of solvents.

Property	PEG200	PEG400	PEG600	DGMBE	DGDEE	DGDBE
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Specific gravity, g/cm^3	1.124	1.13	1.13	0.95	0.91	0.88
Odor	Almost odorless	Almost odorless	Almost odorless	Almost odorless	Weak	Ether-like
Melting point, ^{O}C	-55- - 40	4-8	17-22	-68	-44	-60
Boiling point, ^{O}C	>250	>250	-	226-234	189	254
Flash point, ^{O}C	180	240	270	105	82	118
Soluble in water, g/l	Freely	Soluble	Freely	Soluble	Soluble	3
Ignition temp. , ^{O}C	350	~370	380	225	174	Not available
Viscosity dynamic @20^{O}C, mPa*s	60-70	105-140	175	5.85	1.4	2.4
Molecular weight, g/mole	190-210	380-420	600	162.23	162.23	218.33
LD_{50} (Oral, rat), mg/kg	28000	>15000	>15000	4120	6097	3555

Table 4.2 The properties of twelve types of solvents (continued).

Property	Acetone	Ethanol	1-Butanol	Ethyl acetate	2-Propanol	Toluene
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Specific gravity g/cm^3	0.79	0.79	0.81	0.90	0.78	0.87
Odor	Characteristic	Characteristic	Characteristic	Characteristic	Characteristic	Characteristic
Melting point, ^{o}C	-95.4	-148	-89	-83	-89.5	-95
Boiling point, ^{o}C	56.2	35	116-118	77	82.4	110.6
Flash point, ^{O}C	Less than -20	12	34	-4	17	4
Soluble in water, g/l	Soluble	Soluble	Soluble	Freely85.3	Soluble	0.52
Ignition temp. , ^{o}C	540	425	340	460	425	535
Viscosity dynamic @20^{O}C, mPa*s	-	-	-	-	2.2	0.6
Molecular weight, g/mole	58.08	46.07	74.12	88.1	60.10	92.14
LD_{50} (oral, rat), mg/kg	5800	6200	790	5620	5045	636

4.3 Selection of activators

Activators are added to decompose and remove any oxide film existing in the portion where soldering is going to be carried out, and are usually organic compounds containing halides, typically amine hydrohalogenides, such as diethylamine hydrochloride or weak halide-free organic acids. The resin may be a weak acidic activator but it is also added to protect the metals from oxidation during solder paste reflow. Using additional activators and/or developing improved halide-containing activators is thus not very effective in improving the resistance of solder pastes in aggressive reflow processes.

Additional activators also adversely affect the shelf life of solder pastes and reduce the resistance of the solder paste to drying during the printing process.

The activator should be selected by 2 major factors

1. Flux efficacy, which is the ability of the flux to promote solder wetting. Efficacy is closely related to chemical activity.
2. Flux corrosive, which is the ability of flux residues to affect the soldered products after the soldering process.

From the reflow temperature profile, the temperature of flux action was between 100-235 ^{O}C, then, the melting point of the activator must be within this range. From the information in table 4.3 and the information from the temperature profile, the mort preferred activators are dimethyl ammonium chloride (imported problem), ethyl ammoniumchloride, succinic acid and adipic acid. However, at the present, No-Clean and halide free flux is the most popular which implied that the activators are selected for this research are succinic acid and adipic acid and the most prefer activator was succinic acid

Table 4.3 The properties of five types of activators.

Property	Succinic acid	Adipic acid	DEA. HCl	ETA. HCl	TEA. HCl
Appearance	Solid	Solid	Crystal	Crystal	Crystal
Melting point, ^{O}C	183-187	151.4-154.0	225-227	107-108	256-269
Boiling point, ^{O}C	~235	>250	320-330	-	-
Soluble in water	Soluble	15g/l	Soluble	Freely	1440 g/l
Mw, g/mole	118.09	146.14	109.50	81.55	161.21
Thermal Decomposition, ^{O}C	-	338	>270	>270	-
LD50, mg/kg	2260	~5700	7000	>3200	-

4.4 Selection of thickening agent

The thickening agent gives the thixotropic property of solder paste fluxes and has the purpose of preventing the sagging of the powder particles, and thus producing good resolution during printing or screening. Its effect, however, rapidly vanishes when the temperature is increased and therefore the colophony content of the paste should be above a lower limit, depending on the metal content.

As suggested by the patent no 4,218,248 the suitable thickening agents are hydroxyethylcellulose, methylcellulose and xanthan gum but the preferred thickening is ozokerite wax. In this study ozokerite was the thickening agent of choice.

4.5 Effect of solvent and colophony on viscosity and solubility of solder paste flux

From the physical properties of colophony, solvent, activator and thickening agent, KE604, diethylene glycol diethyl ether, succinic acid and ozokerite wax were chosen for this study.

The influence of solvent and rosin concentration on viscosity and solubility was determined at five different concentrations of KE604 and diethylene glycol diethyl ether.

Figure 4.1 shows the viscosity of solder paste flux increased when the concentration of KE604 increased. In this study, the preferred solder paste flux should have viscosity in the range of 300000 – 450000 centipoises. From Figure 4.1, the formula contained 65 wt% KE604, 30 wt% ethylene glycol diethyl ether gave the most suitable viscosity.

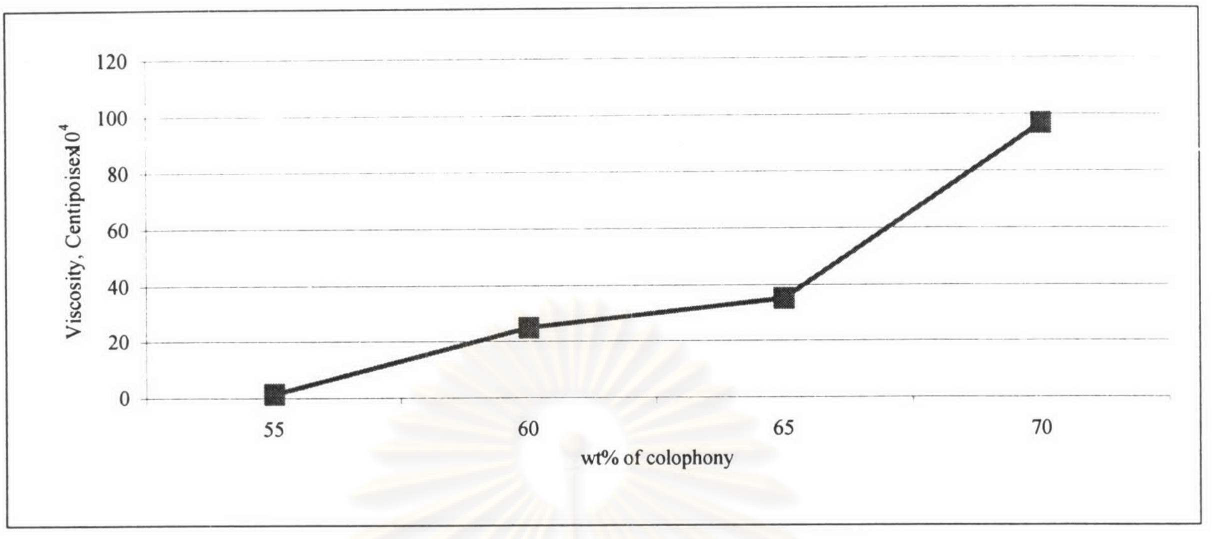


Figure 4.1 Effect of solvent and colophony concentration on solder paste flux viscosity at T = 25 ^{O}C, %RH = 50 ^{O}C for five different concentrations.

4.6 Effect of thickening agent concentration on slump property.

The influence of ozokerite wax concentration on viscosity and solubility was determined at five different thickening agent concentrations (0 – 15 wt %).

From Tables 4.5 and 4.6, it was found that the slump percentage of solder paste flux at 25°C decreased when the concentration of ozokerite increased and stable at the concentration of ozokerite wax more than 12.5 wt%. Figure 4.3 indicated that slump at 150 ^{O}C decreased when the concentration of ozokerite increased and stable at the concentration of ozokerite more than 12.5 wt %.

Figure 4.2 and Table 4.4 indicated that the viscosity of solder paste flux increased when the concentration of ozokerite wax increased. However, at 15 wt% of ozokerite wax the flux became solid.

In this study, the percentage of slump at 25 °C and 150 °C must be less than 5 % and the viscosity of solder paste flux should be in the range of 300000 – 450000 centipoises. Therefore, the formula containing 7.5 wt% of ozokerite was the most suitable one.

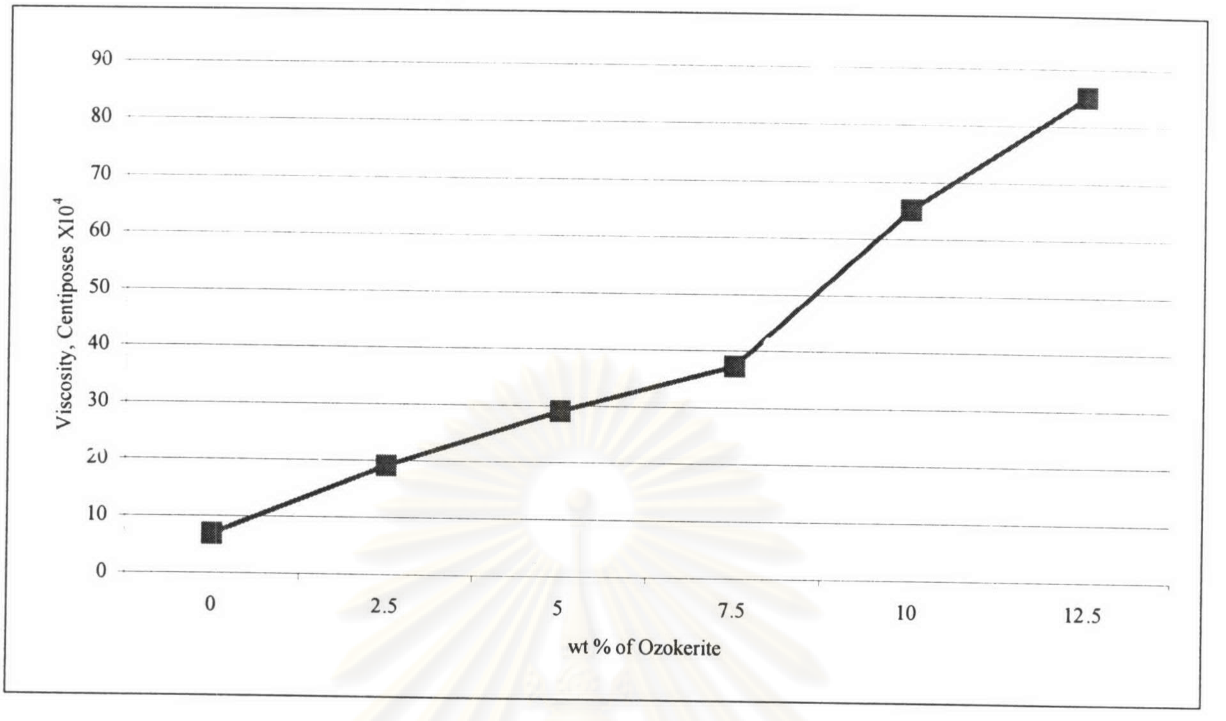


Figure 4.2 Effect of ozokerite concentration of solder paste flux viscosity at T = 25 ^{O}C, %RH = 50 ^{O}C

Table 4.4 Viscosity of solder paste flux at T = 25 ^{O}C, %RH = 50 ^{o}C and various concentrations of ozokerite

% Ozokerite	No. 1	No. 2	Avg.	%Stdv.
0	70	68	69	1.41
2.5	192	189	190.5	2.12
5	292	290	291	1.41
7.5	374	372	373	1.41
10	654	650	652	2.83
12.5	852	849	850.5	2.12

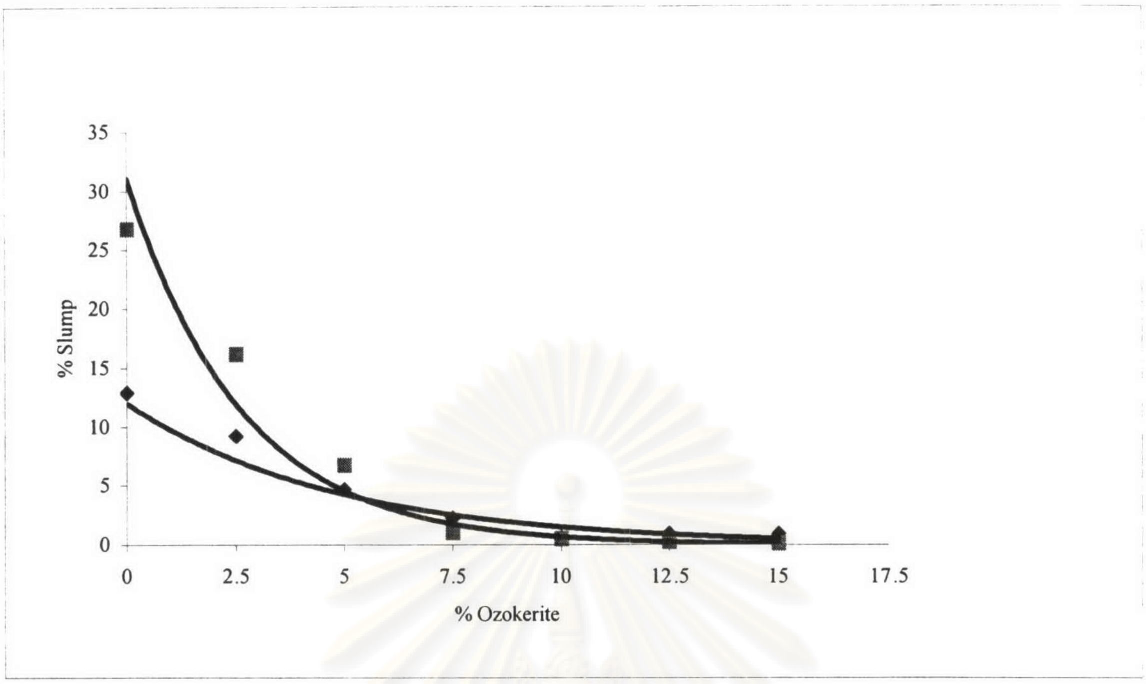


Figure 4.3 Effect of Ozokerite concentration on the slump of solder paste flux viscosity at T = 25 ^{O}C (◆ line) and T = 150 ^{O}C (■ line), %RH = 50 for seven different concentrations.

Table 4.5 The % slump at T = 150 ^{O}C, %RH = 50 of solder paste flux of 10 wt% mixed with solder powder 63/37 Sn/Pb (Type III) 90 wt% and various concentrations of ozokerite.

%Ozokerite	Slump property, %									Average % Slump	Stdv.
	1			2			3				
	D_I	D_H	%Slump	D_I	D_H	%Slump	D_I	D_H	%Slump		
0.0	5.01	6.40	27.74	5.00	6.31	26.20	5.00	6.32	26.40	26.78	0.84
2.5	5.00	5.82	16.40	5.00	5.80	16.00	5.00	5.80	16.00	16.13	0.23
5.0	5.00	5.32	6.51	5.00	5.35	7.00	5.00	5.33	6.60	6.70	0.26
7.5	5.02	5.05	0.60	5.00	5.06	1.20	5.00	5.07	1.40	1.07	0.42
10.0	5.00	5.02	0.40	5.00	5.03	0.60	5.00	5.02	0.40	0.47	0.12
12.5	5.01	5.01	0.00	5.00	5.02	0.40	5.00	5.02	0.40	0.27	0.23
15.0	5.00	5.01	0.20	5.00	5.00	0.00	5.00	5.01	0.20	0.13	0.12

Table 4.6 The % slump at T = 25 ^{O}C, %RH = 50 of solder paste flux and various concentrations of ozokerite.

%Ozokerite	Slump property, %									Average % Slump	Stdv.
	1			2			3				
	D_I	D_H	%Slump	D_I	D_H	%Slump	D_I	D_H	%Slump		
0.0	5.01	5.67	13.17	5.00	5.65	13.00	5.00	5.63	12.60	12.92	0.29
2.5	5.00	5.48	9.60	5.00	5.40	8.00	5.00	5.50	10.00	9.20	1.06
5.0	5.00	5.25	5.11	5.00	5.23	4.60	5.00	5.22	4.40	4.70	0.36
7.5	5.02	5.10	1.59	5.00	5.11	2.20	5.00	5.15	3.00	2.26	0.71
10.0	5.00	5.04	0.80	5.00	5.02	0.40	5.00	5.03	0.60	0.60	0.20
12.5	5.01	5.05	0.80	5.00	5.03	0.60	5.00	5.07	1.40	0.93	0.42
15.0	5.00	5.05	1.00	5.00	5.05	1.00	5.00	5.04	0.80	0.93	0.12

4.7 Effect of thickening agent concentration on tackiness property

The tackiness property of solder paste flux was determined by using five different thickening agent concentrations (0 – 15 wt %).

Table 4.7 shows the tackiness of solder paste flux at various concentrations of ozokerite wax. The tackiness property of solder paste flux containing 0 – 5 wt% ozokerite wax was worse than that of the solder paste flux containing 7.5 – 15 wt% ozokerite wax.

The suitable ozokerite wax concentration giving the good slump behavior, suitable viscosity and good tackiness property was 7.5 wt %.

Table 4.7 The tackiness property at T = 25 ^{O}C, %RH = 50 and various ozokerite concentrations.

%Ozokerite	Time, Hour								
	1	2	3	4	5	6	7	8	24
0.0	-	-	-	-	-	-	-	-	-
2.5	-	-	-	-	-	-	-	-	-
5.0	+++	+++	++	+	+	+	-	-	-
7.5	+++	+++	+++	+++	+++	+++	++	++	-
10.0	+++	+++	+++	+++	+++	++	++	++	-
12.5	+++	+++	+++	+++	+++	+++	+++	++	+
15.0	+++	+++	+++	+++	+++	+++	+++	+++	+

Note: -, where the tackiness property was unacceptable, all solder paste was skinned from glass slide.

+, where the tackiness property was unacceptable, some of solder paste was skinned from glass slide.

++, where tackiness property was acceptable, without solder paste skinned.

+++, where the tackiness property was the best.

4.8 Effect of activator concentration on corrosion properties

The corrosion properties of solder paste flux were determined at 6 different concentrations of succinic acid (0 to 5% wt) by measuring the copper plate corrosion and electrical insulation resistance of solder paste flux.

Figure 4.4 shows the data of Electrical Insulation Resistance (EIR) at different concentrations of succinic acid concentration. The EIR of solder paste flux decreased when the concentration of succinic acid increased.

Table 4.8 shows the corrosion of six concentrations of 0 to 3 wt% succinic acid, the corrosions of solder paste flux did not occur but if the succinic acid concentration was more than 4 wt% the corrosion occurred was clearly visible.

Table 4 .8 The corrosion and electrical insulation resistance at T = 40 ^{O}C, %RH = 90 for 168 hours of various acid concentrations

% succinic acid	Corrosion	Electrical insulation resistance, OHM (x 10^{10})					Average (x 10^{10})	%Stdev.
		1	2	3	4	Average		
0	No corrosion	51.30	69.55	53.78	58.83	58.37	65.23	16.86
		64.80	103.61	66.20	53.75	72.09		
1	No corrosion	21.56	32.91	23.06	25.17	25.67	26.25	4.44
		29.37	31.25	25.50	21.22	26.84		
2	No corrosion	23.70	33.51	20.25	22.61	25.02	20.55	6.37
		14.33	14.51	15.40	20.08	16.08		
3	No corrosion	12.89	12.05	11.70	11.62	12.07	13.02	1.62
		16.67	13.24	13.53	12.42	13.96		
4	Some of corrosion	3.48	2.40	4.05	5.38	3.82	3.57	0.93
		3.36	2.48	3.59	3.80	3.31		
5	Corrosion	1.23	1.39	1.55	1.51	1.42	1.72	0.38
		2.30	2.19	1.63	1.99	2.03		

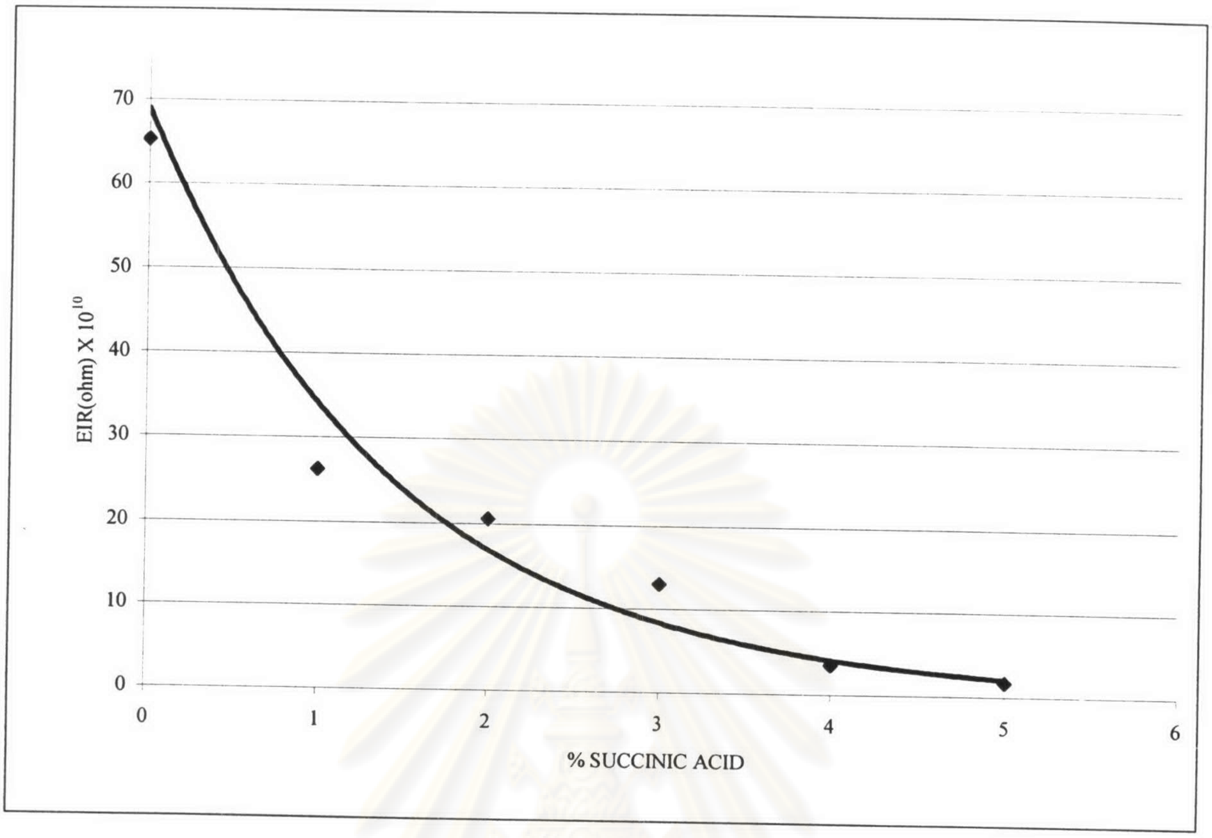


Figure 4.4 Effect of % succinic acid concentration on electrical insulation resistance (Ω) at T = 40 ^{O}C, %RH = 90 for 168 hours.

4.9 Effect of succinic acid on wetting property of solder paste flux.

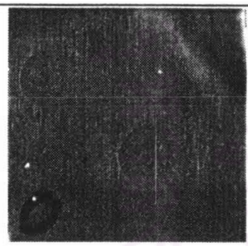
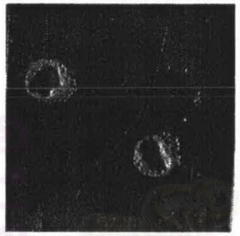
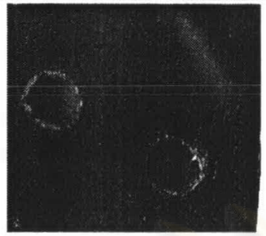
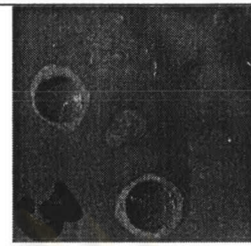
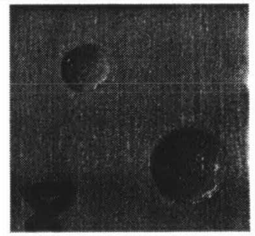
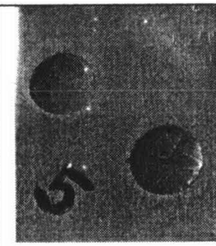
The wetting property of solder paste flux was determined at six different concentrations of succinic acid.

Table 4.9 shows the wetting property of six different concentrations of solder paste fluxes.

When the succinic concentration increased the degree of spread of solder paste flux increased. The acceptable degree of spread was class 1 (Condition where the solder dissolved from the solder paste wets the test plate, and the wetted area becomes larger than the past-coated area) and 2 (Condition where all of coated part by the solder paste was wetted).

From the corrosion, wetting and dewetting test, succinic acid at 3 wt% was the most suitable activator.

Table 4.9 The wetting behavior at T = 235 ^{O}C, %RH = 50 and various succinic concentrations.

% Succinic acid	0	1	2	3	4	5
Picture of wetting result						
Class of spread	4	3	3	2	2	1

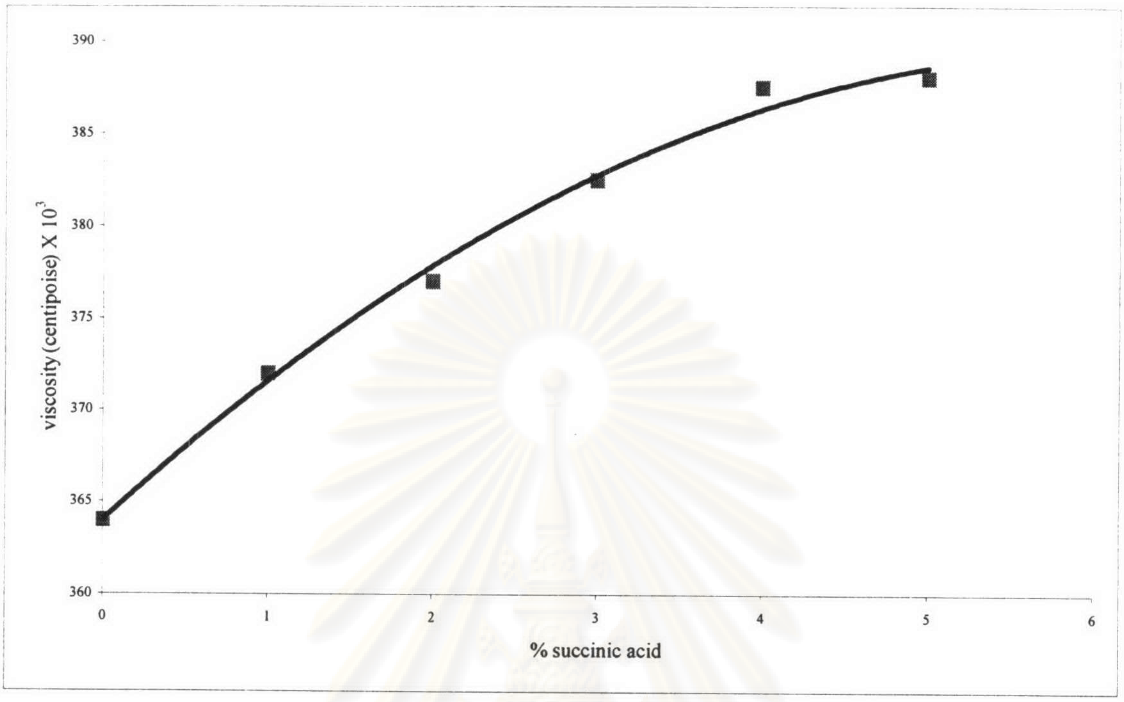


Figure 4.5 Effect of succinic acid concentration on solder paste flux viscosity at T = 25 ^{O}C, %RH = 50 ^{O}C

Table 4.10 Viscosity of solder paste flux at T = 25 ^{O}C, %RH = 50 and various the concentrations of succinic acid

%Succinic acid	No. 1(centipoises) X 10^3	No. 2(centipoises) X 10^3	Average (centipoises) X 10^3	% Stdv
0	368	360	364	5.66
1	374	370	372	2.83
2	376	378	377	1.41
3	380	385	383	3.54
4	386	389	388	2.12
5	390	386	388	2.83

4.10 Comparison of the properties of solder paste flux developed in this study with those commercially available.

In this study, the most suitable solder paste flux was obtained using 61.8 wt% KE604, 28.4 wt% diethylene glycol diethyl ether, 6.9 wt% ozokerite wax and 2.9 wt% succinic acid. Table 4.11 shows a comparison of solder paste flux properties of the present work solder paste flux with Q3 and 5T Asahi solder paste flux. It was found that the properties of the present work solder paste flux, O3 and 5T were similar except that the electrical insulation resistance of O3 and 5T are higher than that of the present work. However, total of solder paste flux properties of the present work are accepted.

Table 4.11 The comparisons of three types of solder paste fluxes.

Item	Developed solder paste flux	Q3-solder paste flux	5-T solder paste flux
1. Appearance	Transparent yellowish paste	Transparent yellowish paste	Transparent yellowish paste
2. Viscosity at T = 25 ^{O}C	374	318	415
3.Wetting property	2	2	2
4. Copper plate corrosion	No corrosion	No corrosion	No corrosion
5. Electrical insulation resistance, Ω	1.30×10^{11}	5.26×10^{12}	6.53×10^{12}
6. Slump property, at T = 25 ^{O}C, %RH = 50	1.07	1.05	0.98
7. Slump property, at T = 150 ^{O}C, %RH = 50	2.26	2.53	1.96
8. Tackiness property	+++	+++	+++

4.11 Effect of storage temperature on quality of solder paste fluxes

The effect of storage temperature was determined at two different temperatures (0-10°C and 11-35 °C) for three months.

Table 4.12 shows the quality of solder paste fluxes stored at 0-10°C, which was the same as those of the fresh solder paste flux. However, the viscosity of solder paste flux stored at 11-35 °C is higher and have some of separated portion at the top of the solder paste flux and the total qualities of solder paste flux were worse than those of the fresh solder paste flux and the solder paste flux stored at 0-10°C.

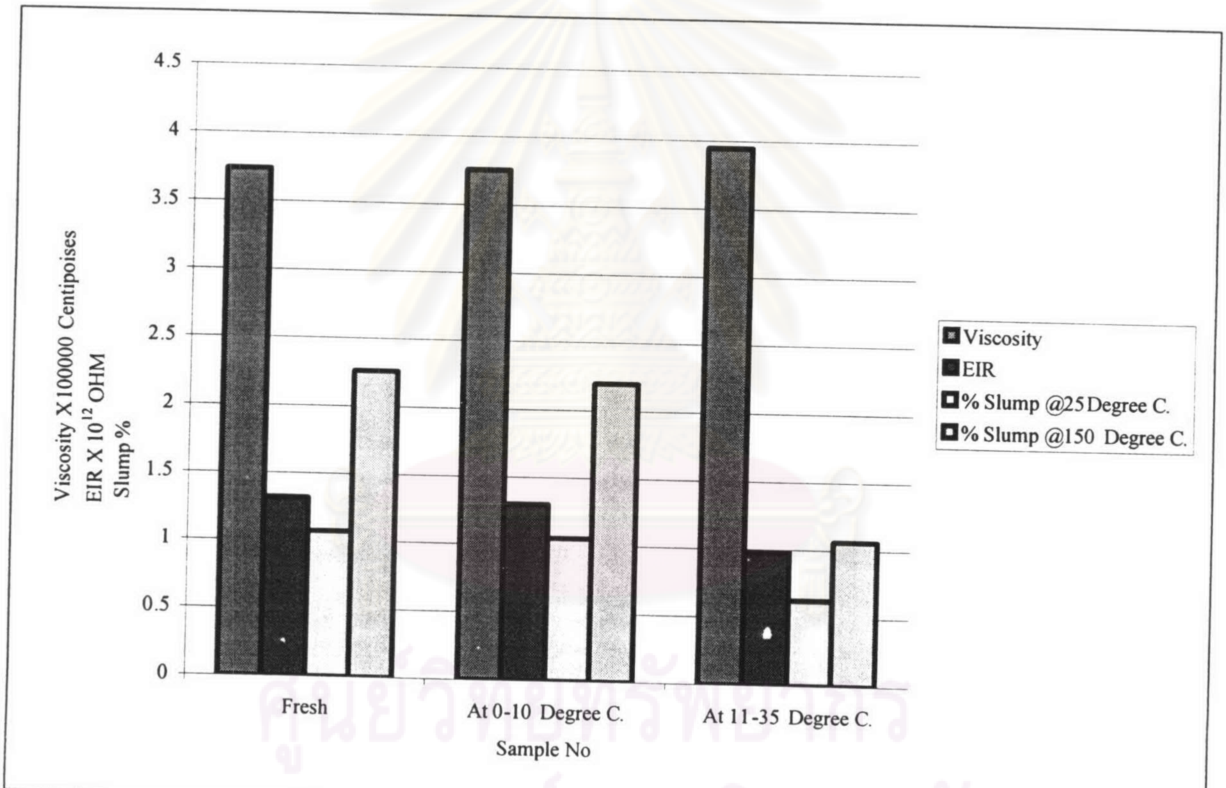
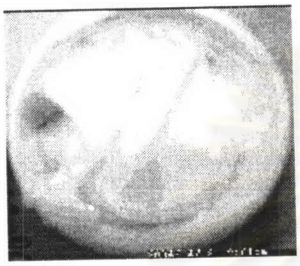
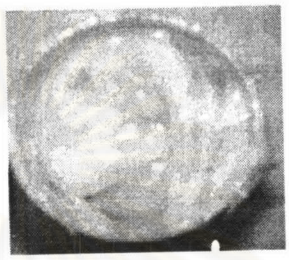
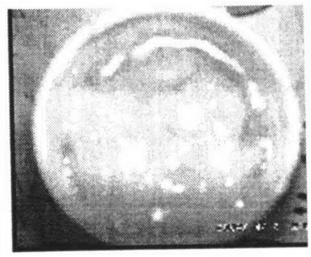


Figure 4.6 Effect of storage temperature on the quality of solder paste flux for two storage conditions (at 0-10 ^{O}C and 11-35 ^{O}C T = 25 ^{O}C, %RH = 50 ^{O}C) compared with the fresh solder paste flux with same composition.

Table 4.12 The qualities data of solder paste fluxes at two different storage temperatures.

Item	Developed solder paste flux		
	Initial	Storage at 0-10°C	Storage at 11-35°C
1. Appearance	Creamy paste without separated 	Creamy paste without separated 	Transparent creamy paste with clear portion on the top. 
2. Viscosity	374	376	395
3.Wetting property	2	2	2
4. Copper plate corrosion	No Corrosion	No corrosion	No corrosion
5. Electrical insulation resistance, Ω	1.30×10^{11}	1.29×10^{11}	0.98×10^{11}
6. Slump property, at T = 25 ^{O}C, %RH = 50	1.07	1.05	0.63
7. Slump property, at T = 150 ^{O}C, %RH = 50	2.26	2.20	1.06
7. Tackiness property	+++	+++	+++