Application of Thermal Latent Carboxylic Acid Derivatives to Pb-Free Microsoldering

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Pb-free microsoldering technology has become important, because complete elimination of lead from electric devices is soon to be enforced. In this work, we studied the application of thermal latent technology of a carboxyl group to Pb-free microsoldering. We found that thermal latent carboxylic acid derivatives could both prevent degradation of a solder alloy under normal conditions and serve as a novel activator when a solder alloy begins to melt. Furthermore, we found that the activator in the flux residue after soldering could be converted into an ester unit which has no influence on electric reliability. Solder paste using thermal latent carboxylic derivatives can be combined to achieve good wettability, high electric reliability and high storage stability, and can be useful for Pb-free microsoldering in response to environmental protection demands.

(Received October 17, 2003; Accepted January 20, 2004)

Keywords: thermal latent carboxylic acid derivative, lead-free solder, soldering flux, solder paste, wettability

1. Introduction

In recent years, many companies and research organizations have conducted much research on Pb-free solders that can be used in electronic products and greater concerns regarding environmental protection and the influence on the human body have been raised worldwide, including Japan and European countries. In some companies, Pb-free solders have already been applied in the production line, and they have accelerated the elimination of lead from various products for the future.^{1,2)} Besides this background, the RoHS Directive of the EU will be enforced from July 2006.

At present, the Sn-Ag-family and Sn-Zn-family of solders have been mentioned as candidates for Pb-free solders. However, all solders have merits, demerits and restrictions regarding their uses. For example, Sn-Ag-family solders have excellent mechanical properties and joint reliability, but they have a major problem in that their melting point becomes higher than that of Sn-Pb eutectic solder, whereby electronic parts and printed-circuit boards would be damaged by the heat. On the other hand, although the Sn-Zn-family solders have a low melting point and their cost is relatively low, they tend to oxidize, resulting in a problem with joint reliability. Therefore, there is no one solder which can be used for all electronic parts, and solders must be appropriately utilized according to the processing conditions of each manufacturer. Due to this background, the development of soldering flux materials applicable to Pb-free solders is very important.

In general, thermoplastic resin, for example, rosin, and an activator, such as a carboxylic acid compound or organic halide compound which can remove the metal oxide layer from the solder alloy surface, are blended into a soldering flux. It is necessary to include a strong activator to remove the surface oxidation layer in the soldering flux for the purpose of achieving excellent wettability, because Pb-free solders form a stable oxide layer on their surface. However, soldering pastes containing higher reactivity activators have been pointed out as having low storage stability and reduced reactivity due to the accompanying reaction of solder and

activator under normal conditions before the solder melts, and as adversely influencing the electric reliability due to the presence of activator in the flux residue. In other words, it depends on the type of soldering flux as to whether wettability, electric reliability and storage stability can be successfully combined.

We applied thermal latent processing of a carboxyl group (protection technique of carboxyl group) to an activator included in a soldering flux for Pb-free solders.

In this present study, the reactivities of the activator applied using the thermal latent processing of a carboxyl group and resultant solder alloys were investigated. Furthermore, in order to improve electric reliability, the neutrality of the activator (esterification of a carboxyl group) in the flux residue after soldering was also examined.

2. Thermal Latent Processing of Carboxyl Group (Protection Technique of Carboxyl Group)

Carboxylic acid compounds are very useful because they have high chemical reactivity, and are lowcost materials which are easily available commercially. However, despite many applications of carboxylic acid compound in various industrial fields, there are inherent drawbacks which limit its technological application.

1. Difficulty in formulating a practical chemical composition because many carboxylic acid compounds have low solubility in organic solvents and poor compatibility with coexisting ingredients because of the strong hydrogen bond.

2. Poor shelf life and short pot life due to high reactivity of a carboxyl group with the coreactive functional group, for example, the epoxy group.

In order to solve the above problems, we developed thermal latent processing of a carboxyl group (the protection technique of a carboxyl group), by which a carboxyl group activated chemically is converted into a hemiacetal ester moiety with alkyl vinyl ethers.³⁾ (Fig. 1)

The thermal latent carboxylic acid derivatives exhibited a liquid form or a low melting point and excellent solubility

Fig. 1 Protection of carboxyl group using alkyl vinyl ether and thermal dissociation of hemiacetal ester.

Fig. 2 Thermal curing reaction pathway between thermal latent carboxylic acid derivative.

and compatibility because hydrogen bonds do not exist in their molecular structure. Furthermore, although the thermal latent carboxyl groups were stable under normal conditions, the corresponding free carboxyl groups can be regenerated easily by thermal dissociation of the hemiacetal ester moiety. Using the protection technique of the carboxyl group, the thermosetting compositions with epoxy resin could form tough cured films which may have practical applications in automotive coatings, coil coatings and protective films for color filters.^{4,5)} (Fig. 2)

The application of thermal latent processing of a carboxyl group to solder pastes using Pb-free solders and their soldering flux can help to prevent solder alloys from degrading and also neutralize the activator that has a carboxyl group in the flux residue with epoxide after the soldering process. As a result, the Pb-free solder paste using thermal latent carboxylic acid derivatives could be combined to achieve good wettability, high electric reliability, and high storage stability.

3. Experimental

3.1 Materials

Glutaric acid, adipic acid, and sebacic acid were purchased from Tokyo Kasei Kogyo Co. Isopropyl vinyl ether was obtained from Nippon Carbide Industries Co. and was purified by distillation. Solder powders were obtained from Mitsui Kinzoku Kogyo Co. The average size of solder powders is 20~30 μm and they are spherical.

3.2 Measurements

¹H-NMR spectra were recorded on a BLUKER AVANCE400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-d (CDCl₃). IR spectra were obtained with JASCO FT/IR-610. Differential scanning

Fig. 3 Hemiacetal esterification of carboxyl group with 2-propyl vinyl ether.

calorimetry (DSC) was performed on Seiko Instruments DSC-6200 at a heating rate of 10°C/min in nitrogen atmosphere. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on Seiko Instruments TG/DTA-200 at a heating rate of 10°C/min in nitrogen atmosphere. Scanning electron microscope (SEM) was performed on HITACHI S-3000N. Quantitative analysis of the carboxyl group was carried out by titration with 0.07 N KOH in ethanol.

3.3 Hemiacetal esterification of a carboxyl group with alkyl vinyl ether (Fig. 3)

Glutaric acid di(2-propoxyethyl) ester

A mixture of 132.1 g (1.0 mol) of glutaric acid and 258.4 g (3.0 mol) of isopropyl vinyl ether in 2-butanone as the dilution solvent was stirred at 65°C for 4 h. Afterwards, completion of the hemiacetal esterification was confirmed by titration. Glutaric acid di(2-propoxyethyl) ester was obtained after removing the dilution solvent and excessive isopropyl vinyl ether under reduced pressure. Yield was 86% based on glutaric acid.

¹H-NMR (CDCl₃) δ 5.49 (2H, q, -COOCH(CH₃)-), 3.19 (2H, m, -OCH(CH₃)₂-), 2.07-2.25 (4H, t, -CH₂-COO-, 2H, m, -OOC-CH₂-CH₂-CH₂-COO-), 1.55 (6H, d, -COOCH(CH₃)-), 1.16 (12H, d, -O-CH(CH₃)₂)

Adipic acid di(2-propoxyethyl) ester

Yield was 83% based on adipic acid.

¹H-NMR (CDCl₃) δ 5.49 (2H, q, -COOCH(CH₃)-), 3.19 (2H, m, -OCH(CH₃)₂-), 2.25 (4H, t, -CH₂-COO-), 1.55-1.68 (6H, d, -COOCH(CH₃)-), 4H, q, -CH₂-CH₂-COO-), 1.16 (12H, d, -O-CH(CH₃)₂)

Sebacic acid di(2-propoxyethyl) ester

Yield was 82% based on sebacic acid.

¹H-NMR (CDCl₃) δ 5.49 (2H, q, -COOCH(CH₃)-), 3.19 (2H, m, -OCH(CH₃)₂-), 2.25 (4H, t, -CH₂-COO-), 1.55-1.68 (6H, d, -COOCH(CH₃)-), 4H, q, -CH₂-CH₂-COO-), 1.16-1.29 (12H, d, -O-CH(CH₃)₂, 8H, m, -(CH₂)₂-CH₂-CH₂-COO-)

3.4 Thermal dissociation of thermal latent carboxylic acid derivatives

Thermal dissociation of thermal latent carboxylic acid derivatives were measured by thermogravimetry. Furthermore, thermal latent carboxylic acid derivatives were heated at respective temperatures for 20 min, and the extent of thermal dissociation was evaluated by titration for the regenerated carboxyl group with 0.07 N KOH in ethanol.

3.5 Reactivity of thermal latent carboxylic acid derivatives with solder alloy

In order to investigate the reactivity of thermal latent carboxylic acid derivative with solder alloys under normal temperature, the surface of solders, which had been mixed with glutaric acid di(2-propoxyethyl) ester, was observed using the scanning electron microscope after letting stand at $40^{\circ}\text{C} \times 1$ week. The mixture has 1.52 mmol of the thermal latent carboxyl group per 1 g of solder powder. In addition, thermal reactivity of the thermal latent carboxylic acid derivative with solder alloy under heating was measured by differential scanning calorimetry. Sn-3.0Ag-0.5Cu solder (mass%) was used for the examination.

3.6 Reactivity of thermal latent carboxylic acid derivative and epoxide

The solution of glutaric acid di(2-propoxyethyl) ester and 4-tert-butylphenyl glycidyl ether with an equimolar mixture of zinc 2-ethylhexanoate and triethanolamine as the reaction catalyst was heated by air reflow and measured by IR at various stages. The equivalent ratio of hemiacetal ester group/epoxy group was 1.0. The catalyst content was 1.79eq.% based on the hemiacetal ester group.

3.7 Preparation of solder paste and its evaluation

The Pb-free solder pastes consisting of thermal latent carboxylic acid derivatives, solvent, epoxide, and rheology control agent were evaluated regarding wettability, storage stability and electric reliability. The soldering property was investigated by soldering the QFP (quad flat package) under each air reflow profile condition. The storage stability was investigated by calculating the ratio between the viscosity of the initial stage and that after preservation at 5°C while sealed. The viscosity was measured on the basis of industry classification JIS Z 3284. The insulation resistance test was measured under $40^{\circ}\text{C} \times 90\%\text{RH}$ or $85^{\circ}\text{C} \times 85\%\text{RH}$ on the basis of industry classification JIS Z 3284.

4. Results and Discussion

4.1 Property of thermal latent carboxylic acid derivatives.

In general, glutaric acid, adipic acid, and sebacic acid, which have high melting points, were included in soldering flux as activators to remove the surface metal oxide of solder alloy. We converted the carboxyl group of the above carboxylic acid compound into hemiacetal ester units by reaction with alkyl vinyl ether. The viscosity of glutaric acid di(2-propoxyethyl) ester was 8.3 mPa·s, while that of adipic acid di(2-propoxyethyl) ester was 8.6 mPa·s and that of sebacic acid di(2-propoxyethyl) ester was 14.9 mPa·s. The obtained thermal latent carboxylic acid derivatives had lower viscosity than ordinary organic solvents and exhibited better solubility and compatibility. It appears that the use of a solder paste and soldering flux produced with thermal latent processing of the carboxylic group could reduce VOC's, because the carboxylic acid compound has poor solubility and a greater amount of organic solvent is required to dissolve it.

4.2 Thermal dissociation of thermal latent carboxylic acid derivatives.

It is necessary to remove the surface metal oxide of solder using the flux ingredient in order to melt the solder alloy. Accordingly, it is important to measure the temperature and rate of free carboxyl group regeneration by thermal dissociation of a hemiacetal ester unit when the thermal latent carboxylic acid derivatives are applied as a flux ingredient.

Ishidoya *et al.*⁶⁾ have reported that thermal dissociation of hemiacetal esters is influenced by alkoxy groups, by demonstrating that the structures and the dissociation temperatures are in the following order: tert-alkoxy < sec-alkoxy < pri-alkoxy.

In this study, the effect of the acidity of a carboxylic acid compound on thermal dissociation of the thermal latent carboxyl group was estimated by TG-DTA and quantitative analysis of the regenerated carboxyl group.

In the TG-DTA curve of the thermal latent carboxylic acid derivatives, a decrease in weight due to volatilization of vinyl ether, which corresponds to the thermal dissociation of the thermal latent carboxyl group, could be observed (Fig. 4). The temperature at which the weight began to decrease was related to the acidity of the carboxylic acid compound in the following order: glutaric acid (152°C) < adipic acid (158°C) < sebacic acid (174°C).

Figure 5 shows the temperature dependence of the conversion of the thermal latent carboxyl group after heating at each temperature for 20 min. The extent of the thermal dissociation reaction increased with an increase in heating temperature and reached approximately 100% after heating at 200°C . It is important that the free carboxyl group is regenerated at a temperature close to the melting point of the solder alloy and then reacts with solder alloy. The thermal latent carboxyl acid derivatives could be applied in soldering flux and solder paste by adjusting the temperature of thermal dissociation.

Fig. 4 TG-DTA diagrams of thermal latent carboxylic acid derivatives. (Heating rate $10^{\circ}\text{C}/\text{min}$.)

Fig. 5 Thermal dissociation behavior of thermal latent carboxylic acid derivatives.

4.3 Reactivity of thermal latent carboxylic acid derivatives with solder alloys

There are many well-known reactions of an organic acid, represented by stearic acid, benzoic acid, and rosin, with metal, metal oxide, or metal hydroxide to obtain metallic soap.

(M represents a metal, such as copper, zinc, or tin.)

That is, the reaction of a metal with rosin or an activator under normal conditions or when preheated by reflow heating proceeds in solder paste, but without exhibiting good wettability. In order to investigate the reactivity of thermal latent carboxylic acid derivative and solder alloys, the surface of solder mixed with glutaric acid di(2-propoxyethyl) ester was observed using a scanning electron microscope after letting stand at 40°C × 1 week. (Table 1) In addition, this same method was utilized to observe free glutaric acid. As a result, the appearance of solder alloys could be seen to change and degrade in the case of free glutaric acid, and the reaction of the carboxyl group with solder alloy yielding metallic soap was confirmed. On the other hand, in the case of glutaric acid di(2-propoxyethyl) ester, the appearance of the solder did not change and was the same as that of original state before examination. It is clear that the thermal latent processing of a carboxyl group could be utilized to lengthen the shelf life of solder paste under normal conditions while improving storage stability.

The thermal reactivity of glutaric acid di(2-propoxyethyl) ester with the solder alloy was estimated by DSC and is shown in Fig. 6. The contents of the samples are shown below.

- (Contents of samples)
A: Sn-3.0Ag-0.5Cu (mass%)

Table 1 SEM images of solder powder.

Solder Alloy Composition	Active agent	
	Glutaric acid/I-PrVE	Glutaric acid
Sn-3.0Ag-0.5Cu		
Sn-8.0Zn-3.0Bi		
Sn-9.0Zn

Fig. 6 Comparison of reactivity with carboxylic acid compounds and Sn-3.0Ag-0.5Cu solder by DSC. (Heating rate 10°C/min.)

- B: Glutaric acid
C: Glutaric acid di(2-propoxyethyl) ester
D: Mixture of Sn-3.0Ag-0.5Cu (mass%) and glutaric acid
E: Mixture of Sn-3.0Ag-0.5Cu (mass%) and glutaric acid di(2-propoxyethyl) ester

In the DSC curve for D, a new exothermic peak, in addition to the endothermic peaks corresponding to the solder alloy and glutaric acid, could be observed at approximately 150°C. Sn-3.0Ag-0.5Cu (mass%) appears to be able to react with glutaric acid to form a metallic soap at 150°C. Furthermore, in the DSC curve for E, an exothermic peak could be observed immediately after the thermal dissociation of glutaric acid di(2-propoxyethyl) ester, which confirms that the reaction of solder alloy with glutaric acid di(2-propoxyethyl) ester could be observed after thermal dissociation of glutaric acid di(2-propoxyethyl) ester and the regeneration of the carboxyl group.

The above result suggests that the thermal latent processing of a carboxyl group can restrain the degradation of solder

Fig. 7 Soldering stages under air reflow condition.

alloy and the decline of the active agent during storage or the preheating stage in air reflow, and that the thermal dissociation temperature to regenerate the carboxyl group must be designed to approximately the melting point of the solder alloy to remove the surface metal oxide of solder alloy effectively.

4.4 Reactivity of thermal latent carboxylic acid derivatives with epoxide

The reactivity of glutaric acid di(2-propoxyethyl) ester with 4-tert-butylphenyl glycidyl ether under air reflow heating was measured by IR at each stage under the reflow condition.

Figure 7 shows the reflow profile and Fig. 8 shows the IR spectra of fractions obtained at each stage. On the basis of these spectra, we concluded that the thermal dissociation reaction of glutaric acid di(2-propoxyethyl) ester and the esterification of the regenerated carboxylic acid with the epoxide that accompanied it did not occur at stage A or B. On the other hand, new peaks corresponding to a carboxyl group from 3000 to 3500 cm^{-1} and a hydroxyl group at approximately 3500 cm^{-1} could be observed at stages C and D. This result suggested that the thermal dissociation reaction of the glutaric acid di(2-propoxyethyl) ester and the esterification of regenerated carboxylic acid with epoxide that accompanied it began to proceed approximately from stage C, which is the point at which preheating is completed. (Fig. 2) At stage E, the broad peak corresponding to the carboxyl group from 3000 to 3500 cm^{-1} finally disappeared, while the peak corresponding to the hydroxyl group could be observed at approximately 3500 cm^{-1} . This result suggested that the completion of the reaction does not occur at stage D, which is when the solder alloy begins to melt, but rather, at stage E. In addition, the solution of glutaric acid di(2-propoxyethyl) ester and 4-tert-butylphenyl glycidyl ether exhibit high storage stability for a $40^\circ\text{C} \times 1\text{ month}$ storage period and exhibit no rise in acidity or viscosity.

4.5 Application to Pb-free solder paste

Pb-free solder pastes consisting of thermal latent carboxylic acid derivatives were evaluated regarding their soldering

Fig. 8 IR spectra of mixture of glutaric acid/i-PrVE and epoxide at each stage in air reflow.

Table 2 Representative characteristics of solder paste.

Solder Powder	Sn-3Ag-0.5Cu	Sn-8Zn-3Bi	Sn-9Zn
Soldering State			
Preheat	150°C	150°C	150°C
Condition	100s	100s	100s
Peak Temperature	237°C	220°C	220°C
Reflow Atmosphere	Air	Air	Air
Insulation Resistance			
40°C, 90%RH	$1.0 \times 10^{10}\Omega$	$1.0 \times 10^{11}\Omega$	$1.0 \times 10^{11}\Omega$
85°C, 85%RH	$1.0 \times 10^9\Omega$	$1.0 \times 10^{10}\Omega$	$1.0 \times 10^{10}\Omega$

property, storage stability, and insulation resistance. Table 2 shows the soldering properties and insulation resistances. The photographs showing the appearance of the soldering state indicate that the Pb-free solder pastes consisting of thermal latent carboxylic acid derivatives exhibit excellent soldering properties for all of the solder alloys used in this evaluation. Due to the effect of the neutralization of the carboxyl group to 2-hydroxyethyl ester, the insulation resistance was satisfactory.

Figures 9 and 10 show the influence of the application of thermal latent processing of a carboxyl group in an activator on the storage stability of solder pastes. The storage stability

Fig. 9 Change of viscosity during storage (1). (Storage Temperature 5°C.)

Fig. 10 Change of viscosity during storage (2). (Storage Temperature 25°C.)

of solder paste consisting of a free carboxylic acid compound is also shown for comparison. The viscosity of a solder paste without thermal latent processing of the carboxyl group increased even at 5°C. In particular, in the case of Sn-8.0Zn-3.0Bi (mass%), a sharp rise in viscosity was observed during the production of the solder paste. On the other hand, the solder paste with thermal latent processing applied to the carboxyl group in the soldering flux exhibited good storage stability under room temperature conditions, which is suitable for industrial application as a Pb-free solder paste.

5. Conclusions

Developing a soldering flux that can be applied to Pb-free solders has become important, because complete elimination of lead from electrical and electronic devices is soon to be enforced. In this study, the synthesis of thermal latent carboxylic acid derivatives, their thermal dissociation reaction, and their reactivity with solder alloy or epoxide were examined. Furthermore, a Pb-free solder paste consisting of thermal latent carboxylic acid derivatives was evaluated. The following results were obtained.

- (1) Protection of the carboxylic group can prevent degradation of the solder alloy under normal conditions.
- (2) Because thermal latent carboxylic acid derivative does not function as a carboxylic acid when the protection of

the carboxyl group by vinyl ether can be accomplished, designing the thermal dissociation temperature of the regenerated free carboxyl group makes it possible to remove the surface metal oxide of solder alloy more effectively without reducing its active power.

- (3) The activator in the flux residue after soldering could be converted into an ester unit by reaction with epoxide which has no influence on electric reliability.
- (4) The Pb-free solder paste using thermal latent carboxylic acid derivatives could be combined to achieve good wettability, high electric reliability and high storage stability.

REFERENCES

- 1) M. Kitajima and T. Shono: *Journal of Japan Institute of Electronics Packaging* **6** (2003) 380–385.
- 2) T. Shima: *Journal of Japan Institute of Electronics Packaging*, **6** (2003) 386–393.
- 3) Y. Nakane and M. Ishidoya: *Shikizai* **67** (1994) 766–774.
- 4) K. Sato and M. Ishidoya: *Journal of Network Polymer, Japan* **19** (1998) 215–221.
- 5) K. Sato and M. Ishidoya: *Journal of Network Polymer, Japan* **22** (2001) 124–131.
- 6) N. Nakane and M. Ishidoya: *Journal of Network Polymer, Japan* **19** (2001) 123–129.