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CHARACTERIZATION OF NITROGEN-BLANKETED WAVE SOLDERING REACTIONS USING THERMAL ANALYSIS

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Abstract

Thermal analysis techniques have been employed to elucidate the mechanism of low solids soldering flux activation. Metal oxides (SnO, PbO and PbO_2) are converted to carboxylate salts, which are displaced in the solder wave, rendering a solderable metal surface. Neither of the activators tested, namely succinic acid and adipic acid, react with SnO_2 at soldering wave temperatures and therefore cannot yield a solderable surface when SnO_2 is present. Further, adipic acid reacts with SnO to form a salt that can decompose to cyclopentanone, so the preheating of the printed circuit board must be carefully controlled to yield a solderable surface.

Keywords: soldering flux, dicaboxylic acid, metal oxide

Introduction

In the last few years, the use of low solids soldering fluxes has become prevalent in the circuit pack assembly industry. These fluxes are based on short-chain carboxylic acids that vaporize during wave soldering, leaving minimal flux residues on the soldered circuit. Minimal residues mean that post-soldering circuit pack cleaning becomes optional, allowing for the elimination of chlorofluorocarbon cleaning solvents from the assembly process.

A printed circuit board consists of a substrate, generally of epoxy-glass or paper-phenolic material, with copper circuit traces that form the conductive pathways. The copper is protected against oxidation between the manufacture of the printed circuit board and its use in the assembly process with a thin coating of Sn–Pb solder, or with an organic corrosion inhibitor. During the assembly process, the board is populated with components that have leads with a Sn–Pb solder finish. In the wave soldering machine, the board is coated with a soldering flux and enters a pre-heat zone, where the flux solvent evaporates and activation occurs. Activation is the process whereby solder oxides on the

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component leads and the printed circuit board are converted to other compounds that can be displaced from the surface, allowing a good solder bond to be formed. The board then enters the solder wave, which is a molten wave of solder typically at temperatures 235 to 250°C, where the printed circuit board and components bond. After cooling, cleaning may be required if flux residues remain.

The primary function of a wave soldering flux is to render a solderable surface from oxidized Sn–Pb printed wiring board pads and component leads. This is accomplished by reaction of the respective oxide with an activator material in the flux; a good activator will yield a low soldering defect rate. In the case of low solids fluxes, the activator is normally a short chain dicarboxylic acid (succinic, glutaric, adipic or malic). The study of the interaction of flux activators which have long been in use, such as rosin, amine hydrochloride, and stearic acid, with metal oxides has been the subject of several investigations [1–5]. Elucidation of the mechanism of activation can be used to optimize soldering process parameters and also to design better activator systems. Knowledge of the temperature of activation and other thermal parameters is crucial to the success of the system [6].

Much work has been reported on the characterization of surface oxide layers of tin–lead alloys; some are more specifically concerned with the oxide layers of 63/37 eutectic Sn–Pb alloys typically used in wave soldering processes [7–11]. Most studies have concluded that the tin is preferentially oxidized as SnO as it diffuses to the surface. They also find that SnO_2, PbO, and PbO_2 are present whenever the availability of O_2 exceeds the rate of Sn diffusion to the surface.

The focus of this investigation is the reactions of two of the most widely used acids in low solids flux products, adipic and succinic acids, with the metal oxides that are found on the surface of oxidized solder, namely SnO, SnO_2, PbO, and PbO_2. Several different analytical techniques are used to identify and quantify reaction by-products and to classify the end products that remain on the circuit pack or are deposited in the solder wave. Specifically, thermogravimetry (TG), differential scanning calorimetry (DSC), and thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) are used to study these reactions. These techniques are ideal for the study of the interaction of soldering fluxes with metal oxides since the conditions closely mimic the soldering preheat and wave soldering operations. Diffuse reflectance FTIR was used to analyze the final reaction products.

Experimental

Reagent grade adipic acid, succinic acid, tin(II) oxide, tin(IV) oxide, lead(II) oxide, and lead(IV) oxide (Aldrich Chemical, Milwaukee, WI) were used in their finely divided powder form. Reactants were dried, weighed, mixed in the solid state, and ground together to a fine dust in a mortar and pestle. Excesses of metal oxide were used since they exhibit no measurable weight gain or loss and no measurable heat gain or loss in the temperature range studied that might interfere with the measurements. They also provided a large surface area on which the acids could react. Between 55 and 65 milligrams of each mixture were analyzed.

A Mettler Instruments Model DSC 30, capable of heating from liquid nitrogen temperature to 600°C, was employed for DSC analysis (closed pan with pinhole). A Mettler Instruments Model TGA 50, capable of heating from ambient temperatures to 1000°C, was employed for TG analysis (open pan). Both DSC and TG instruments were operated with N_2 flowing through the system at 20 millilitres per minute. This atmosphere mimics that of a nitrogen-blanketed soldering machine, which is often used in conjunction with low solids fluxes. Scans were from 35 to 300°C with a heating rate of 20°C per minute. (Solder waves are typically run at a temperature of 235 to 250°C.)

A Model FTS-40 Fourier transform infrared (FTIR) absorption spectrometer (Bio-Rad Industries, Cambridge, MA) was used for the identification of evolved gases from the TG when indicated. The TG/FTIR interface was a thermostatted, insulated copper transfer line set to maintain a temperature of 250°C, connected to a Bio-Rad gas chromatography/FTIR gold light pipe. The FTIR, operated in the diffuse reflectance mode, was also utilized to identify solid reaction end products. This was greatly facilitated by the use of the Mini 'D' Diffuse Reflectance Accessory (International Crystal Labs, Garfield, NJ).

Results and discussion

Adipic acid

Adipic acid was analyzed using TG, DSC, and TG-FTIR to obtain baseline results with which to compare the adipic acid/metal oxide experiments. Observable weight loss began at about 160°C on the TG run, with adipic acid vapor being evolved as detected by TG-FTIR. Carbon dioxide and water were also evolved in the temperature range 275 to 300°C. The major carbonyl stretch of adipic acid occurs at 1779 cm^{-1} in the vapor phase, while the major infrared absorption band in carbon dioxide is the antisymmetric CO_2 stretch near 2335 cm^{-1} (P branch) and near 2360 cm^{-1} (R branch), while water exhibits vibrations with many rotational features in the area of 4000 to 3500 cm^{-1}, and also 2000 to 1300 cm^{-1} [12]. The DSC run yielded results that agreed well with the literature values of ΔH_{fusion}=238 J/g and a melting point of 153°C [13].

Adipic acid:SnO

A mixture of adipic acid and SnO in a 1:10 weight ratio was subjected to TG, DSC, and TG-FTIR analyses. The TG and DSC traces are shown in Fig. 1. The

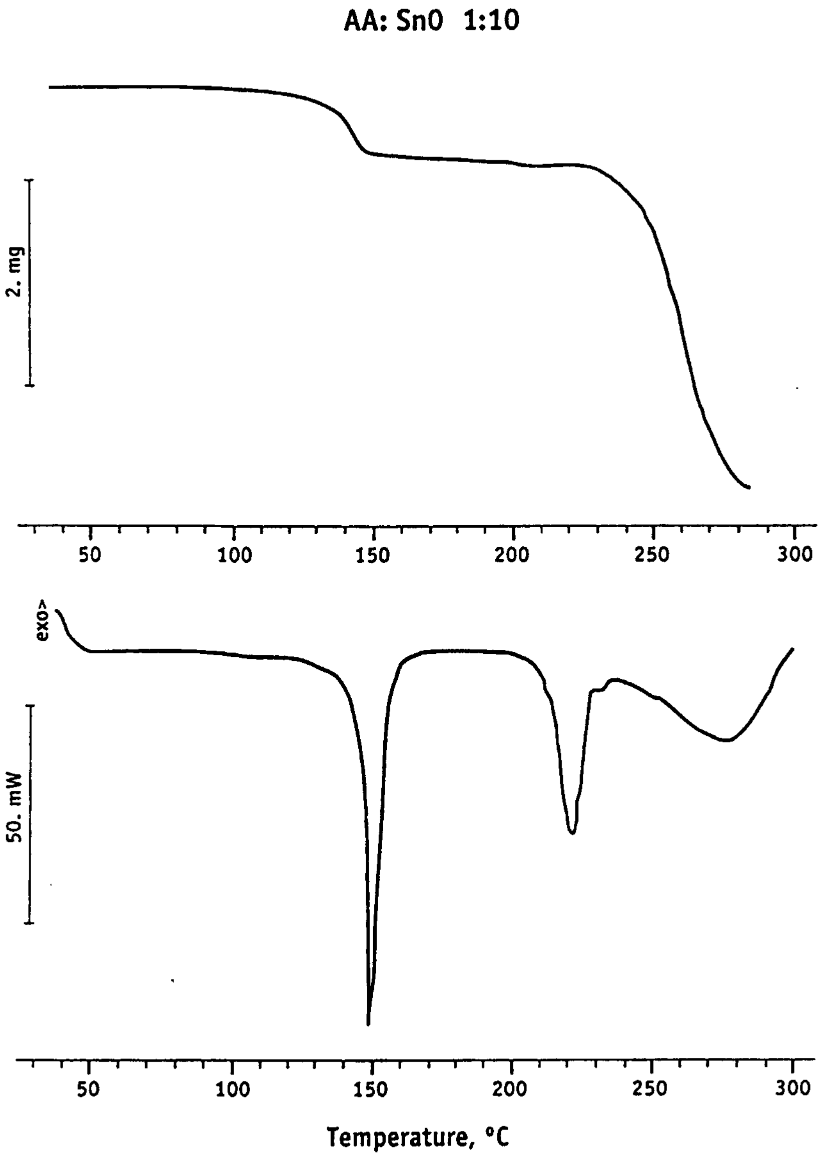

Fig. 1 TG and DSC scans of a mixture of adipic acid and SnO in a 1:10 weight ratio (56.88 mg and 57.80 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

TG run revealed a weight loss of 1.2% at a peak deflection temperature around 145°C and another weight loss of 6.4% at a peak deflection temperature around 260°C. The TG-FTIR results showed that H_2O is evolved in the first weight loss, while CO_2 and cyclopentanone (with a vapor phase carbonyl stretch at 1766 cm^{-1} and smaller absorptions at 2977, 2893, 1419, and 1144 cm^{-1}) are evolved in the second weight loss. Specifically, the evolution of H_2O is associated with the endotherm at 142°C, while the evolution of CO_2 and cyclopentanone is associated with the broad endotherm at 270°C, which begins at lower temperatures and ends at a temperature above 300°C.

The loss of H_2O is probably the result of an acid-base neutralization reaction between the adipic acid and the SnO. This neutralization reaction occurs around 145°C, which is the peak deflection temperature of the first weight loss in the TG scan, the peak deflection temperature of the first endotherm in the DSC scan, and the temperature at which H_2O appears in the TG-FTIR spectrum. The weight loss at this temperature corresponds to a 1:1 mole ratio between adipic acid and H_2O; thus, both available hydrogens from the adipic acid are involved in the neutralization reaction. Further, it appears that the adipic acid must melt for the neutralization reaction to occur. Conversion of the adipic acid to the liquid state apparently greatly increases its mobility and/or reactivity, allowing the reaction to proceed.

A sample retrieved from the TG at a temperature of 200°C had its most intense carbonyl stretch at 1515 cm^{-1}, which is typical for a carboxylic acid salt [14, 15]; the salt is probably tin(II) adipate. The overall reaction that occurs around 145°C is endothermic; in a wave soldering machine, this energy is supplied by preheaters before the printed circuit board reaches the soldering wave. Endothermic contributions to this reaction include melting of the adipic acid and volatilization of the water that is produced, while the neutralization reaction itself is presumably exothermic.

As the sample is heated to soldering wave temperatures (250°C) and beyond to 300°C, decarboxylation of the tin(II) adipate salt is noted. The decarboxylation starts around 230 °C as noted on the TG-FTIR scan, and the production of cyclopentanone also appears to begin either simultaneously with the decarboxylation or soon thereafter. Adipic acid is known to form cyclopentanone at temperatures above 225°C at a slow rate [16, 17]; however, certain adipate salts are known to decompose rapidly to cyclopentanone [17, 18]. The tin(II) adipate species decomposes rapidly to cyclopentanone, CO_2, SnO, and $SnCO_3$, according to the FTIR spectrum of the solid product removed from the TG instrument at 300°C and also according to the stoichiometry of the reaction. One mole of cyclopentanone and 0.5 mole of CO_2 were produced per mole of adipic acid in this reaction. The consequences of this reaction will be discussed below. Other mixing ratios, namely 1:4 and 1:20, of adipic acid and SnO were analyzed with substantially the same results.

Adipic acid:SnO_2

A 1:10 mixture by weight of adipic acid and SnO_2 was analyzed. The TG scan of this mixture resembled that of adipic acid by itself, while the DSC run exhibited a sharp endothermic peak at 155°C (melting point of adipic acid) and a broader endothermic peak around 280°C. The TG-FTIR run revealed that a decomposition product with a carbonyl stretch at 1700 cm^{-1} and smaller absorptions at 2952, 2917, 2875, 1463, 1430, 1406, 1358, 1286, 1199, and 932 cm^{-1} is produced at temperatures as low as 170°C. At 250°C and beyond, CO_2 and H_2O are emitted, and as the temperature reaches 300°C, vapor phase adipic acid is also evolved. The substance with the carbonyl stretch at 1700 cm^{-1} is most likely a ketone with the C=O group in conjugation with a C=C group. For example, the carbonyl stretching frequency in 3-methyl-2-cyclohexen-1-one is 1700 cm^{-1} and in 3,5-dimethyl-2-cyclohexen-1-one is 1701 cm^{-1} (12).

The diffuse reflectance FTIR spectrum of the mixture at 250°C showed that it was virtually the same as adipic acid mixed with SnO_2. It therefore appears that no stable non-volatile reaction products are formed.

Adipic acid:PbO

A 1:10 mixture by weight of adipic acid and PbO was subjected to analysis; Fig. 2 shows the scan traces. The TG run showed a weight loss of about 1.3% at a peak deflection temperature of 145°C and another weight loss that started around 260°C and was not completed by the time that 300°C was reached. Both weight losses were caused by the evolution of CO_2 as observed by TG-FTIR. The DSC run showed a sharp endotherm at 150°C, followed by a sharp exotherm at 153°C, and a broad endotherm starting around 280°C.

Similar to the adipic acid/SnO reaction, the adipic acid melts around 150°C as observed by the endotherm on the DSC scan, and then immediately the exothermic reaction with PbO occurs. However, the evolution of water was not detected in this reaction as it was in the adipic acid–SnO reaction; CO_2 was evolved instead, so additional experiments were run to explain the absence of H_2O evolution. Diffuse reflectance FTIR of the adipic acid/PbO mixture, unheated and at room temperature, showed that there is an immediate reaction between adipic acid and PbO upon mixing in the mortar and pestle at room temperature. As seen in Fig. 3, in adipic acid only the 1695 cm^{-1} carbonyl stretch is observed by diffuse reflectance FTIR; after mixing, carbonyl stretches at both 1695 and 1523 cm^{-1} at about equal intensity are observed, so a partial reaction between the adipic acid and the PbO occurs upon mixing. It is possible that one carboxylate group per adipic acid molecule is produced, while the other remains acidic in nature.

As seen in Fig. 3, the diffuse reflectance FTIR spectrum of the reaction product removed from the TG instrument at 250°C had its most intense carbonyl

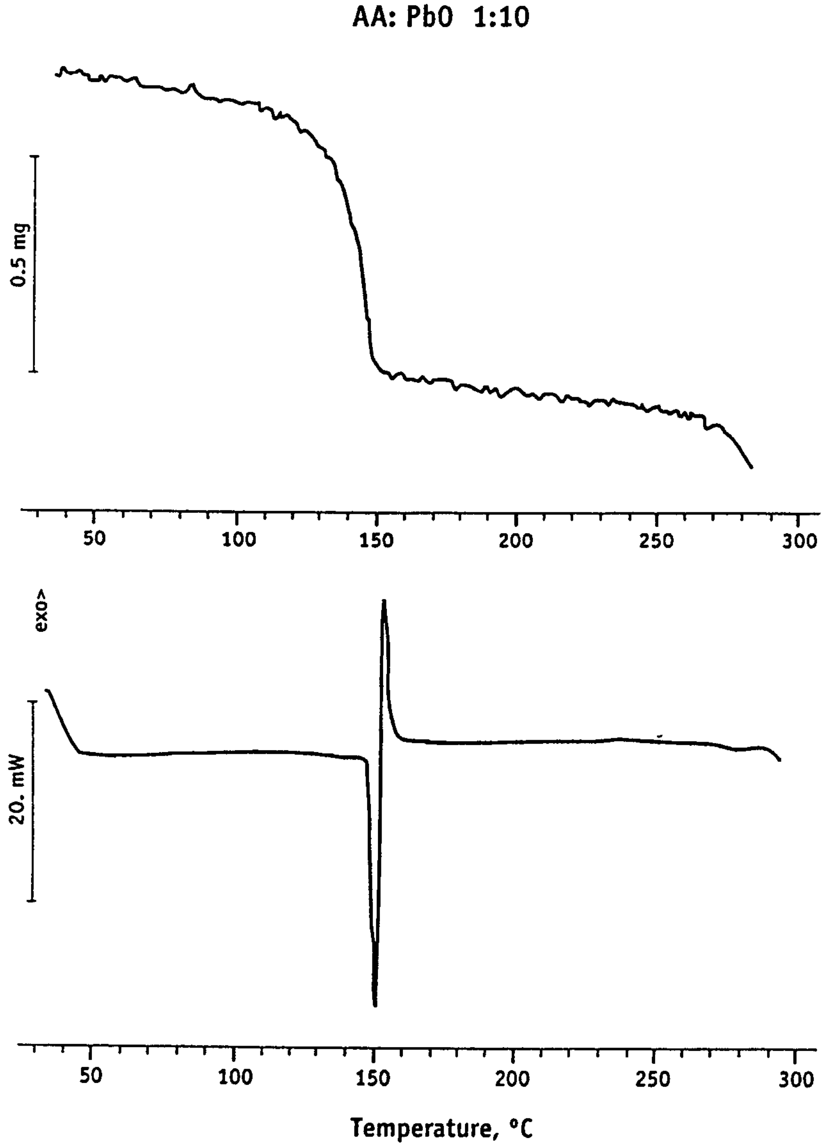

Fig. 2 TG and DSC scans of a mixture of adipic acid and PbO in a 1:10 weight ratio (55.98 mg and 56.60 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

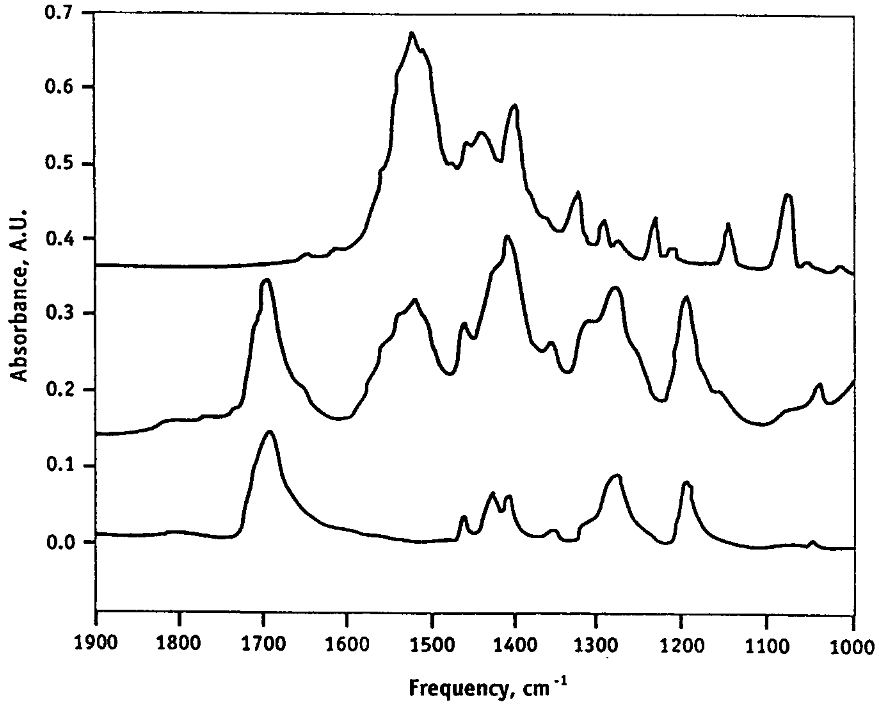

Fig. 3 Diffuse reflectance FTIR spectra. Bottom trace: Adipic acid. Middle trace: Mixture of adipic acid and PbO in a 1:10 weight ratio mixed in a mortar and pestle at room temperature. Top trace: Mixture of adipic acid and PbO in a 1:10 weight ratio heated to 250°C at a rate of 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1} in the TG instrument, then immediately cooled to room temperature

stretching frequency at 1523 cm^{-1} (and none at 1695 cm^{-1}), which is consistent with a carboxylic acid salt [14, 15]. Since CO_2 is evolved at approximately 0.5 mole per mole of adipic acid reactant around 160°C, this salt may be a mixture of lead(II) pentanoate and lead(II) hexanedioate. The FTIR spectrum of the solid product also has sharp peaks indicative of a well-defined crystalline structure. The decarboxylation that occurs at higher temperatures (beyond 260°C) is not expected to occur at the lower wave soldering temperatures (250°C).

Adipic acid:PbO_2

A 1:10 mixture of adipic acid and PbO_2 was analyzed as above, with the results in Fig. 4. The TG run showed a weight loss of about 5.4% at a peak deflection temperature of 155°C, then a slow linear weight loss, followed by another weight loss after about 260°C that was not completed by the end of the run. The TG-FTIR run revealed that only CO_2 was evolved until a temperature around 235°C was reached, when CO_2 and H_2O were both evolved. An endotherm was observed on the DSC scan at 152°C, followed by an exotherm at 180°C, with some smaller exotherms at 185, 210, and 240°C. Each one of these thermal transitions have concomitant weight losses.

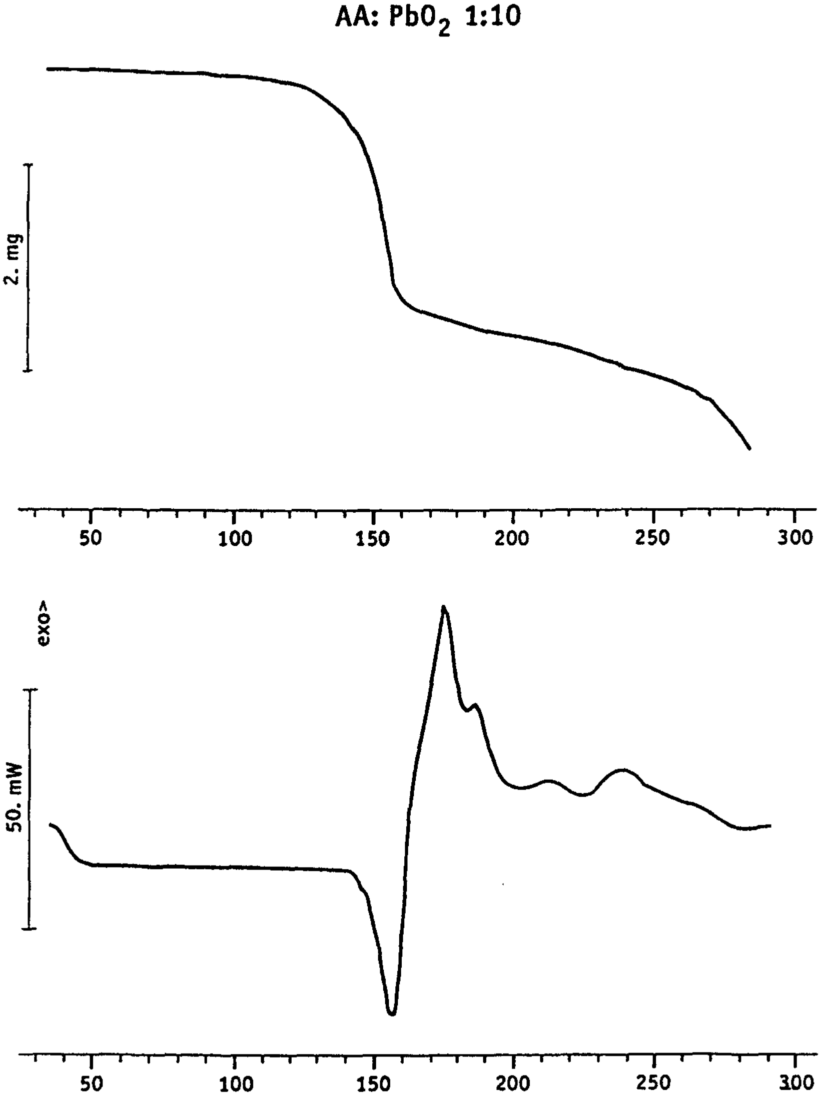

Fig. 4 TG and DSC scans of a mixture of adipic acid and PbO_2 in a 1:10 weight ratio (58.54 mg and 61.40 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

Like PbO, the PbO_2 appears to react with adipic acid at room temperature upon mixing in the mortar and pestle. In the diffuse reflectance FTIR spectrum of the mixture after mixing at room temperature, the carbonyl stretching vibrations occur at 1695 and 1530 cm^{-1}, indicating that a reaction has occurred. As in the adipic acid:PbO reaction, CO_2 is the volatile reaction product during the

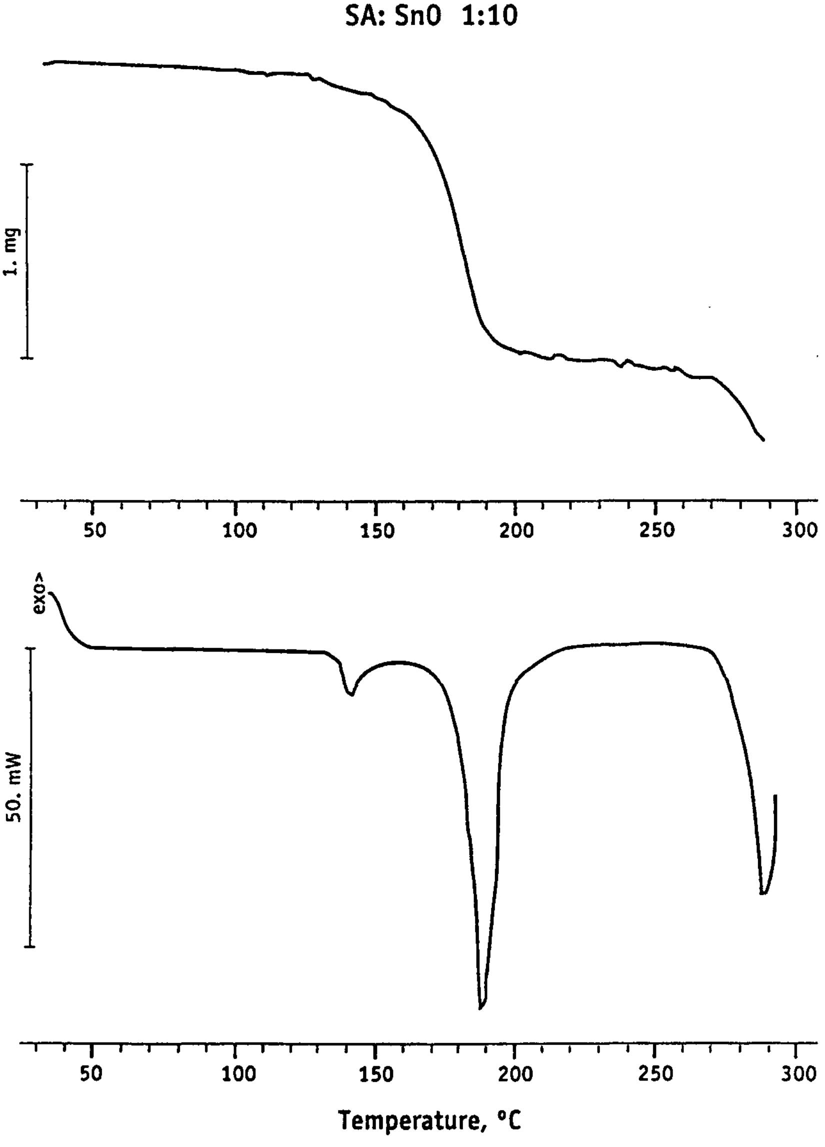

Fig. 5 TG and DSC scans of a mixture of succinic acid and SnO in a 1:10 weight ratio (58.54 mg and 57.10 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

initial reaction. The stoichiometry is unclear due to the continual weight loss, but it appears that approximately 2 moles of CO_2 are lost per mole of adipic acid reactant at the temperature of 260°C. The solid product at that stage is most likely a Pb(IV) or possibly Pb(II) butanoate type salt. As the reaction proceeds, the carbonyl stretching band grows at 1522 cm^{-1}, and the band at 1695 cm^{-1} disappears completely. Like the previous reactions, the melting of adipic acid as observed on the DSC scan precedes the subsequent exothermic reactions.

Succinic acid

Succinic acid was subjected to TG, DSC, and TG-FTIR analysis so a baseline could be established for the ensuing reactions. Succinic acid had an observable weight loss starting at about 170°C. The TG-FTIR run indicated an evolution of succinic acid around 200°C, followed by loss of H_2O and some CO_2 in the range 235 to 300°C. After 300°C was reached, CO_2, succinic acid, and succinic anhydride are evolved. Major vapor phase infrared vibrations occur in succinic acid at 1781, 1725, and 1120 cm^{-1}, and in succinic anhydride at 1872, 1812, 1205, 1045, and 900 cm^{-1}. The DSC run showed a small endotherm at 127°C as a result of the α to β phase change in succinic acid [19]. A sharp endotherm at 185°C marked the melting point of succinic acid; another endotherm at 235°C occurs as the succinic acid dehydrates to form the anhydride; and the endotherm at 260°C indicates the boiling point of succinic anhydride. These values agree will with those in the literature [13].

Succinic acid:SnO

Figure 5 shows the data obtained from a 1:10 ratio by weight mixture of succinic acid and SnO. The TG scan revealed a weight loss of 0.2% at 135°C, a weight loss of 2.4% at a peak deflection temperature of 182°C, and another weight loss that started around 260°C and had not ended by the end of the scan. H_2O and some succinic acid were lost in the first step; along with some succinic anhydride, they were also lost in the first part of the second weight loss, along with CO_2 in the latter part of the second weight loss. The final weight loss consisted of CO_2 and H_2O, but occur at temperatures higher than those encountered during soldering. The DSC scan had three endotherms, a small one at 140°C, a larger one at 182°C, and another around 290°C that was not completed by the end of the run.

The first small weight loss (0.2%) on the TG scan occurring at 135°C peak temperature is probably correlated with the small endotherm on the DSC scan at 140°C peak temperature. Diffuse reflectance FTIR analysis of the solid removed from the TG instrument at 120 and 140°C showed that a reaction to form the carboxylate salt (with a carbonyl stretch at 1514 cm^{-1}) occurs in this temperature range. The signal at 1695 cm^{-1} indicates that some succinic acid still remains; a small amount of H_2O is evolved in this reaction. This reaction may occur when both reactants are present in the solid state, or it may be preceded by the SnO dehydrating some of the succinic acid to form succinic anhydride, which would explain the small amount of water released. The melting point of

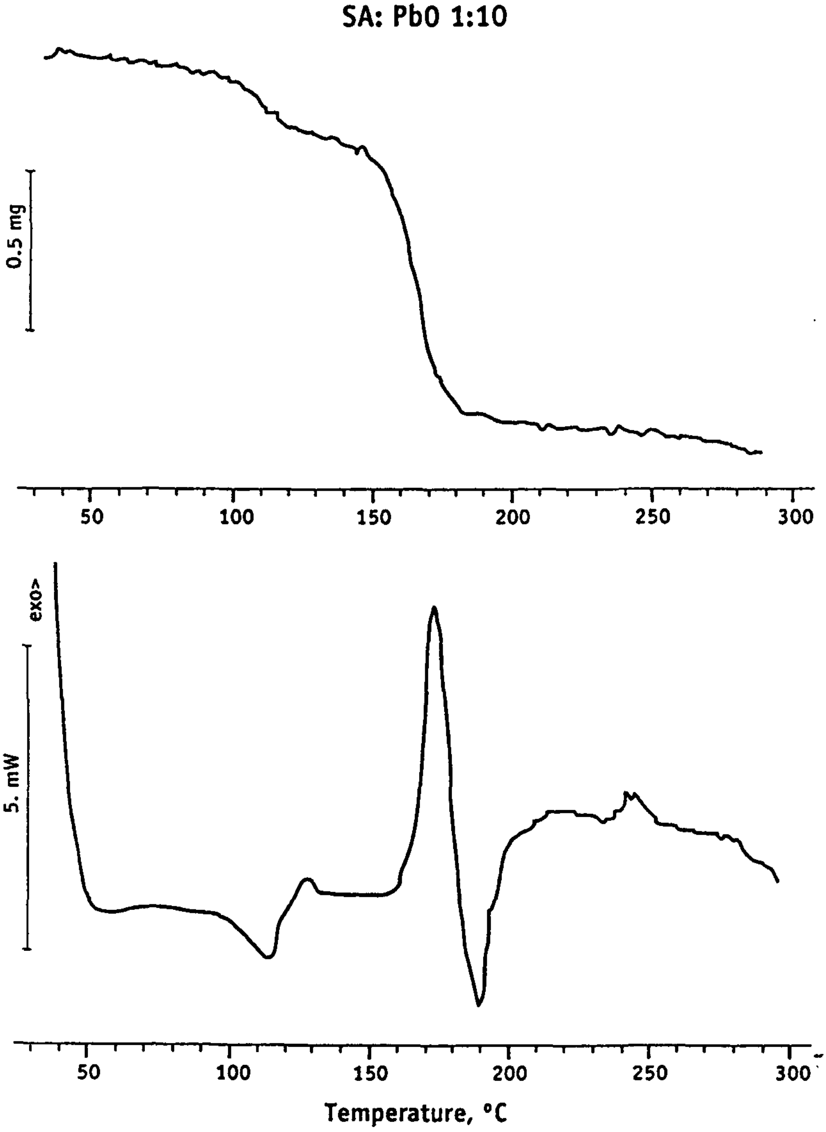

Fig. 6 TG and DSC scans of a mixture of succinic acid and PbO in a 1:10 weight ratio (64.28 mg and 60.0 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

succinic anhydride is 120°C, so any succinic anhydride formed would be melted in the temperature range of the first weight loss and endotherm, and probably reacts with the SnO to form the carboxylate salt with the carbonyl stretch at 1514 cm^{-1}. A solid state reaction can be explained by the Hedvall effect, which states that solid substances are more reactive during phase transitions [20]. Succinic acid has an α to β phase transition at 127°C [19], and so may be more reactive than usual at this temperature as the crystal rearrangement occurs. In either case, it is possible that only the substances on the surfaces of the finely ground particles react. Most of the succinic acid apparently melts and reacts in the major weight loss and endotherm around 182°C. This overall reaction is endothermic; during soldering, the required heat is supplied in the preheat cycle of the soldering process.

The stoichiometry of the second weight loss suggests that 0.5 mole of H_2O and 0.5 mole of CO_2 are lost per mole of succinic acid reactant. The diffuse reflectance FTIR spectrum of the solid product removed at 250 °C had a carbonyl stretching band with highest intensity at 1498 cm^{-1}, indicating that a different carboxylate salt was present than the one at lower temperatures, perhaps a Pb(IV) propanoate salt. There was no diffuse reflectance FTIR evidence for reaction at room temperature upon mixing using the mortar and pestle.

Succinic acid:SnO_2

A 1:10 mixture by weight of succinic acid and SnO_2 was analyzed. The TG, DSC, and TG-FTIR scans of this mixture were nearly identical to that of succinic acid. There does not appear to be a reaction between succinic acid and SnO_2.

Succinic acid:PbO

A 1:10 ratio by weight mixture of succinic acid and PbO was analyzed, as seen in Fig. 6. The TG curve shows a weight loss at 110°C of 0.35% and one at 165°C of 1.4%. The TG-FTIR run showed that the first weight loss was CO_2 and the second one was CO_2 with some H_2O. The magnitudes of the weight losses suggest that 0.5 mole of CO_2 is released for each mole of succinic acid present. The DSC curve was complex, with endotherms at 113 and 187°C, and exotherms at 126, 173 and 245°C.

Similar to the adipic acid/lead oxide cases, a reaction at room temperature upon mixing in the mortar and pestle was noted by the appearance of carbonyl stretching bands at both 1695 (acid) and 1527 cm^{-1} (salt) in the diffuse reflectance FTIR spectrum.

This system was the only one studied that exhibited differences in the DSC and TG scans with changing succinic acid:PbO ratios. At the 1:20 weight ratio, the exotherm at 245°C became large (5.3 kJ/mole succinic acid) compared to the 1:10 (0.8 kJ/mole succinic acid) and the 1:4 (0.4 kJ/mole succinic acid) ratios. No change in weight is associated with this irreversible exotherm. A series of diffuse reflectance FTIR spectra were obtained for the different ratios of succinic acid to PbO heated to various temperatures in the TG and immediately

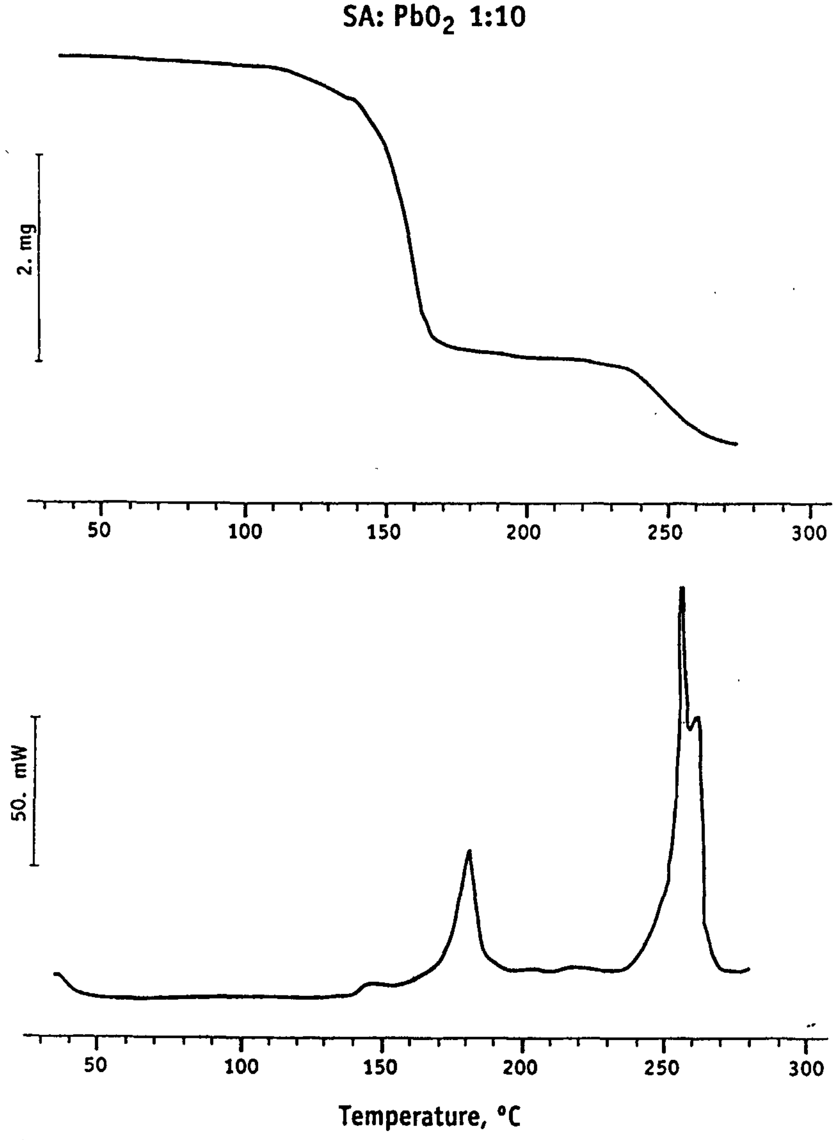

Fig. 7 TG and DSC scans of a mixture of succinic acid and PbO_2 in a 1:10 weight ratio (57.60 mg and 56.53 mg, respectively) heated at 20 deg·min^{-1} in nitrogen flowing at 20 ml·min^{-1}

cooled to room temperature, in an attempt to understand the changes occurring at each step.

As noted above, there appears to be a reaction at room temperature between succinic acid and PbO upon mixing in the mortar and pestle as evidenced by carbonyl stretching vibrations at both 1695 cm^{-1} (succinic acid) and 1527 cm^{-1}. For the 1:20 ratio, the band at 1527 cm^{-1} is broad and featureless at room temperature and also in a sample heated to 100°C at 20°C per minute and no hold time, then cooled to room temperature; however, when heated to 150°C and cooled to room temperature, the infrared spectrum shows sharp peaks indicative of a well-defined crystalline structure(s) of the product(s). After being heated to 200°C and cooled to room temperature, no major changes are noted from the 150°C spectrum. At 250°C, however, new vibrations at 1221 and 654 cm^{-1} arise. These vibrations were present in the 1:4 and 1:10 ratio mixtures at 200°C, so stoichiometry does have an effect on the DSC and the FTIR data. These vibrations are linked to the irreversible exotherm at 245°C observed on the DSC scan and probably involve a crystal rearrangement.

The weak phase transition at 160°C of Pb(II) succinate was observed when the 1:20 ratio was cooled at a controlled rate from 300°C. This is a tetragonal (low temperature) to cubic (high temperature) transition [21]. The solid product produced at 250°C is probably a mixture of Pb(II) succinate and some other salt, possibly Pb(II) propionate since some, but not all, of the FTIR peaks match the published spectrum of Pb(II) succinate [21] and that of synthesized Pb(II) succinate [procedure in Ref. (22)].

Succinic acid:PbO_2

Figure 7 shows the data obtained when a 1:10 by weight mixture of succinic acid and PbO_2 was analyzed. The TG curve shows a 5.1% weight loss at 160°C attributable to CO_2 and H_2O and further weight losses at 250°C and continuing but not completed by the end of the run, also attributable to CO_2 and H_2O. The stoichiometry suggests that 1 mole of both CO_2 and H_2O for each mole of succinic acid reactant are lost in the first step. The DSC curve showed exotherms at 145, 185, 255 and 265°C. The diffuse reflectance FTIR spectra showed that a partial reaction had occurred during the room temperature mixing because the carbonyl stretch at 1695 cm^{-1} from succinic acid is joined by a broad absorption centered at 1545 cm^{-1}. The solid product removed from the TG at 200°C had a carbonyl stretch at 1558 cm^{-1} and no trace of absorption at 1695 cm^{-1}, indicating a complete reaction to a carboxylate salt had occurred; when removed from the TG at 250°C, the highest frequency carbonyl absorption occurred at 1538 cm^{-1}, indicating that further reaction had occurred.

Conclusions

Since thermal analysis techniques were employed, and since the activation of solder oxides with the organic acids is a thermal process, these conclusions can be used to design better soldering fluxes and also to predict the behavior of soldering fluxes that contain a specific activator. The mechanism of activation appears to be the formation of metal carboxylate salts from the metal oxides on the surface of the solder, which is a neutralization reaction. These salts most likely separate from the molten solder during wave soldering, exposing unoxidized solder on the printed wiring board and component leads, allowing good wetting and therefore a good solder bond to be made.

Diffuse reflectance FTIR evidence of the formation of metal carboxylate salts was found for the reactions of adipic or succinic acids with PbO, PbO_2, and SnO at preheat and soldering wave temperatures; thus, these acids are effective activators for solder surfaces that have these oxidation products present. However, if heated for too long at too high a preheat temperature, the carboxylate salt produced by the reaction of adipic acid with SnO could decompose to CO_2, cyclopentanone, $SnCO_3$, and SnO. This would, of course, defeat the purpose of the activation step and would re-create a nonsolderable surface or leave a white $SnCO_3$ residue. The temperatures of the preheat zones and solder wave, along with conveyor speed, could be optimized empirically to avoid this decomposition.

Neither succinic nor adipic acids activate SnO_2 at preheat or soldering temperatures. If a board is very heavily oxidized from being stored for an extended period of time and SnO_2 is present on the surface, then it likely will not be solderable using low solids soldering fluxes that employ these acids. A recent study has correlated excessive amounts of SnO_2 with degradation in solderability [23].

The reactions of adipic and succinic acids with SnO are endothermic, and so the preheat temperatures must be set to complete the reaction to the carboxylate salts before the solder wave is reached. In the case of adipic acid reacting with SnO, as mentioned above, care must be taken to not provide too much heat so that the carboxylate salt is not decomposed.

Partial reactions of PbO and PbO_2 with succinic and adipic acids occur by mixing the reagents at room temperature. These reactions, for the most part, are exothermic after the acid is melted and produce stable carboxylate salts at soldering wave temperatures. Adipic and succinic acids do not react with SnO at room temperature upon mixing, and produce H_2O as the first volatile product when they are heated. These reactions are classical neutralization reactions. On the other hand, adipic and succinic acids react with PbO and PbO_2 at room temperature with mixing, and produce CO_2 as the first observable volatile reaction product. In general, adipic acid must melt before complete conversion to carboxylate salts occurs, but these reactions can occur with succinic acid at temperatures lower than its melting point. This may be related to succinic acid's ability to form succinic anhydride, which has a lower melting point than succinic acid. It may also be related to the Hedwall effect, since succinic acid has an α to β phase transition at about the same temperature. This may explain why succinic acid is generally considered a stronger activator than adipic acid within the soldering flux industry.

Thermal analysis techniques in conjunction with FTIR have been shown to yield valuable information about the reaction of soldering flux activators with metal oxides found on the surface of printed wiring boards and component leads. This work was done in a nitrogen atmosphere to replicate the atmosphere inside a nitrogen-blanketed soldering machine, but a debate concerning the advantages and disadvantages of nitrogen versus a regular air atmosphere continues. These experimental techniques should be able to provide information about the mechanistic details of activation for nitrogen versus air atmospheres. Further, some printed wiring boards are now being supplied in a 'bare' copper form, where azole-type coatings are used to passivate the copper pads until ready for soldering. This work could be extended to include the oxides of copper that may be present on these surfaces. Lastly, these techniques can be used for further evaluation of new organic acid activators. The temperature at which reactions occur, their endothermic or exothermic nature, and other side reactions that may occur that may jeopardize the activation process can be studied to evaluate new activator systems for new low solids soldering fluxes.

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Zusammenfassung — Metalloxide (SnO, PbO und PbO_2) werden in ihre Carboxylatsalze überführt, in dessen Folge eine lötfähige Metalloberfläche ermöglicht wird. Keiner der getesteten Aktivatoren, namentlich Bernsteinsäure und Adipinsäure reagiert mit SnO_2 bei Lötofentemperatur, weshalb in Gegenwart von SnO_2 keine lötfähige Oberfläche erzielt werden kann. Weiterhin reagiert Adipinsäure mit SnO und bildet ein Salz, welches sich zu Cyclopentanon zersetzen kann, weshalb das Vorwärmen der gedruckten Leiterplatte sorgfältig überwacht werden muß, um eine lötfähige Oberfläche zu erhalten.