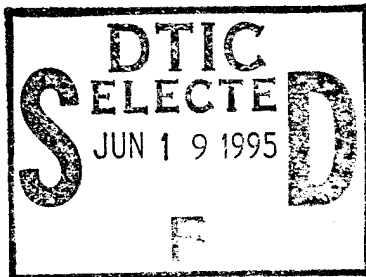


An Investigation of the Chemistry of Citric Acid in Military Soldering Applications

by

Robin Nissan, Larry Merwin,
John Fischer, Jim Smith,
Jerry Maurice, Roger Nickell,
and Loretta Lusk
Engineering Department



JUNE 1995

NAVAL AIR WARFARE CENTER WEAPONS DIVISION
CHINA LAKE, CA 93555-6001



Approved for public release; distribution is unlimited.

19950616 003

DTIC QUALITY INSPECTED 5

Naval Air Warfare Center Weapons Division

FOREWORD

As a result of the phase-out of ozone-depleting chemicals (ODC), the military and its contractors are facing the problem of developing alternative materials and processes which currently employ these materials. Electronics are a particularly challenging problem because efficient removal of post-soldering flux residues is critical to the long-term performance of high-reliability electronics. The use of water soluble flux offers an attractive option because all cleaning would be accomplished using only water. Until recently, the military has not allowed this type of flux because of the highly corrosive fluxing action usually associated with these materials. However, a new flux ingredient, citric acid, is gaining favor within the electronics manufacturing industry. Citric acid offers excellent fluxing ability, efficient removal of residues with water, and non-ionic flux formulations.

This report examines the chemistry of this material under simulated soldering conditions in an effort to gain an improved understanding of thermal reactions and degradation products which may have an effect on long-term reliability of military electronic hardware. This report has been reviewed for technical accuracy by A. P. Chafin and W. S. Wilson.

Approved by
R. L. DERR, *Head*
Research and Technology Division
26 April 1994

Under authority of
D. B. McKINNEY
RAdm., U.S. Navy
Commander

Released for publication by
S. HAALAND, *Head*
NAWCWPNS Research and Engineering Group

NAWCWPNS Technical Publication 8199

Published byScientific and Technical Documentation
CollationCover, 20 leaves
First printing145 copies

REPORT DOCUMENTATION PAGE

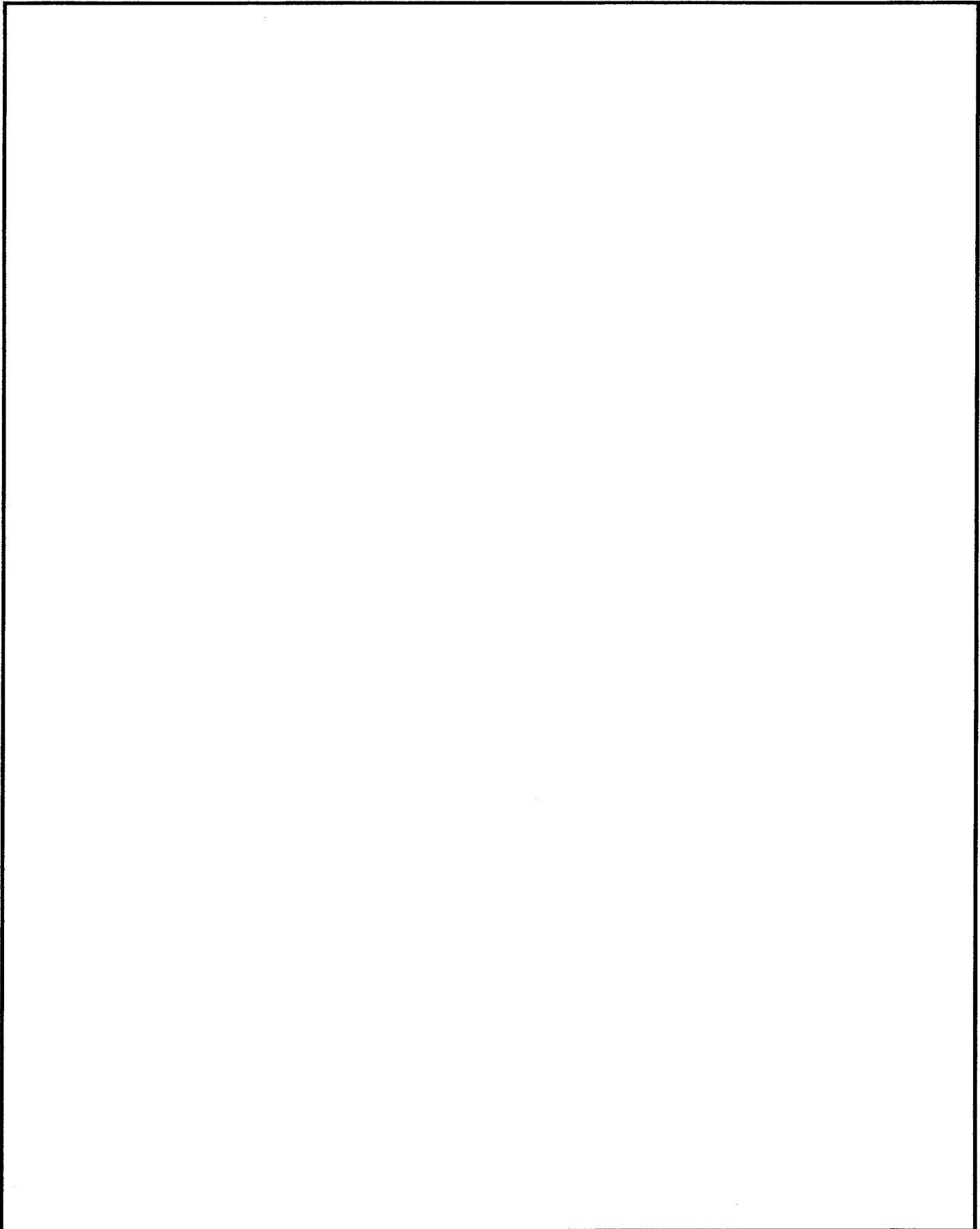
Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1995	3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE An Investigation of the Chemistry of Citric Acid in Military Soldering Applications			5. FUNDING NUMBERS	
6. AUTHOR(S) John Fischer, Loretta Lusk, Jerry Maurice, Larry Merwin, Robert Nickell, Robin Nissan, and Jim Smith				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Weapons Division China Lake, CA 93555-6001			8. PERFORMING ORGANIZATION REPORT NUMBER NAWCWPNS TP 8199	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12A. DISTRIBUTION/AVAILABILITY STATEMENT A statement; unlimited distribution			12B. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) (U) As a result of the phase-out of ozone-depleting chemicals (ODC), the military and its contractors are facing the problem of developing alternative materials and processes which currently employ these materials. Electronics are a particularly challenging problem because efficient removal of post soldering flux residues is critical to the long-term performance of high reliability electronics. The use of water soluble flux offers an attractive option because all cleaning would be accomplished using only water. Until recently, the military has not allowed this type of flux because of the highly corrosive fluxing action usually associated with these materials. However, a new flux ingredient, citric acid, is gaining favor within the electronics manufacturing industry. Citric acid offers excellent fluxing ability, efficient removal of residues with water, and non-ionic flux formulations. This report examines the chemistry of this material under simulated soldering conditions in an effort to gain an improved understanding of thermal reactions and degradation products which may have an effect on long-term reliability of military electronic hardware.				
14. SUBJECT TERMS Ozone depleting chemicals, citric acid, resin, flux, ionic, non-ionic post-soldering flux residues, water soluble flux, simulated soldering conditions			15. NUMBER OF PAGES 41	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNLIMITED	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

CONTENTS

Introduction	3
General Experimental Approach.....	6
Instrumentation	7
Samples	7
Conclusions	25
References	28
Figures:	
1. Atmospheric Halocarbons Continue to Increase (Adapted From References 2 and 3)	3
2. Flow Chart of the Wave Soldering Process	5
3. Solder Reflow Process Time/Temperature Profile	8
4. ^{13}C CP/MAS NMR Spectrum of Anhydrous CA	9
5. CA Structure	9
6. Anhydrous CA Spectrum	10
7. ^{13}C CP/MAS NMR Spectra of Lead Citrate and Tin Citrate	11
8. ^{13}C CP/MAS NMR Spectra (Carbonyl Region Only) of the Monosodium, Disodium and Trisodium Salts of CA	12
9. ^{13}C NMR Spectra of CA Heated in the Presence of Tin/Lead Solder	13
10. ^{13}C NMR Spectrum of CA Heated in the Presence of Tin/Lead Solder for 45 Seconds Past Solder Liquidus	14
11. Destructive Distillation of CA	15
12. ^1H NMR Series of CA at Solder Liquidus	15
13. ^{13}C NMR Series of CA at Solder Liquidus	16
14. Expanded Decomposition Pathway for CA Involving Decarboxylation and Dehydration	17
15. Decomposition of CA Involving Dehydration at 2,3 Position	18
16. ^1H NMR Spectrum of Itaconic Anhydride in D_2O	20
17. ^{13}C NMR Spectrum of Itaconic Anhydride in D_2O	20
18. ^1H NMR Spectrum of Citraconic Anhydride in D_2O	21
19. ^{13}C NMR Spectrum of Citraconic Anhydride in D_2O	21
20. ^1H NMR Spectrum of Aconitic Acid in D_2O	22
21. ^{13}C NMR Spectrum of Aconitic Acid in D_2O	22
22. Heteronuclear Multiple Quantum Coherence (HMQC) Spectrum for Sample CA60	23

23. Total Correlation Spectroscopy (TOCSY) for CA Decomposition
for 60 Seconds at Solder Liquidus 24

24. TGA Plot of Anhydrous CA 26

25. TGA Plot of Monosodium Salt of CA 26

26. TGA Plot of Disodium Salt of CA 27

27. TGA Plot of Trisodium Salt of CA 28

Tables:

1. CFC Replacement Methods 4

2. ¹³C NMR Chemical Shift Data for CA and Related Compounds..... 11

3. Thermogravimetric Data Under Nitrogen Atmosphere for CA
and Some CA Salts 25

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTRODUCTION

The ozone-depleting chemical (ODC) cleaning solvents methyl chloroform and freons (chlorofluorocarbons (CFCs)), have been in use in the electronics industry for decades. The relative stability, low toxicity, and nonflammability of these ODCs made them easy to use, while their ability to clean thoroughly and leave little or no residue made them the ideal cleaning agent for military and aerospace applications. Unfortunately, the identification of these materials' role in the depletion of the earth's stratospheric ozone layer has led to a ban on their production in the United States beginning in 1996. Depletion of the ozone layer has been implicated in an increase in the number of cases of skin cancer, cataracts, and crop damage. In early 1992, a NASA study was published indicating that the erosion of the earth's ozone layer, as a result of the widespread uses of several ODCs, was occurring faster and extending farther than had previously been believed (Figure 1). The ban on these substances is having a significant impact on the electronics manufacturing industry as a whole and the manufacture of military specification electronics components in particular (References 1 and 2).

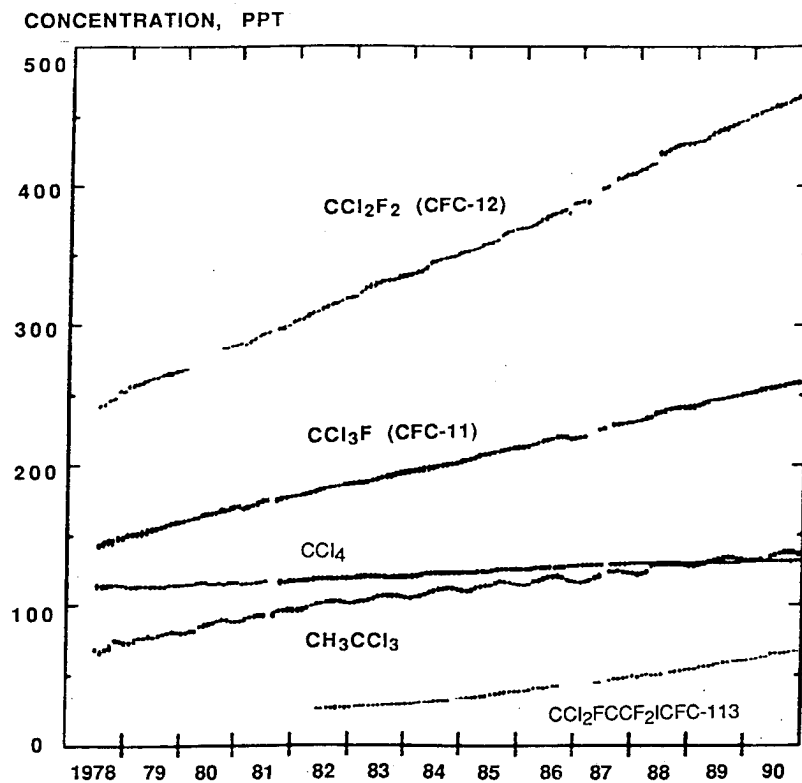


FIGURE 1. Atmospheric Halocarbons Continue to Increase (Adapted from References 2 and 3).

In standard wave soldering processes, the circuit board and components are pretreated with a flux (Figure 2). As the board is soldered, the flux serves to remove or break down the oxide layer present on the surface of the circuit board and component leads. This results in faster solder wetting (higher manufacturing volume) as well as a stronger and more reliable solder joint. Traditionally, the flux compound of choice has been rosin moderately activated (RMA). This pine-pitch-based material is a complex mixture of terpenoids with a quaternary alkyl amine hydrohalide activator. While this material works well as a solder flux, the chemical residues are corrosive to electronics and *not* water soluble. RMA flux requires an efficient cleaning system such as has been provided by ODC solvent cleaning and degreasing.

One option for the manufacture, rework, and repair of electronics that does not require the use of an ODC solvent cleaning system is the implementation of a process using only water-soluble fluxes. Water-soluble fluxes have traditionally not been allowed on military systems because of the highly corrosive nature of these materials. Recently however, aqueous citric acid (CA) has received attention as a flux because it is chemically active, yet very easy to remove after soldering. CA is readily available, inexpensive, and has taken the early lead in the area of "environmentally green" fluxes since only warm water is required for cleaning and disposal of the rinsates is cost effective on both large and small scales. CA-based fluxes have been shown to exhibit excellent soldering properties (Table 1). However, an understanding of the fundamental chemistry of these materials and their thermal degradation products are required before they can be certified for military applications.

TABLE 1. CFC Replacement Methods.^a

Methods	Plus	Minus
Aqueous (tap/DI H ₂ O)	Requires H ₂ O soluble flux No CFC problem No VOC problem No polyglycols Better solder joint (CA)	Heavy metals in waste stream
Semi-aqueous (hydrocarbon surfactant in H ₂ O)	Recycle agent and first rinse through decant and R/O system	High cost of chemicals and equipment VOC content (<1 lb/day)
No-clean (inert atmosphere)	Very small amounts of flux	Significantly increased quality assurance monitoring Poor visual appearance Generally not tenable for military applications

^a There is *NO* drop-in replacement for CFCs—especially for MIL-STD applications.

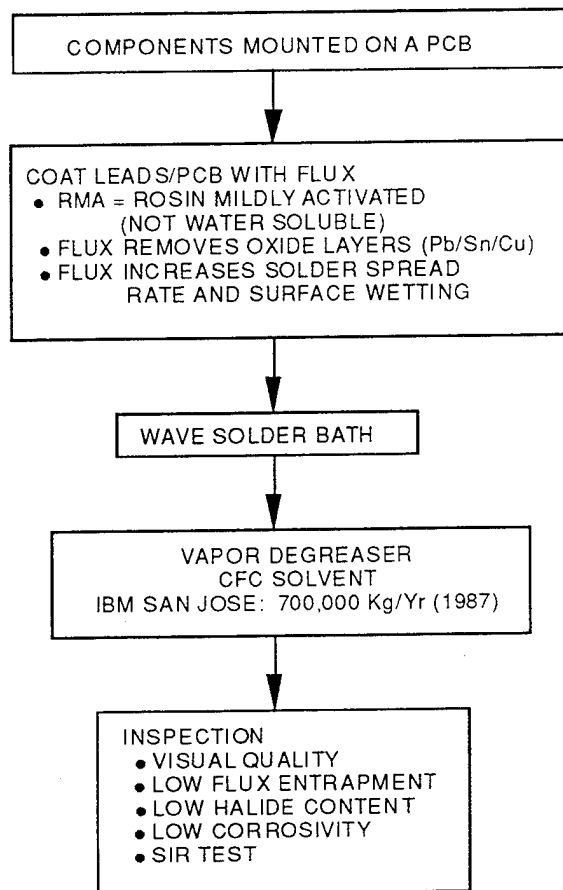


FIGURE 2. Flow Chart of the Wave Soldering Process.

Military requirements for electronics are significantly more stringent than those for most commercial applications. Military hardware must remain functional in severe environments for prolonged periods or may be stored for years prior to use and the storage conditions may involve temperature and humidity cycling. It is therefore imperative that military circuit boards pass the required surface insulation resistance (SIR) and solvent extraction tests designed to identify organic and ionic contaminants that may, at some future time, lead to corrosion or to dendritic growth between the traces, thereby resulting in circuit failure (Reference 4). While it is clear that the ODC ban will force a change to the use of alternative cleaning technologies and non-rosin fluxes, it is essential that the elimination of CFCs and other ODCs should not have an adverse effect on the reliability of military hardware. Given that water-based cleaning technologies will be an interim, if not final, solution to the fabrication of clean electronic circuitry for military hardware, it is important that a clear understanding of the underlying chemistry be reached.

CA has been one of the most studied alternatives to rosin-based fluxes by industry as well as the military. Preliminary investigations have concluded that CA performs at least as well, if not better, than conventional rosin flux technology (Reference 5). However, CA and other organic acids that are presently under investigation are new ingredients in soldering processes and, therefore, must be studied thoroughly prior to large-scale utilization. This report details the study of the interaction of CA with metals likely to be found in the soldering process as well as the decomposition pathways of CA under typical soldering conditions. It is essential that a good understanding be obtained of the contaminants likely to be found and of the potential for these contaminants to cause problems with long-term reliability.

GENERAL EXPERIMENTAL APPROACH

Before CA will gain widespread military approval as a soldering flux, several questions must be answered. These include:

1. What products are formed during the thermolysis of CA at solder liquidus?
2. Are any tin, lead, or other metal citrates formed?
3. How much residue remains after the soldering process?
4. What is the chemical composition of these residues?

The answers to these questions provide the basis for an understanding of the use of CA-based fluxes, their cleanability, and the ultimate effect on long-term circuit board reliability.

The first portion of this study was focused on the use of nuclear magnetic resonance (NMR) spectroscopy to answer the above questions. NMR techniques were used to characterize neat CA, CA salts, and CA thermolyzed under the specific conditions noted below. Solid-state NMR was used to characterize the solids "as received" to avoid any interferences or solubility problems that may occur when dissolving the materials. Solution-state NMR was used to determine, as closely as is possible, the exact structure of the compounds formed.

In addition to the above, thermal decomposition studies of neat CA were undertaken. Thermogravimetric analysis (TGA) was used to characterize the decomposition profile of CA and to determine the amount of solid residue that remains after heating to solder liquidus temperatures.

Neat reference chemicals were obtained from a number of commercial sources. CA, the sodium and potassium salts of CA, and citraconic acid were purchased from Aldrich, Milwaukee, Wisconsin. Nickel citrate was obtained from ICN Biomedicals,

Inc., Irvine, Calif. Stannous citrate and lead citrate were prepared by Polarchem, Garden Grove, Calif. Itaconic acid and anhydride were purchased from Pfizer & Co. New York, New York and J. T. Baker, Phillipsburg, New Jersey, respectively.

INSTRUMENTATION

Solution-state NMR spectra were run on a Bruker AMX-400 NMR spectrometer operating at a magnetic field strength of 9.4 Tesla. This corresponds to ^1H and ^{13}C frequencies of 400.1 and 100.6 MHz, respectively. Chemical shift values are reported (with respect to external tetramethylsilane (TMS) using the high-frequency positive convention (Reference 6)).

Solid-state NMR spectra were run on a Bruker MSL-200 NMR spectrometer operating at a field of 4.7 Tesla with a corresponding ^{13}C frequency of 50.3 MHz. All spectra were obtained using magic-angle spinning at speeds of ca. 3 to 4 kHz. Both Bloch decay and cross polarization experiments were performed. ^{13}C shift values are reported with respect to TMS and were measured by replacing the sample with the secondary reference, adamantane (high-frequency line = 38.5 ppm with respect to TMS) (Reference 7).

Thermogravimetric analyses were run on a TA Instruments TGA 2950 high-resolution thermogravimetric analyzer linked to a Dupont Thermal Analyst 2100 data station. Exact analysis profiles are provided herein.

SAMPLES

The amount of decomposition products formed on a circuit board are relatively small. Therefore, a method was required for forming sufficient quantities of decomposition products for NMR analysis. At the same time, the CA had to be exposed to conditions similar to those of a typical wave solder process (Figure 3). To accomplish these conditions, a number of glass test tubes were prepared, each containing several grams of CA and a ca. 5-mm-diameter ball of military specification (QQ-S-571, 63/37 tin/lead) solder. The tubes were then immersed into a molten solder bath and allowed to remain for 5, 10, 15, 30 and 60 seconds past the point at which the solder in the tube liquified. The ends of the tubes were then sealed with parafilm until the decomposition products could be removed for analysis. (Note that the sample number CA5 denotes the residue of CA at 5 seconds past solder liquidus, CA10, 10 seconds, etc.) Samples were first examined by solid-state NMR. The samples were then dissolved in D_2O or d_6 -acetone for solution-state NMR analysis. Ultimately, D_2O was the solvent of choice since the residues were far more soluble and gave clear solutions with no turbidity as compared to the cloudy acetone solutions.

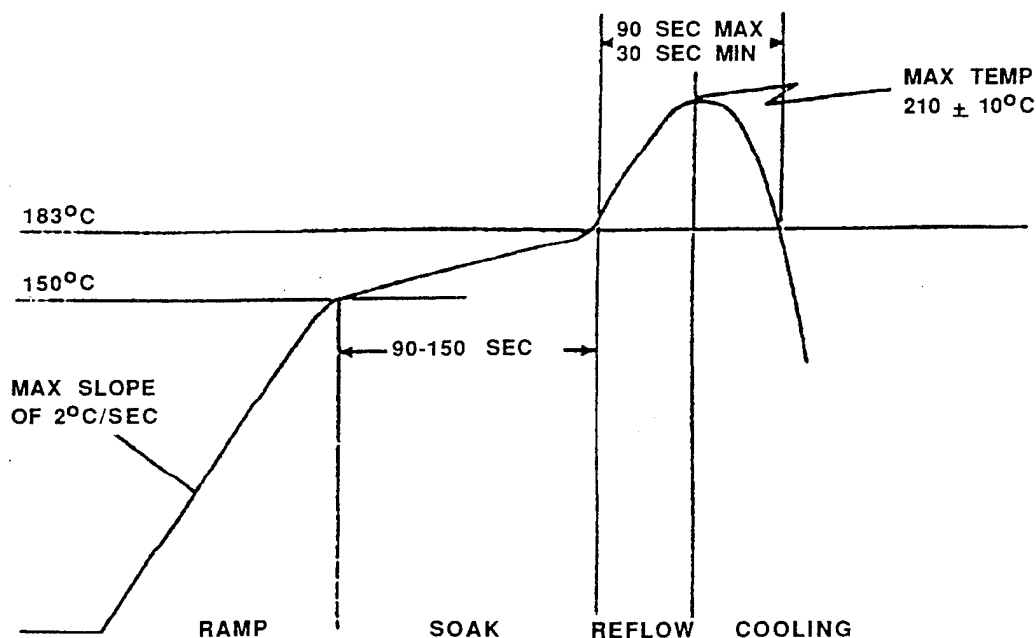


FIGURE 3. Solder Reflow Process Time/Temperature Profile.

Solid-State NMR Data for Known CA Reference Standards

Solid, anhydrous CA has a ^{13}C NMR spectrum consisting of six lines (Figure 4). The three lines at 179.5, 176.6 and 175.0 ppm arise from the carbon atoms of the carboxylic acid groups (Figure 5). The sharp resonance at 72.9 ppm corresponds to the central carbon of the molecule and the lines at 44.2 and 43.3 ppm may be assigned to the two methylene carbons. It will be noted that this line multiplicity reflects the fact that in the solid, the carboxylic acid groups are strongly hydrogen bonded to neighboring groups, thus rendering the three carbonyl carbons inequivalent. There also exists a solid form of CA in which the crystal lattice contains one molecule of water per molecule of CA. The ^{13}C spectrum of commercially obtained CA monohydrate indicated that the sample contained ca. 30% anhydrous CA (Figure 6). If the anhydrous CA component is subtracted from the spectrum of the mixture, a spectrum of only the monohydrate results. This spectrum is similar to the anhydrate in line multiplicity, but the chemical shift values are significantly different (Table 2). No evidence of CA monohydrate was found in any other sample examined.

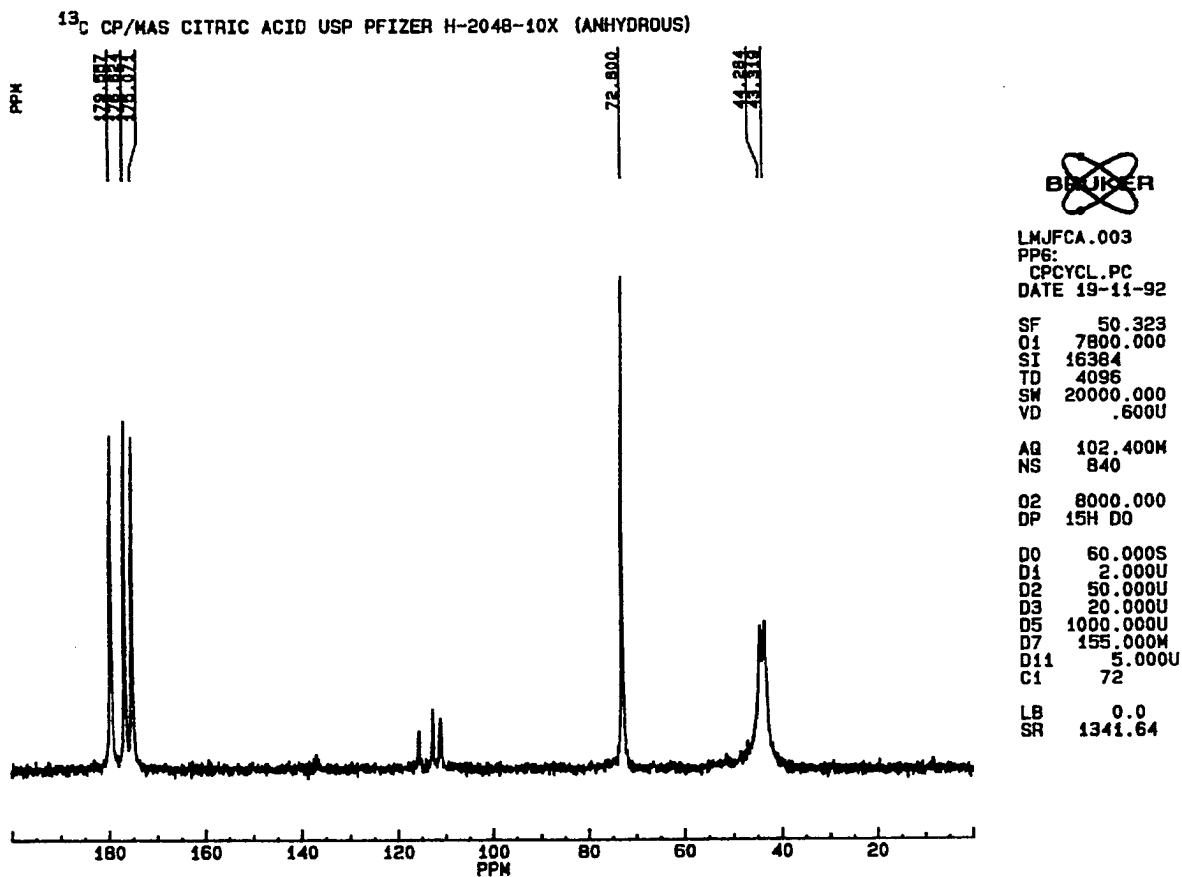


FIGURE 4. ¹³C CP/MAS NMR Spectrum of Anhydrous CA.

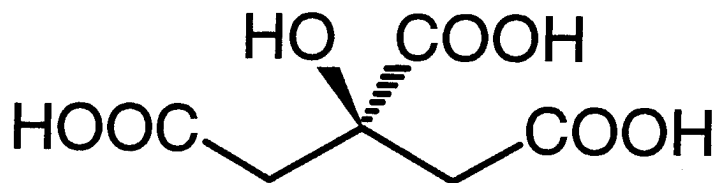


FIGURE 5. CA Structure.

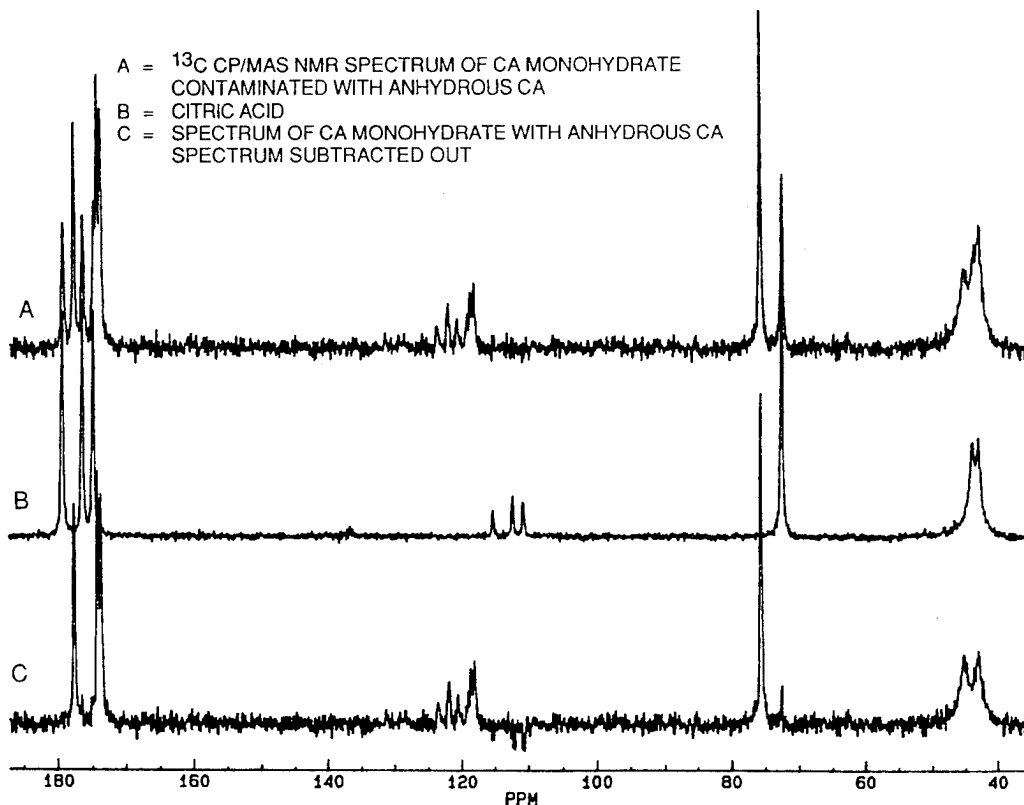


FIGURE 6. Anhydrous CA Spectrum.

The ^{13}C spectrum of tin (stannous) citrate is similar in appearance to that of CA, but with the lines shifted somewhat by the presence of the tin (Figure 7 and Table 2). However, in the lead citrate there is a doubling of the number of lines in the carbon spectrum. This apparently occurs due to the presence of two differing types of citrate anions in the lead citrate unit cell.

The ^{13}C NMR data for three sodium salts and one potassium salt of CA are given in Table 2 and Figure 8. The trisodium and tripotassium salts have line multiplicity similar to that of CA but, again, significantly different shift values. The monosodium salt spectrum contains small resonances, the source of which are not readily apparent. These may be either minor crystal phases or impurities; however, the shift values for the minor components do not correlate to any other CA compound examined in this study. The carbonyl region of the disodium salt spectrum consists of four lines in a 2:1:2:1 ratio. This reflects the presence of 1.5 waters of crystallization (i.e., two molecules of water for every three CA molecules in the crystal lattice).

Several aspects of the data presented in the previous paragraph must be emphasized. First of all, the solid-state ^{13}C NMR results for CA and its related compounds show assignable spectra that consist of narrow lines that are all well resolved. Furthermore, each compound examined has a unique set of resonances that may be used as a "fingerprint" to identify that component, even in a complex mixture.

TABLE 2. ^{13}C NMR Chemical Shift Data^a for CA and Related Compounds.

Compound	Solid-state ^{13}C shift values/ppm ^b (solution-state values in parentheses)		
	-COOH	C-OH	-CH ₂ -
CA (anhydrous)	179.5, 176.6, 175.0	72.8	44.2, 43.3
CA (monohydrate)	177.9, 174.5, 174.0	75.9	45.7, 43.4
CA (D ₂ O solution) ext. Tss reference	(178.4, 175.2 (2C _s))	(75.1)	(44.9)
Stannous citrate	184.7, 182.0, 178.7	80.1	51.3, 47.8
Plumbous citrate	185.0, 184.3, 181.5, 180.7, 178.2, 177.5	78.9, 76.0	51.5, 48.3, 45.8
CA monosodium salt	180.2, 173.4,	73.3	49.9, 41.9
CA disodium salt ($\cdot 1.5$ H ₂ O)	184.2, 181.5 180.6, 179.6	74.3	48.9, 45.0
CA trisodium salt ($\cdot 2$ H ₂ O)	186.1, 181.4, 178.1	75.8	47.5, 42.9
CA tripotassium salt	182.2, 178.1	76.8	53.5, 51.6
	C=O	Olefin C, CH, CH ₂	Alkane CH ₂ , CH ₃
Aconitic acid in D ₂ O	(176.7, 171.4, 170.6)	(141.6(q), 132.6 (CH))	(35.3)
Itaconic acid	180.0, 172.8	136.5, 132.2 (q)	37.5
Itaconic anhydride(D ₂ O solution)	(178.1, 172.2)	(135.8, 133.1)	(39.7)
Citraconic acid	174.2, 172.6	135.9, 131.1 (q)	20.2
Citraconic anhydride (D ₂ O solution)	(175.5, 170.4)	(149.5, 122.5)	(22.0)

^a NB: Both nickel and copper citrate gave no ^{13}C result due to the paramagnetic nature of metal cation.

^b ^{13}C shifts reported with respect to external TMS, error ± 0.1 ppm.

q = quaternary.

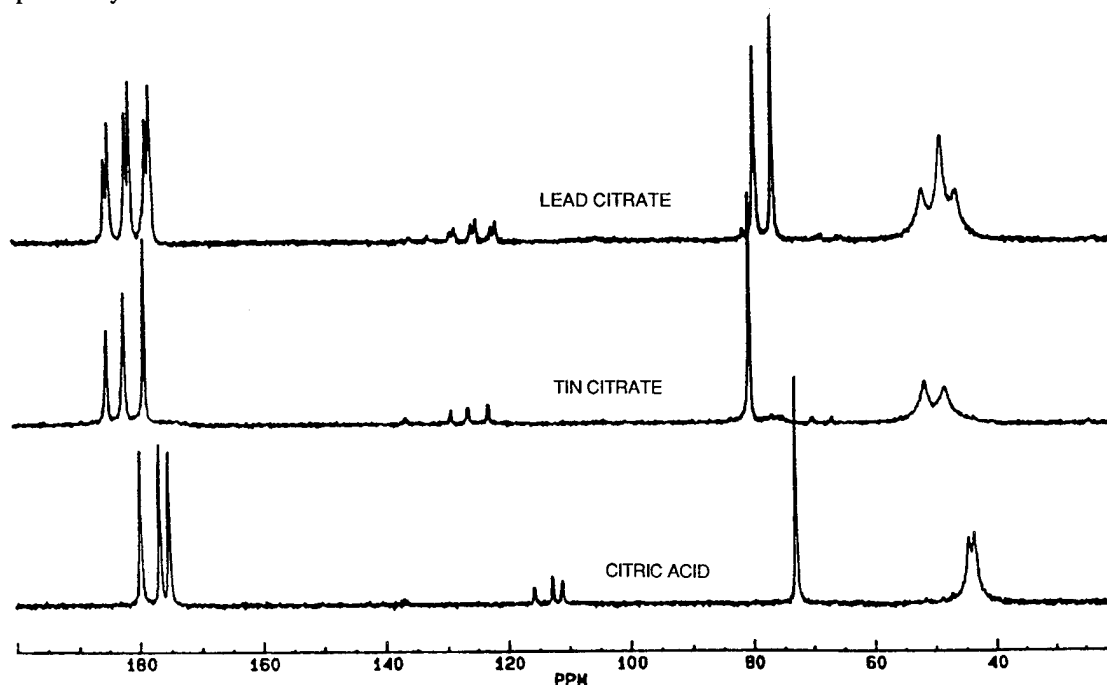


FIGURE 7. ^{13}C CP/MAS NMR Spectra of Lead Citrate and Tin Citrate.

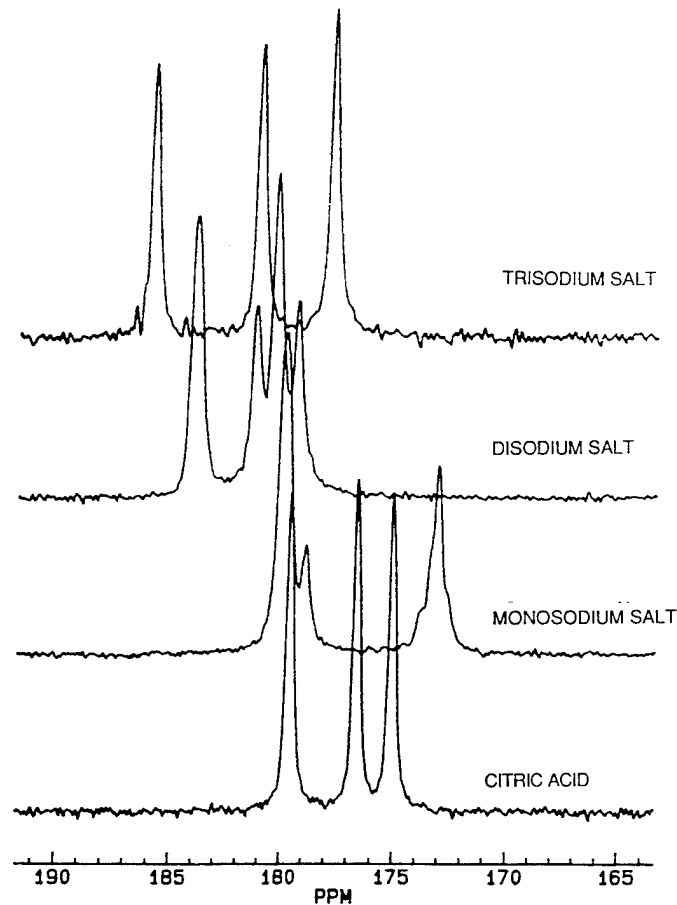


FIGURE 8. ^{13}C CP/MAS NMR Spectra (Carbonyl Region Only) of the Monosodium, Disodium and Trisodium Salts of CA.

Solid-State NMR Results of Thermolyzed CA

After thermolysis in the presence of solder, the sample CA5 appeared light brown in color and was of a viscous, amorphous consistency. A small amount of white, crystalline CA had apparently spattered upwards and coated the inside of the test tube. Samples CA10, CA15, and CA30 were similar in appearance. Samples CA45 and CA60 were a darker, red-brown in color with little or no remaining CA on the tube sides. Solid-state NMR spectra of the brown material from samples CA5, CA30, and CA60, along with the spectrum of CA as reference, are shown in Figure 9. The spectra at 5 and 30 seconds past liquidus show only very minor changes from the spectrum of neat CA. The methylene region at ca. 45 ppm broadens and the resonance associated with the central, quaternary carbon (72 ppm) shifts slightly. There is an increase in line multiplicity in the carbonyl region (175 to 185 ppm), but this is not accompanied by any new lines in the 0 to 80 ppm region, which one would expect to observe if new compounds or salts were being formed. This suggests that the multiplicity in the carbonyl region is associated with changes in hydrogen bonding (possibly associated with loss of water) for the carboxylic acid groups. There is also no evidence of resonances that could be correlated to tin or lead citrate.

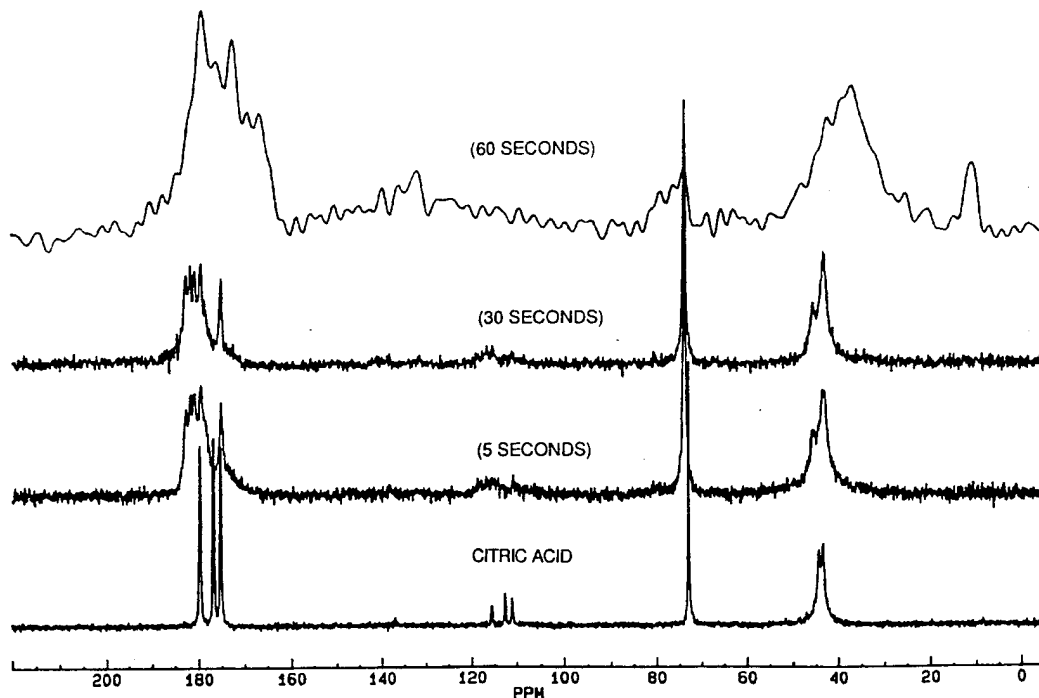


FIGURE 9. ^{13}C NMR Spectra of CA Heated in the Presence of Tin/Lead Solder.

At 45 seconds past liquidus, the ^{13}C NMR spectrum clearly shows evidence of chemical changes in the sample (Figure 10). The carbonyl region has broadened considerably as has the quaternary resonance. The methylene resonance has not only broadened, but also exhibits a considerable increase in relative intensity in the spectrum. Most notably, there is a new resonance that has appeared at ca. 132 ppm indicating the presence of an olefinic carbon species. In the spectrum of the 60-second sample, the intensity of the CA quaternary carbon has significantly decreased, indicating that a significant portion of the CA has been converted to other compounds (Figure 9). There is some structure to the carbonyl region. Three of the features in this region and the maximum of the broad resonance at ca. 40 ppm correspond to itaconic anhydride (see Solution State NMR Results section). In addition, there is a resonance at 10.5 ppm which may correspond to the methyl group in citraconic acid or anhydride. Citraconic anhydride has a melting point of 8°C , but may form a eutectic in this type of system. It is interesting to note that when a sample of the 60-second material was placed in a vacuum oven overnight at 80°C , this methyl resonance disappeared. This would seem to suggest that the low melting point citraconic anhydride was present. There is no evidence for the presence of metal citrates or alkali metal citrate salts.

In conclusion, the solid-state NMR results suggest little or no reaction of the CA for times of 30 seconds or less. At 45 seconds, there is clear evidence of chemical changes taking place. The 60-second spectrum indicates the possible presence of itaconic and citraconic anhydrides. There is no evidence of metal or alkali citrate salts in any of the spectra recorded.

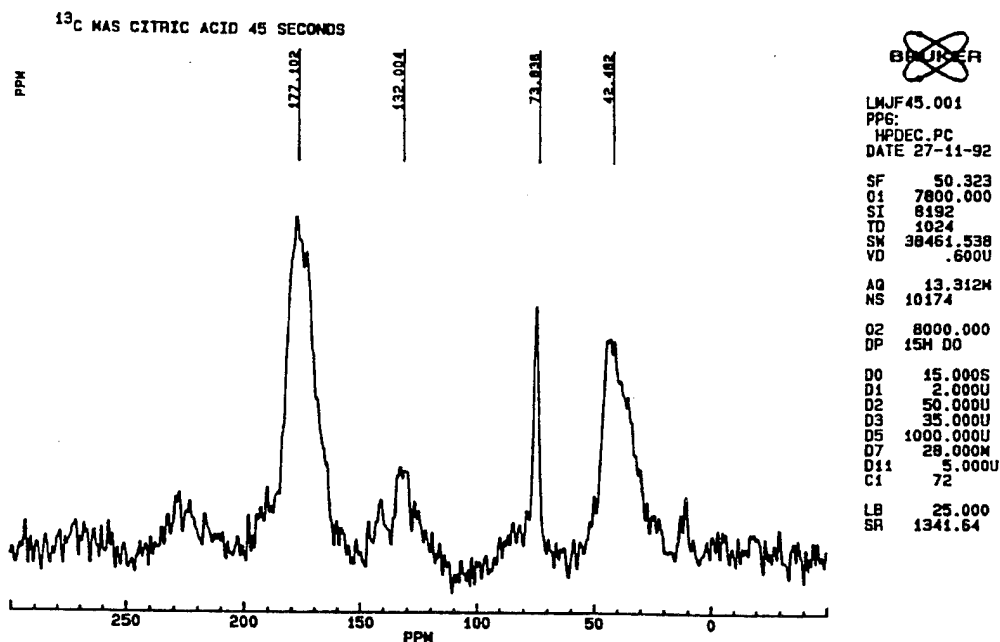


FIGURE 10. ¹³C NMR Spectrum of CA Heated in the Presence of Tin/Lead Solder for 45 Seconds Past Solder Liquidus.

Solution-State NMR Results

Samples of CA and several samples of thermally aged CA (see General Experimental Approach section) were subjected to a battery of solution state NMR experiments. Both ¹H and ¹³C solution state NMR results will be discussed in this section. The goal of this work was to identify the decomposition products that might be formed under standard wave solder conditions with CA-based fluxes. The bulk of the materials formed by thermal decomposition in the presence of liquid solder were water soluble, and solutions in D₂O were analyzed by NMR methods. The destructive distillation of CA is described in Reference 8 and is shown in Figure 11.

Figures 12 and 13 display the ¹H and ¹³C NMR spectra of CA and three samples of CA that were allowed to thermally decompose for 5, 30, and 60 seconds in the presence of liquid solder. The initial spectrum of CA is characterized as an AB quartet centered near 2.9 ppm assigned to the methylene protons of CA. The peak near 5.5 ppm is residual HDO from the solvent. After just 5 seconds at solder liquidus, several dramatic changes were observed in the ¹H NMR spectrum. Residual HDO appears near 4.9 ppm—a result in the change in acidity of the solution. The growth of new resonances at 2.1, 3.1, 3.8, and 6.9 ppm is noted. The appearance of these resonances after 5 seconds at solder liquidus indicates that dehydration and decarboxylation steps are occurring in the early stages of CA decomposition. The CA30 sample is very similar to the 5-second sample with additional small peaks growing in the olefinic region (between 5 and 7 ppm). The sample that had been thermolyzed for 60 seconds at solder liquidus changed dramatically. While there is still a small amount of CA present, the majority of product is represented by singlets or slightly broadened singlets in the aliphatic and olefinic regions.

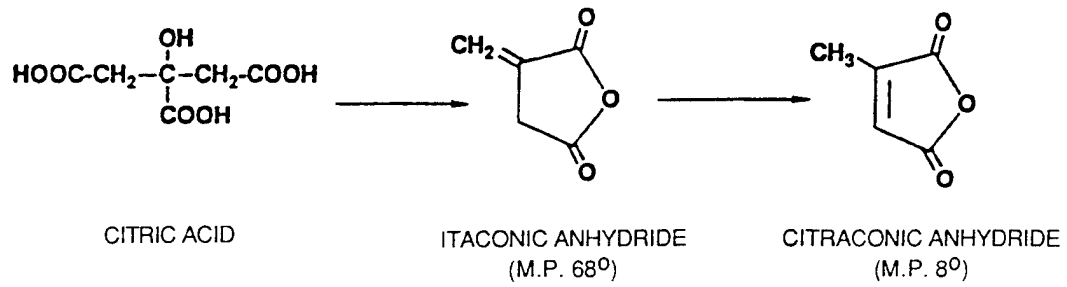


FIGURE 11. Destructive Distillation of CA.

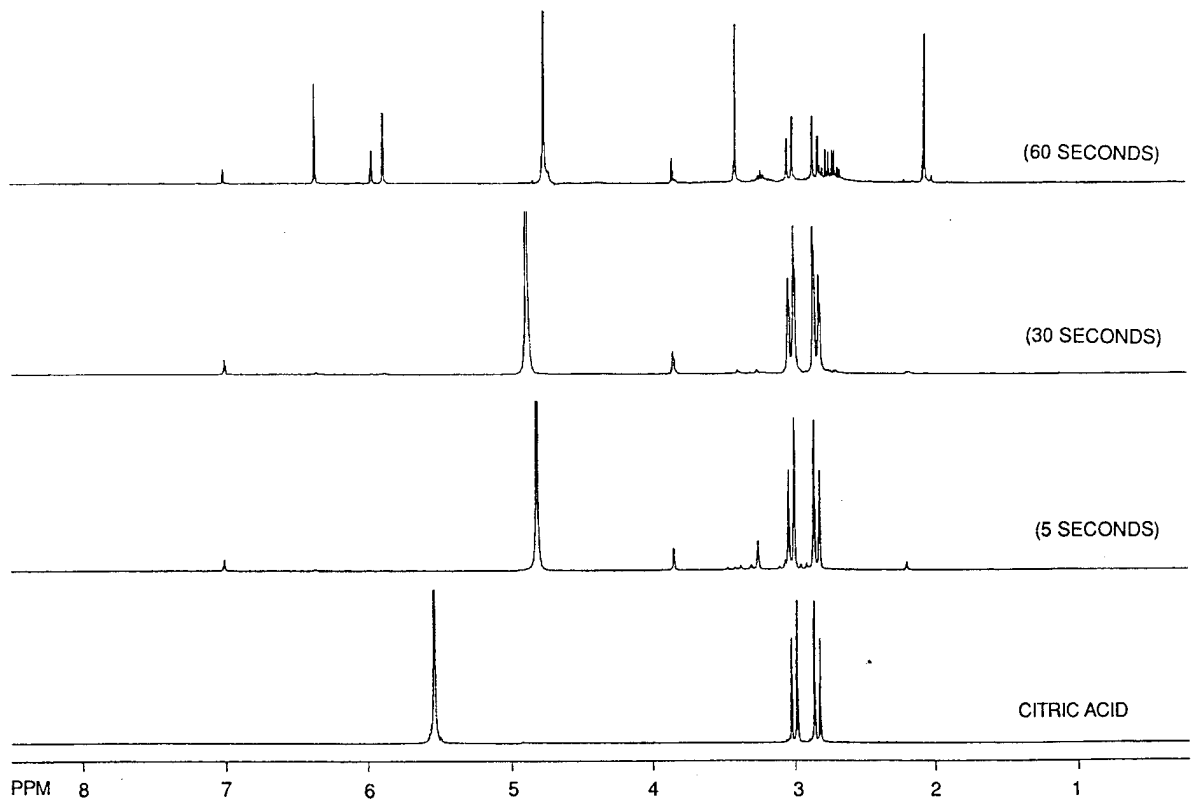


FIGURE 12. ¹H NMR Series of CA at Solder Liquidus.

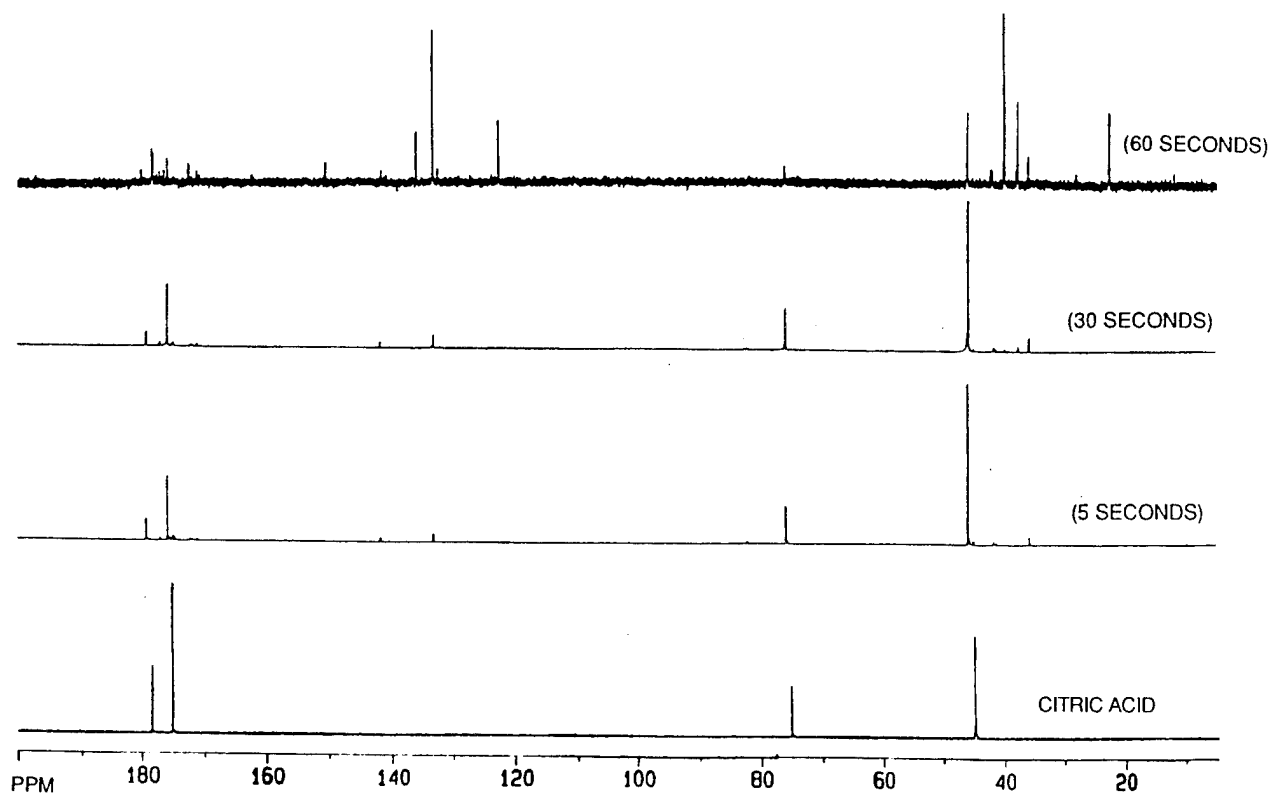


FIGURE 13. ^{13}C NMR Series of CA at Solder Liquidus.

The ^{13}C NMR series yields further evidence that CA is present in large quantities after 5 and 30 seconds at solder liquidus (Figure 13). The CA methylene, 45 ppm, quaternary, 75 ppm, and carboxyl resonances, 178 and 175 ppm, in the ^{13}C NMR spectrum are prominent in the CA5 and CA30 samples. Once again there are definite indications of new materials containing olefinic carbons (120 to 150 ppm) as well as some new aliphatic resonances (20 to 50 ppm) appearing in the early stages of thermal decomposition. After 60 seconds of thermolysis, the ^{13}C NMR indicates that a small amount of CA is still present and compounds containing olefinic carbons are dominating the spectrum, thus confirming the ^1H NMR results. The major decomposition products have been identified using an array of 1- and 2-dimensional NMR techniques described in the following paragraphs.

The CA60 sample was used for a series of NMR experiments to study the thermolysis of CA at solder liquidus. It is instructive to first consider how CA might decompose thermally. From these simple considerations, four materials were identified that appeared to be present in the thermally aged samples. Decarboxylation and dehydration are the most likely paths of decomposition for CA. Indeed, the destructive distillation of CA is known to lead to itaconic and citraconic anhydrides (Reference 8, Figure 11). If decarboxylation is considered first, there are two sites where a reaction could occur (Figure 14). Decarboxylation at either of the two sites adjacent to a methylene group leads, after dehydration, to either itaconic or citraconic anhydride, **2** or **3** (for simplicity, it was assumed that anhydrides are formed that are later rehydrated when dissolved in D₂O for solution-state NMR experiments.) On the other hand, if decarboxylation is performed first at the central carbon of CA, then the result might be 3-hydroxyglutaric acid, **4**, which could dehydrate to form a dehydroglutaric acid, **5**. There is clear evidence for **4** in the ¹H and ¹³C NMR, but evidence for **5** is not compelling. One last decomposition pathway for which there is clear evidence involves dehydration prior to any decarboxylation step. This pathway is depicted in Figure 15 and the products, as shown, are cis or trans aconitic acid, **6**, or aconitic anhydride, **7**. Cis aconitic acid is closely related to CA in the Krebs cycle (Reference 8). It is known that CA reacts with hydrochloric acid to give aconitic acid when heated (Reference 9).

NMR evidence suggests that under thermal conditions, CA undergoes both decarboxylation and dehydration to yield many of the products shown in Figures 14 and 15. Data also shows that the initial step in thermolysis of CA is dehydration to form aconitic acid derivatives, which are observed in the earliest stages of reaction.

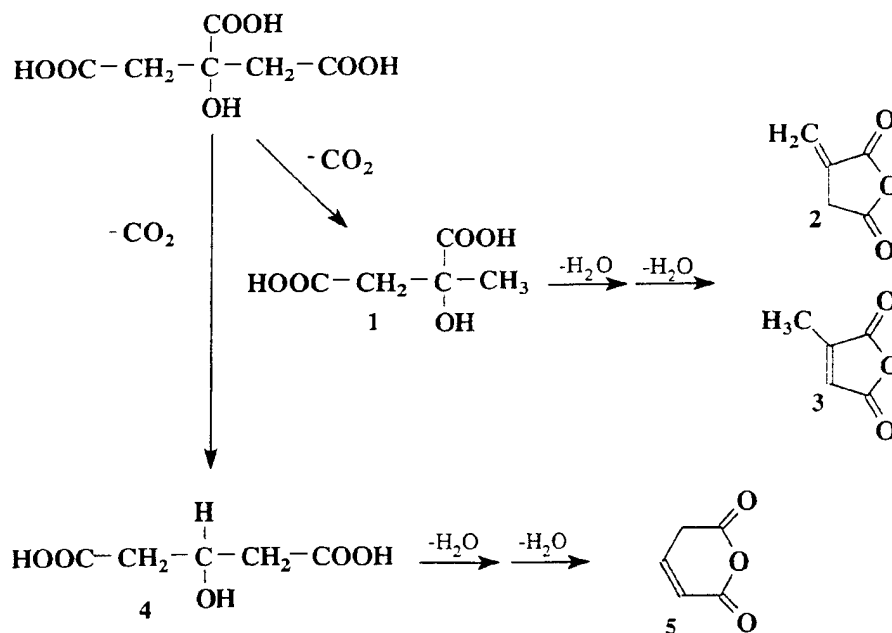


FIGURE 14. Expanded Decomposition Pathway for CA Involving Decarboxylation and Dehydration.

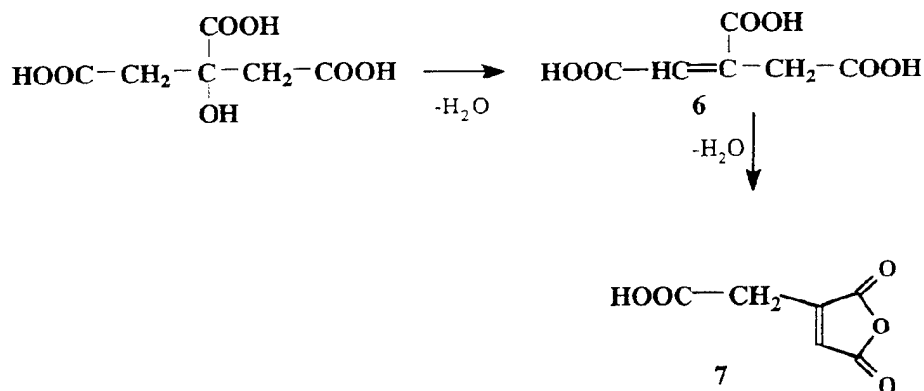


FIGURE 15. Decomposition of CA Involving Dehydration at the 2,3 Position.

Itaconic and citraconic anhydrides, 2 and 3, are seen in the CA60 sample as is aconitic acid or anhydride 6 or 7 (see 1H and ^{13}C NMR spectra of actual materials Figures 16 through 21). Citraconic anhydride is evident in the CA5 sample, but only at very low concentrations. However, an aconitic acid derivative can be clearly identified in the CA5 and CA30 samples. HMQC (Reference 10) and TOCSY (Reference 11) 2-dimensional NMR experiments were performed in order to confirm our conclusions (Figures 22(a), 22(b) and 23). The HMQC experiment allows direct correlation of 1H resonances with their directly bonded ^{13}C resonances. Figure 22(a) displays the HMQC data for the aliphatic region and Figure 22(b) displays the olefinic region. Direct evidence for the presence of citraconic and itaconic acids or anhydrides is found in both regions of this 2-dimensional data. The methyl carbon/protons for the citraconic derivative are observed near 2.1 and 22 ppm in the 1H and ^{13}C dimensions, respectively, and the olefinic CH is observed near 122 and 6.0 ppm (see Figure 22(a)). Close examination of the 1H resonance near 6.0 ppm reveals a quartet structure, $^4J_{H-H} = 1.6$ Hz from coupling to the methyl protons in the citraconic derivative (see inset Figure 22(b)).

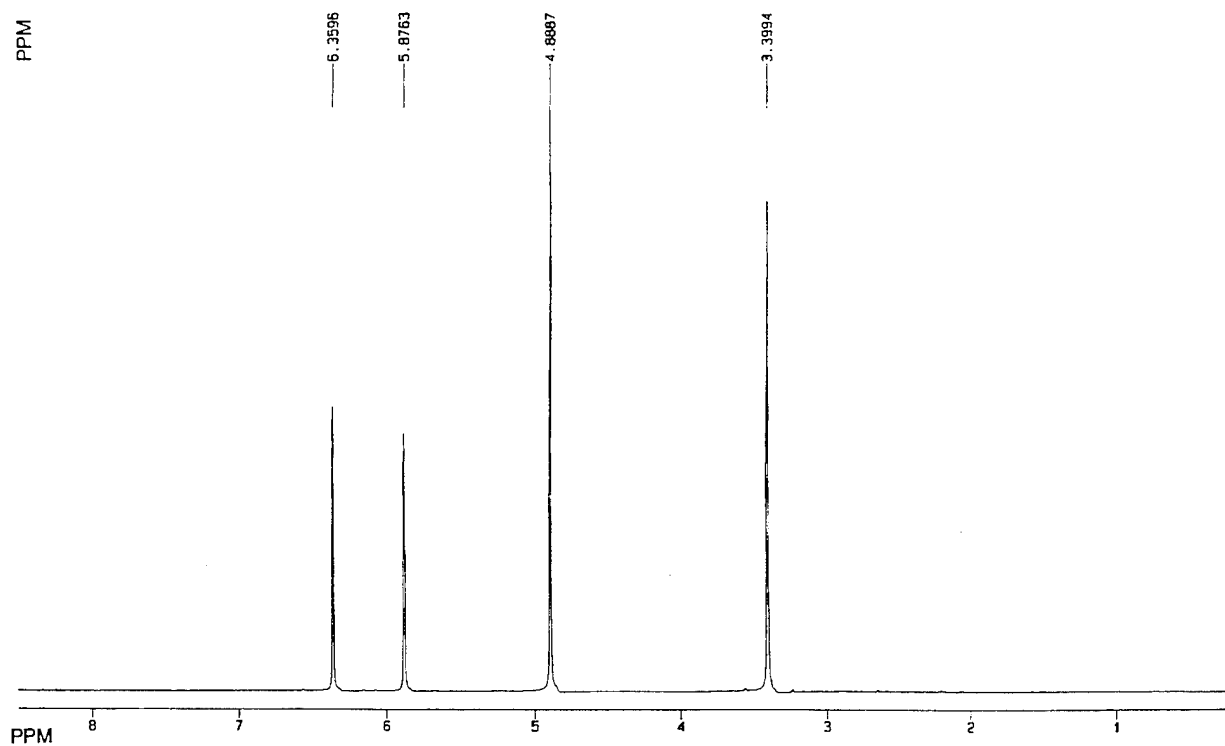
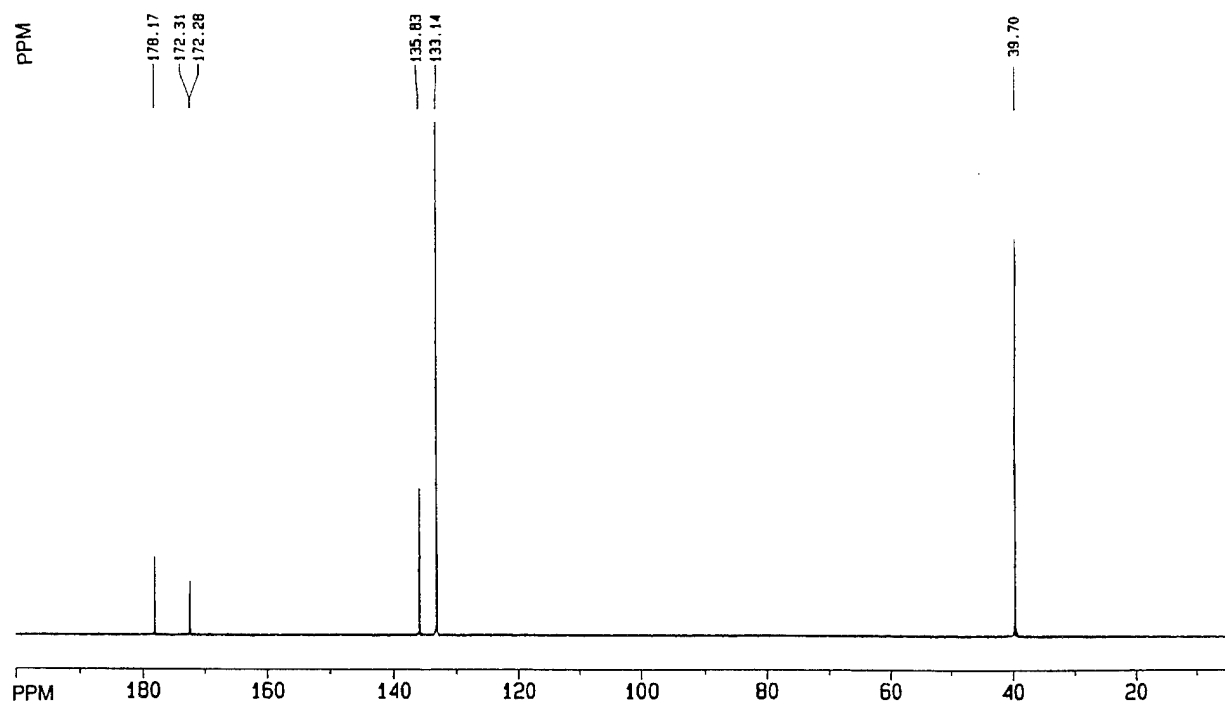
The evidence for an itaconic derivative is equally compelling, with a methylene resonance observed near 3.4 and 39 ppm in the 1H and ^{13}C dimensions, and a pair of inequivalent olefinic protons near 5.9 and 6.4 ppm displaying a correlation to a carbon resonance near 133 ppm. This corresponds well to the expectation for itaconic acid or anhydride. The evidence for 3-hydroxy glutaric acid, 4, as a decomposition product centers upon two multiplet resonances in the 1H spectrum of the 60-second aged material. A quartet of doublets centered near 2.7 ppm and an apparent triplet centered near 3.2 ppm

have the correct multiplicity and ratio of integrated areas to be assigned to the methylene and methine protons of **4**. Evidence for aconitic acid derivatives includes the resonance near 7.0 and 133 ppm in Figure 22(b) and also the resonance near 3.8 ppm and 36 ppm, which was assigned to the methylene group of aconitic acid or anhydride.

One further conclusion, based upon the ^1H spectra at 5 and 30 seconds thermolysis in Figure 12 and comparison to the spectra of aconitic acid in Figures 20 and 21 is that the initial decomposition pathway involves dehydration at the 2,3 position of CA. The appearance of singlets at 7.0 and 3.9 ppm would indicate that aconitic acid derivatives are present in the earliest stages of thermolysis and each of the six ^{13}C resonances of aconitic acid in the ^{13}C NMR spectra of CA5 and CA30 can be identified (Figure 13).

The TOCSY experiment allows for correlation between all coupled proton spins within a molecule (Figure 23). This technique is very helpful for looking at samples that contain mixtures of materials. Off-diagonal resonances correspond to coupled spin systems and must indicate resonances that are within the same molecule. There is a clear correlation (off-diagonal peak) between two olefinic peaks near 6.4 and 5.9 ppm and each of these olefinic resonances has an additional correlation to a resonance near 3.4 ppm. This corresponds exactly to what would be expected for itaconic acid. If focus is placed on the other major olefinic resonance near 6.0 ppm, a correlation with a resonance near 2.0 ppm can be identified. These resonances were assigned to the olefin and methyl resonances of citraconic acid. The evidence for 3-hydroxyglutaric acid, **4**, is the off-diagonal resonance near 2.7 and 3.2 ppm, indicating a strong, probably vicinal, coupling between these two resonances. An authentic sample of **4** could not be found, however, comparison to malic acid, which contains similar methine and methylene protons, does indicate a similar coupling pattern. Finally, one other correlation is observed in the TOCSY experiment between protons near 7.0 and 3.9 ppm and this can be assigned to the 4-bond coupling between olefin and methylene protons of an aconitic acid derivative.

In conclusion, the thermal decomposition of CA in the presence of liquid solder leads to many of the possible organic products associated with dehydration and decarboxylation. Thus far, these efforts have not lead to the identification of any metal salts, however, their presence is not precluded by these investigations. Indeed, many of the anticipated citrate salts are only sparingly soluble in water or acetone, and might not be observed by the techniques employed herein. A further extension of this work will be to monitor CA/solder flux products by atomic absorption methods.

FIGURE 16. ^1H NMR Spectrum of Itaconic Anhydride in D_2O .FIGURE 17. ^{13}C NMR Spectrum of Itaconic Anhydride in D_2O .

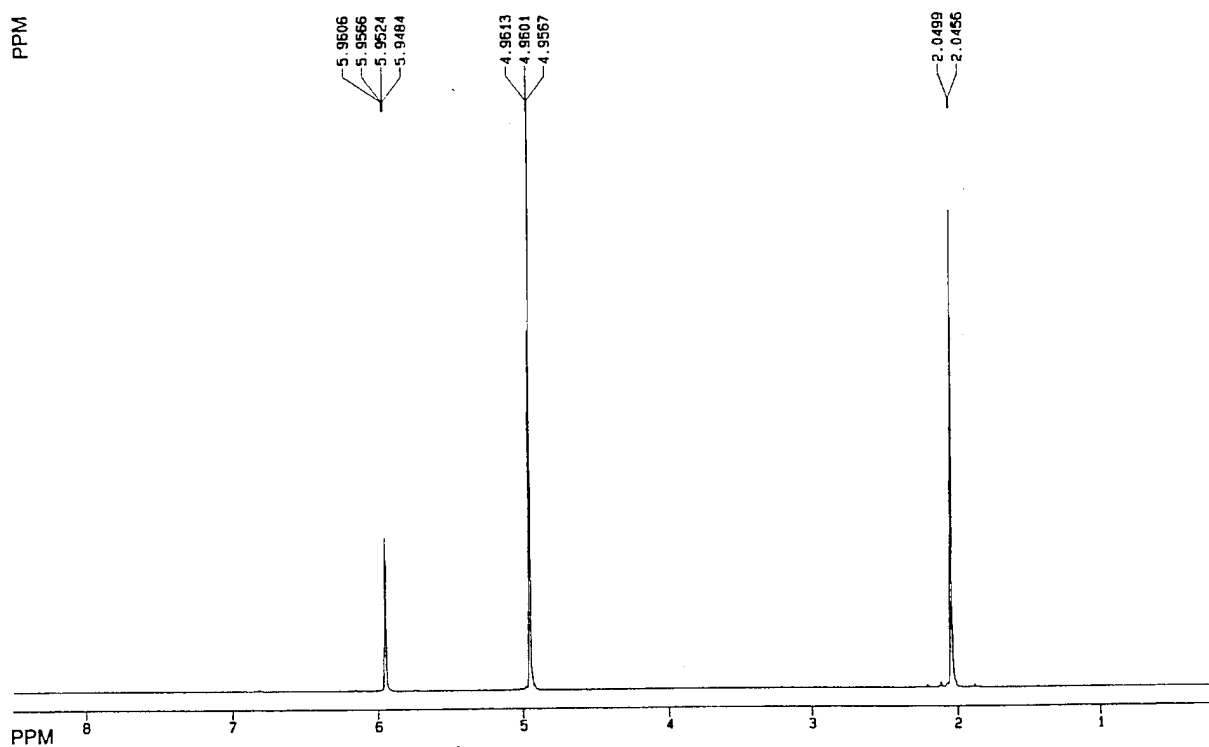


FIGURE 18. ¹H NMR Spectrum of Citraconic Anhydride in D₂O.

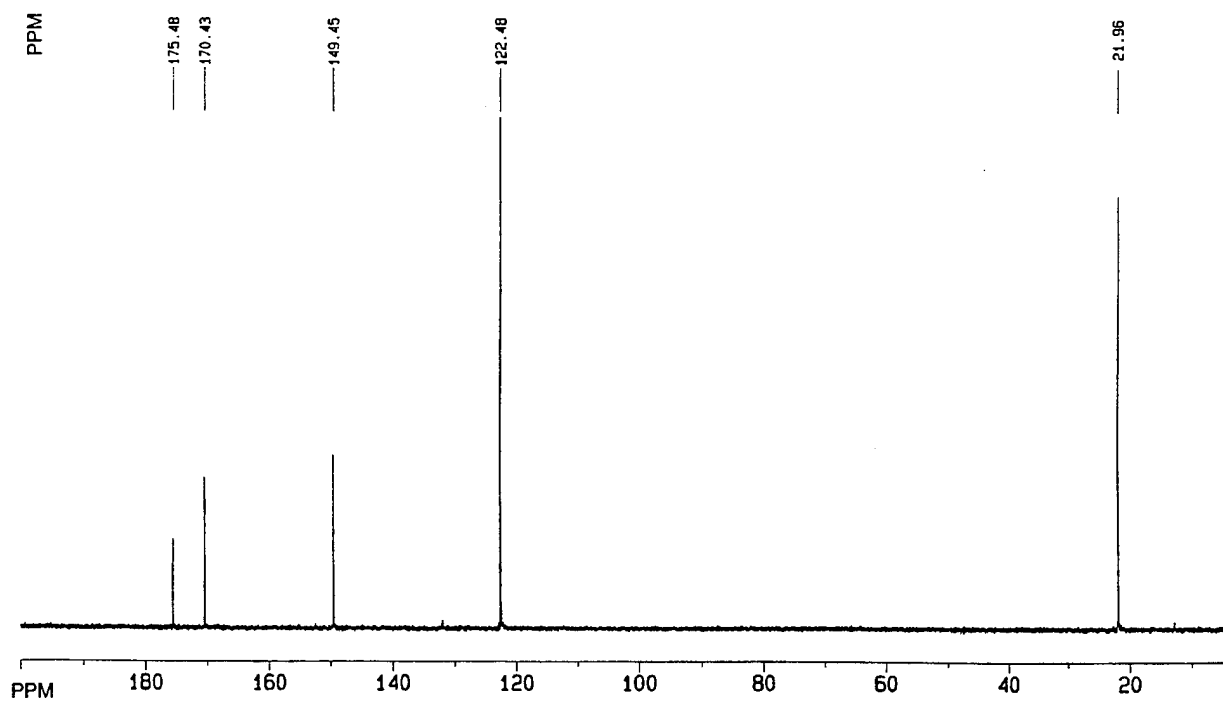


FIGURE 19. ¹³C NMR Spectrum of Citraconic Anhydride in D₂O.

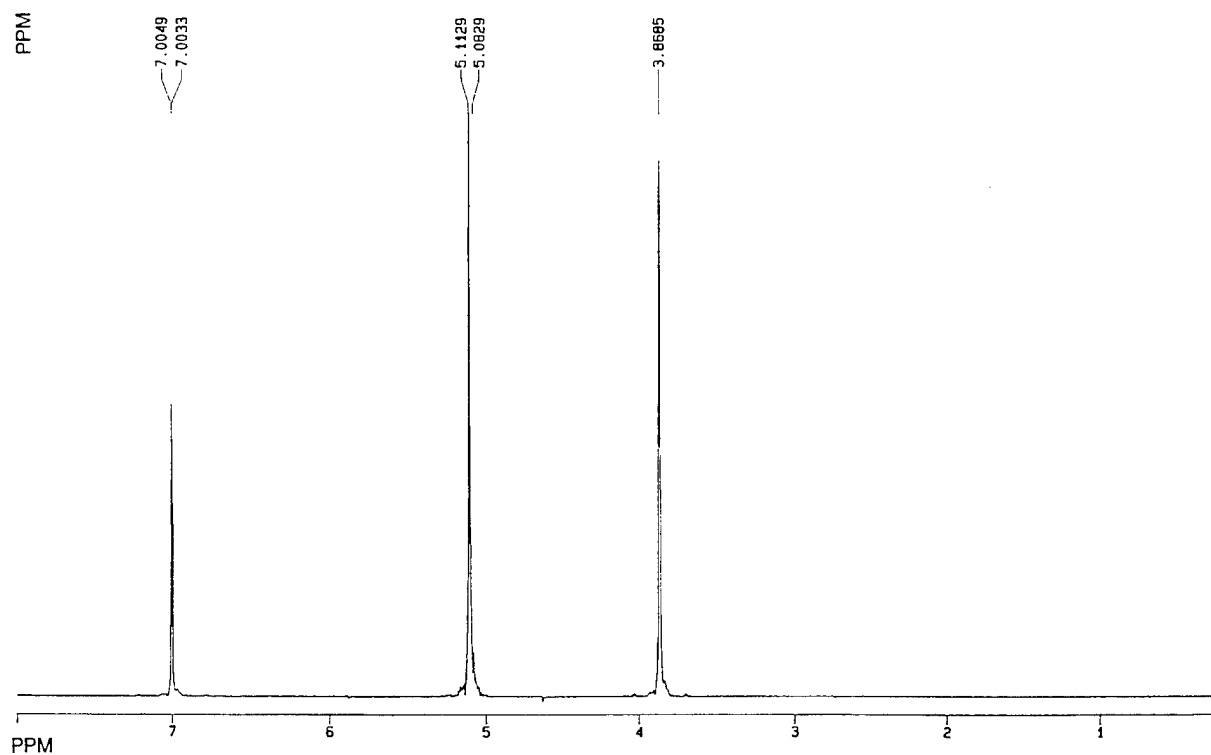


FIGURE 20. ¹H NMR Spectrum of Aconitic Acid in D₂O.

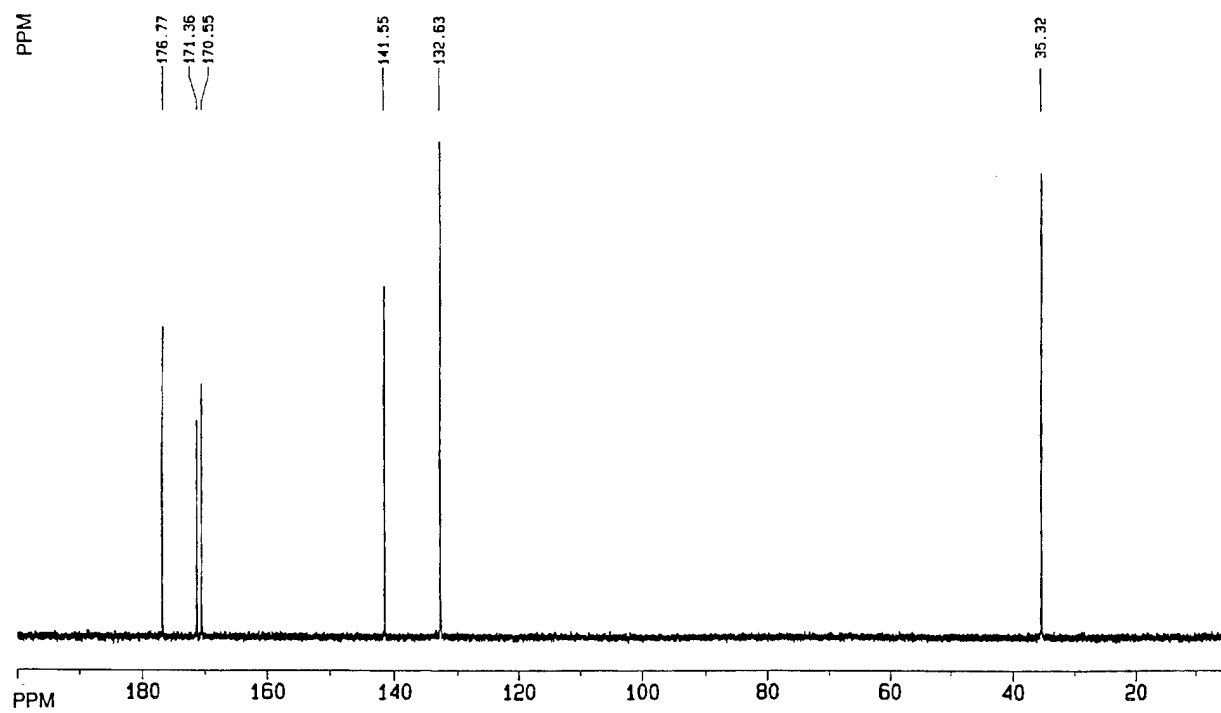
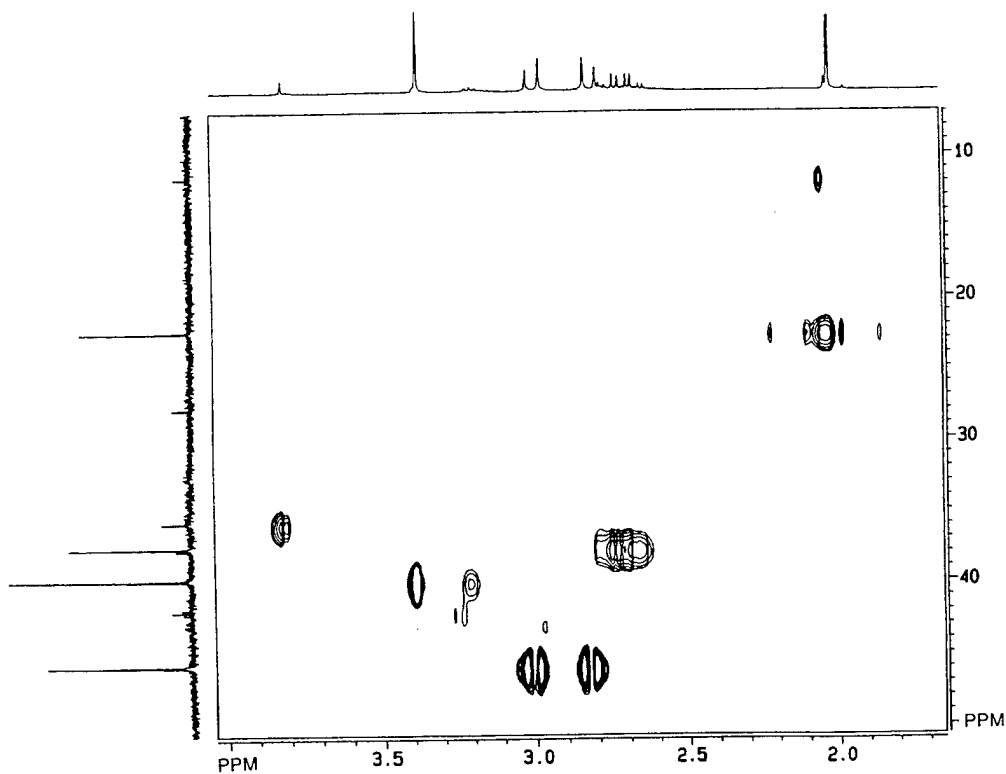
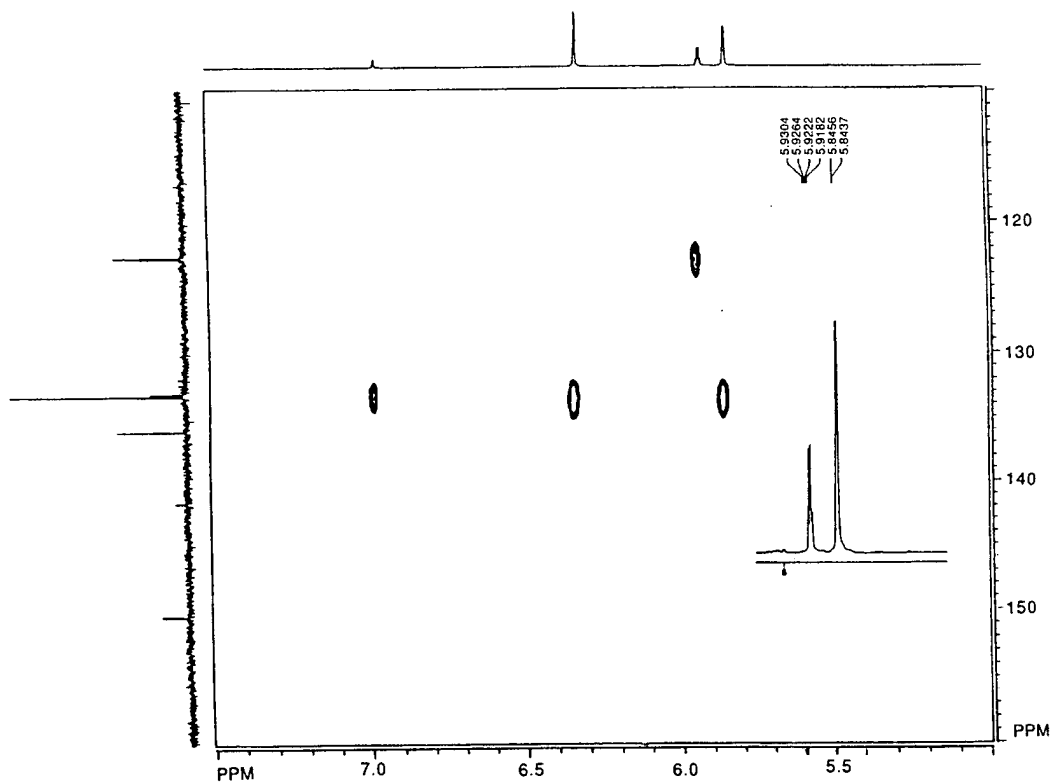


FIGURE 21. ¹³C NMR Spectrum of Aconitic Acid in D₂O.



(a) Aliphatic regions.



(b) Olefinic regions (inset expansion of proton region near 6 ppm).

FIGURE 22. Heteronuclear Multiple Quantum Coherence (HMQC) Spectrum for Sample CA60.

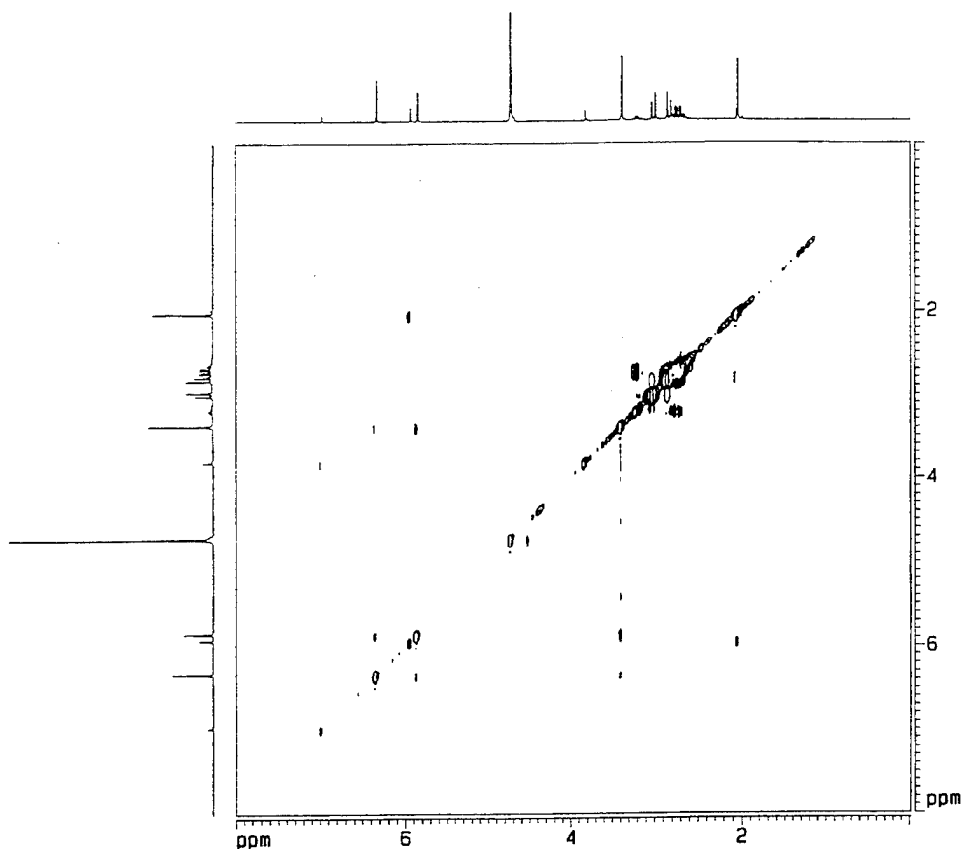


FIGURE 23. Total Correlation Spectroscopy (TOCSY) for CA Decomposition for 60 Seconds at Solder Liquidus.

TGA Results

TGAs were run on neat CA and on several alkali metal citrates. TGA provides an extremely accurate measure of sample weight as a function of temperature. The method provides a clear picture of the decomposition profile of the material as a function of temperature, as well as an accurate measure of the amount of residue after sample decomposition. For the data presented herein, an initial sample size of 2 to 10 mg was used. The heating profile began at room temperature and was ramped at 5°C per minute. During heating, the sample was maintained under a nitrogen atmosphere. The onset of sample decomposition is reported as the temperature at which 1.0% of the sample weight has been lost.

TGA results for the compounds of interest are reported in Table 3. Anhydrous CA begins to decompose at ca. 166°C and leaves 3.1 weight percent residue at 250°C (Figure 24). The onset temperature of 97.4 °C for the monohydrate represents the loss of the water of hydration. An inflection in the TGA curve at ca. 165°C represents the actual onset of CA decomposition. Again, the amount of residue is small.

TABLE 3. Thermogravimetric Data Under Nitrogen Atmosphere for CA and Some CA Salts.

CA sample	Onset of decomposition, °C*	Sample residue at 250°C, %	Sample residue at 300°C, %
Anhydrous	166.5	3.1	2.2
Monohydrate	97.4	1.9	1.5
Monosodium salt	194.9	45.5	41.5
Disodium salt sesquihydrate	138.8	74.5	67.1
Trisodium salt dihydrate	154.0	87.6	86.1
Tripotassium salt monohydrate	144.3	94.0	84.6

* Onset of decomposition defined as temperature where 1.0 weight percent has been lost.

Of importance here is the large amount of residue remaining from the decomposition of the CA alkali metal salts (Figures 25 through 27). For the monosodium salt, over 45 weight percent remains at 250°C. As the amount of residue scales with the amount of cation present, it is believed that the product consists mainly of the alkali metal carbonate, though this has not been conclusively proven. This result argues strongly for the use of alkali-cation-free water in making up the flux solutions, as it is clear that the presence of even small amounts of these salts may result in large amounts of residue remaining on the soldered board and components.

CONCLUSIONS

In summary, a careful chemical evaluation of CA and the products formed when CA is thermolyzed in the presence of tin/lead based solder were completed. There is no evidence of the formation of metal citrate salts in the solid-state NMR spectra. Solution-state NMR evaluation was used to identify the thermolysis products. The results support the presence of itaconic anhydride, citraconic anhydride, 3-hydroxyglutaric acid and aconitic anhydride, all of which can be derived by dehydration and/or decarboxylation of CA. These products are all water soluble and should pose no problem in the production of circuit boards by wave solder operations, if water or steam cleaning processes are subsequently used. TGA results demonstrate the low residue of neat CA, but also indicate that the presence of alkali metal salts will result in significantly increased weight of residue.

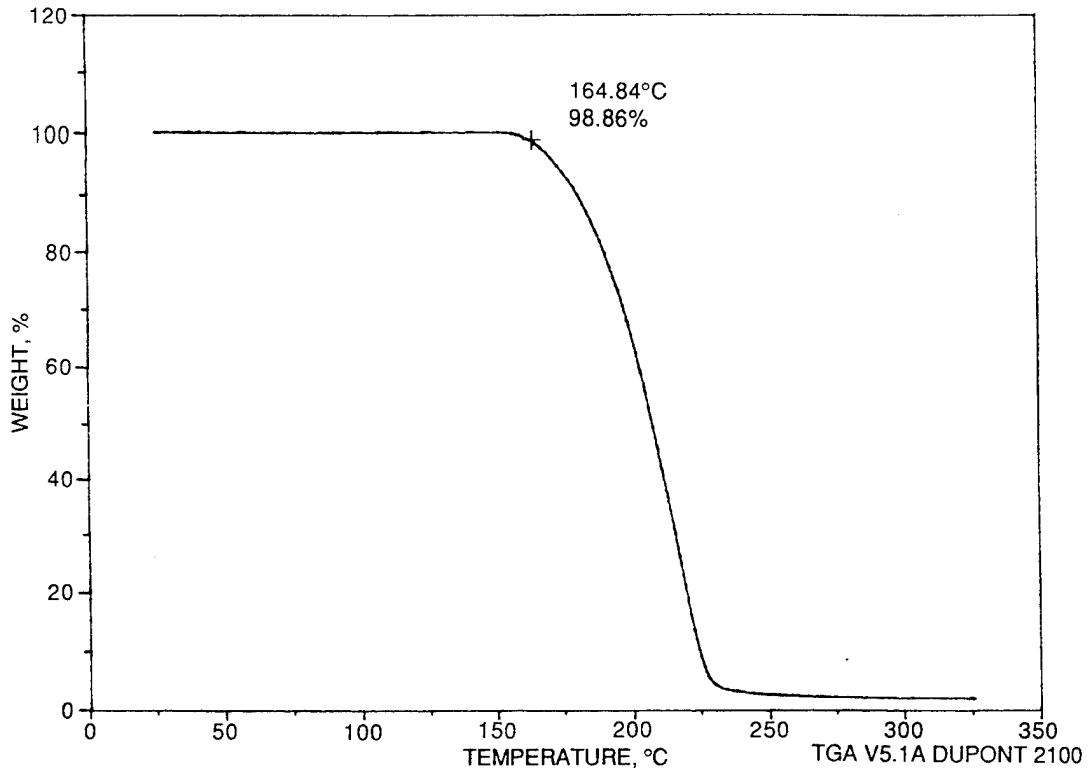


FIGURE 24. TGA Plot of Anhydrous CA.

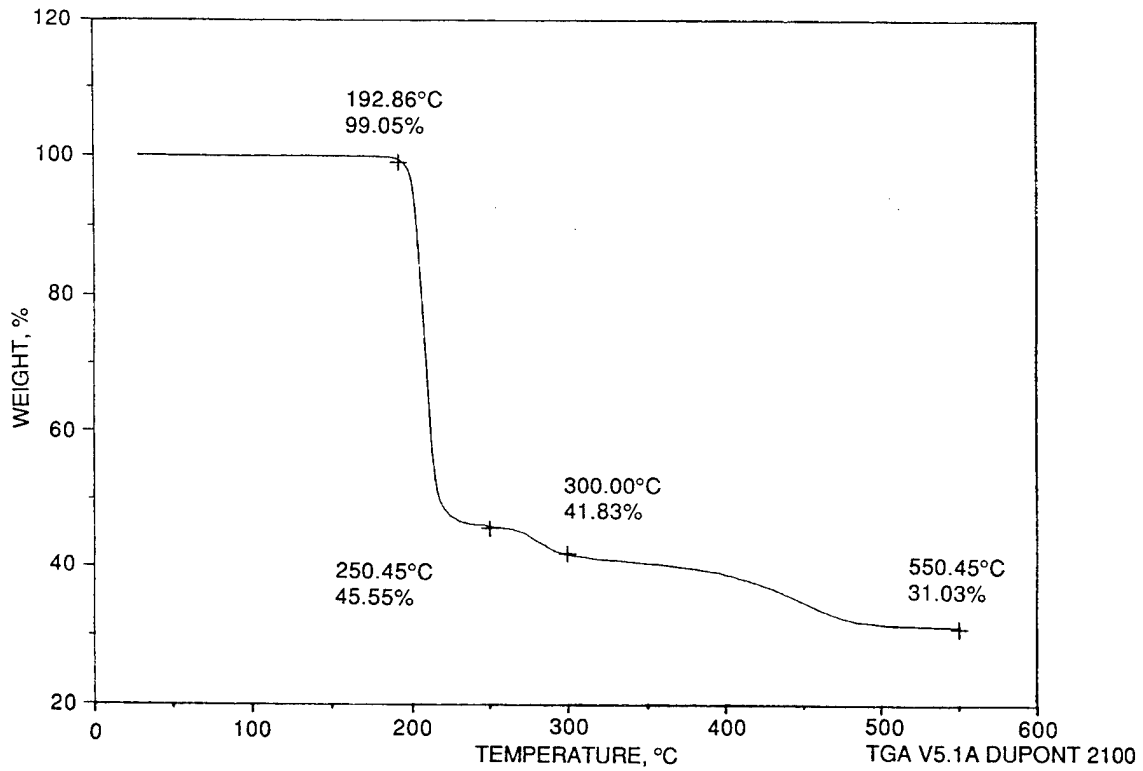


FIGURE 25. TGA Plot of Monosodium Salt of CA.

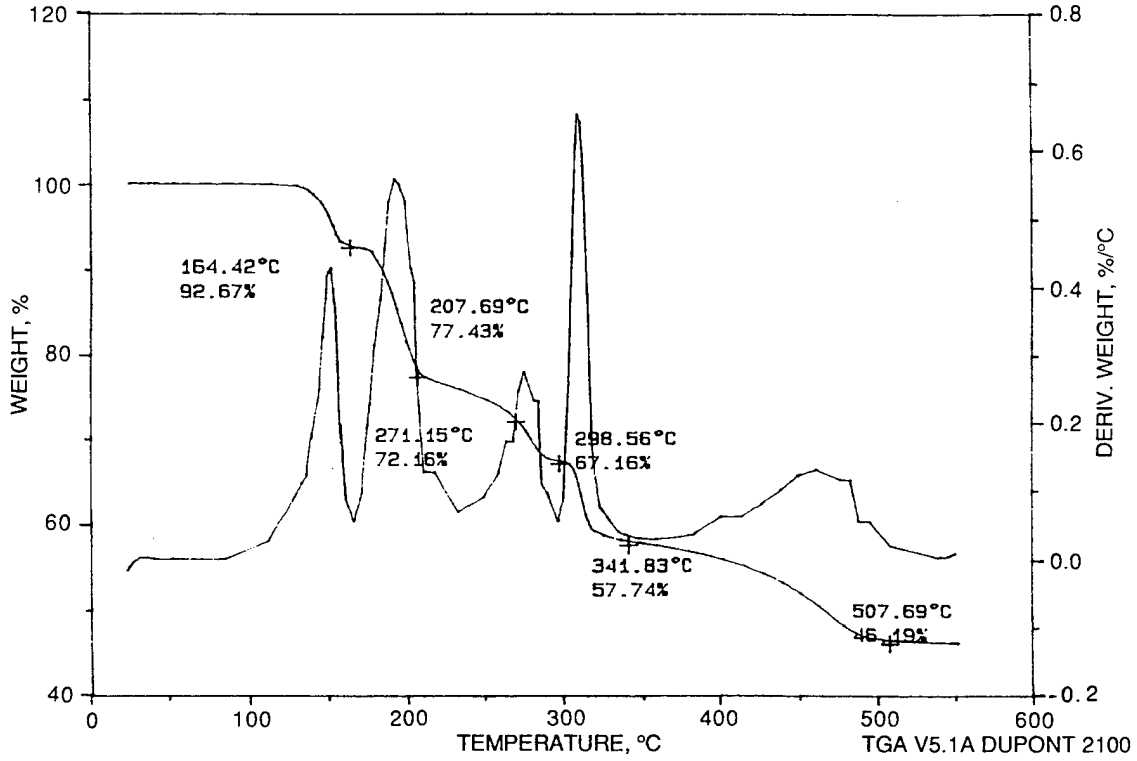


FIGURE 26. TGA Plot of Disodium Salt of CA.

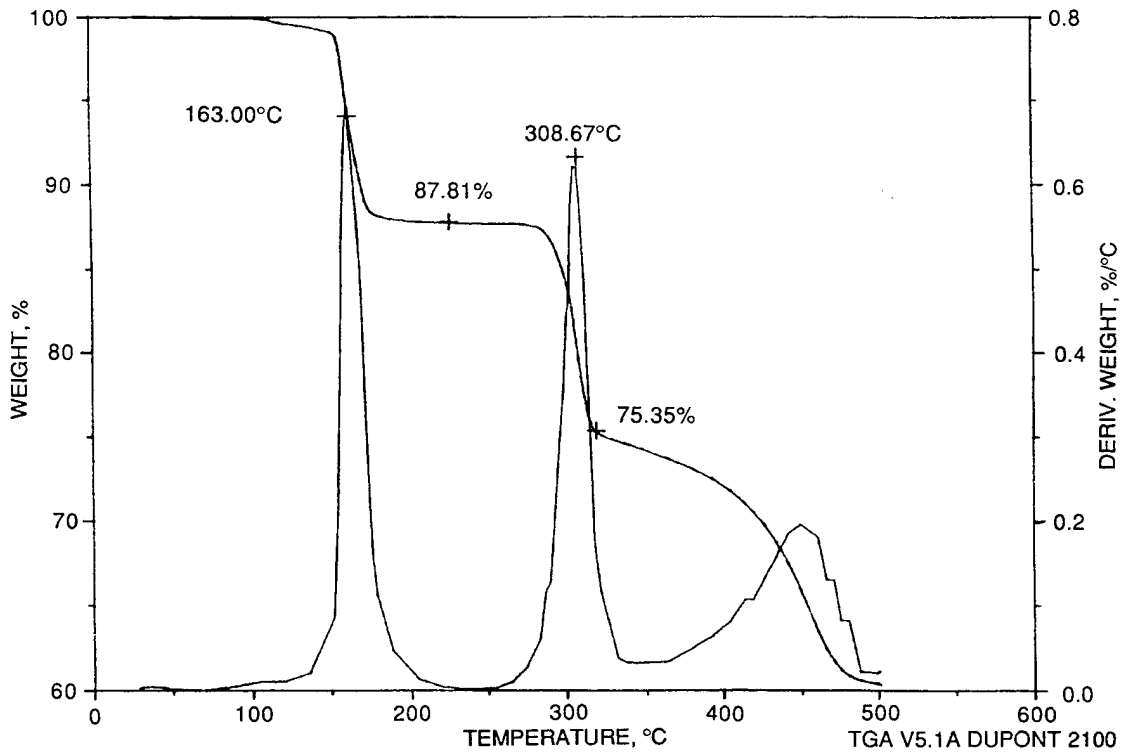


FIGURE 27. TGA Plot of Trisodium Salt of CA.

REFERENCES

1. Tekla S. Perry. "Cleaning Up," *IEEE Spectrum*, Vol. 30, No. 12 (February 1993) pp. 20-26.
2. Pamela S. Zurer. "Industry, Consumers Prepare for Compliance With Pending CFC Ban," *Chemical and Engineering News*, Vol. 70, No. 25 (June 22, 1992) pp. 6-13.
3. Bette Hileman. "Web of Interactions Makes It Difficult To Untangle Global Warming Data," *Chemical and Engineering News*, April 27, 1992, p. 7.
4. Naval Air Systems Command. *Flux, Soldering/Liquid, Paste Flux, Solder Paste and Solder-Paste Flux, (For Electronic/Electrical Use) General Specification for*. Washington, D.C. NAVAIR. (MIL-F-14256, document UNCLASSIFIED.)
5. Ray L. Turner. "HF-1189 The Environmentally Green Flux," *17th Annual Electronics Manufacturing Seminar Proceedings* (NAWCWPNS TP 8096) December 1992 pp. 137-146. (Paper UNCLASSIFIED.)
6. Robin K. Harris and Brian E. Mann. *NMR and the Periodic Table*, London, England, Academic Press, 1978.
7. Shigenobu Hayashi and Kikuko Hayamizu. "Shift References in High-Resolution Solid-State NMR," *Bulletin of the Chemical Society of Japan*, Vol. 62 (July 1989) pp. 2429-2430.
8. L. F. Fieser and M. Fieser. *Advanced Organic Chemistry*, New York, Rheinhold Publishing Corporation. 1961.
9. G. A. Hill, and L. Kelley. *Organic Chemistry*, The Blakiston Company, Philadelphia, p. 398. 1943.
10. A. Bax and S. Subramanian. "Sensitivity Enhanced Two-Dimensional Homonuclear Shift Correlation NMR Spectroscopy," in *J. Magn. Reson.* Vol. 67, pp. 565-569 (1986).
11. A. Bax and Donald G. Davis. "MLEV-17-Based Two-Dimensional Homonuclear Magnetization Transfer Spectroscopy." in *J. Magn. Reson.* Vol. 65, pp. 355-360 (1985).