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Pyrolysis of Epoxies Used for Thermal-Battery Headers

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Pyrolysis of Epoxies Used for Thermal-Battery Headers

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Abstract

Thermally activated batteries use an epoxy for encapsulation of the electrical feedthroughs in the header of the battery. When the thermal battery is thermally abused, the encapsulant can pyrolyze and generate large internal pressures. This causes the battery to vent in extreme cases. The nature of these gases has never been adequately documented. Therefore, a study was undertaken to address this deficiency. The pyrolysis of various encapsulants that have been used, or are being considered for use, in thermally activated batteries was studied over a temperature range of 155°C to 455°C. The composition of the pyrolysis decomposition products was determined by gas chromatography/mass spectrometry (GS/MS). This determination is helpful in assessing the potential environmental and health effect for personnel exposed to such gases. In addition, the thermal stability of the various epoxies was measured by thermogravimetric analysis (TGA).

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Pyrolysis of Epoxies Used for Thermal-Battery Headers

Introduction

Many thermal batteries use an epoxy to encapsulate the header of the battery. The header is basically a stainless-steel plate that contains glass-to-metal electrical feedthroughs that provide electrical connections to the battery stack, to the electric match used to fire the battery, and to the thermal switch (monitor) used to determine whether the battery has been fired. The encapsulant is applied to the internal surface (battery side) of the header using a mold that provides the desired potting thickness. The igniter (or the percussion cap when it is used in place of the igniter) is also encapsulated in the epoxy along with the electrical leads to the battery stack. In addition to protecting the electrical feedthroughs from shock and vibration, the encapsulant supports the thermal-battery stack.

Under certain operating conditions, a thermal battery may overheat during activation or discharge. At such times, the epoxy encapsulation may also overheat. In severe cases, pyrolysis of the encapsulation can occur, which could generate a high enough pressure to cause the battery case to bulge. In extreme cases, the glass-to-metal seals rupture, venting the pyrolysis gases into the surrounding environment.

The composition of the gases that are generated during pyrolysis of the encapsulant is of interest from a health and safety perspective. While thermal batteries are being tested, personnel can be exposed to such gases should a thermal runaway occur that will cause the thermal battery to rupture its case. Initial work regarding the outgassing

products of heated epoxies has been reported by C. Mauldin at the Department of Energy's Pinellas Plant.¹ Although Mauldin's work formed the basis for this present study, it was limited to a maximum temperature of 250°C.

To better define the products of the thermal-decomposition process, various epoxy encapsulants were subjected to heating under controlled conditions at temperatures of 150°C to 445°C. We then determined the composition of the gases that were generated. This report describes the results of such tests with a number of epoxy materials that have been used (or that have been considered for use) as encapsulants for headers in thermal batteries designed at Sandia National Laboratories (SNL) for nuclear weapon applications for the Department of Energy (DOE).

Experimental Procedures

Materials

A total of five different epoxies were evaluated for this study. The first one was the primary epoxy that has been used for thermal batteries in the past. It is based on Epon 828 resin (Shell Chemical Co., Houston, TX) and is cured with Agent Z (Shell Oil Co., Houston, TX). The Epon 828 resin is a reaction product of epichlorohydrin and bisphenol-A. Agent Z contains methylenedianiline (MDA) and *m*-metaphenylenediamine (*m*-PDA). Because MDA has been classified as a suspect-carcinogen by the Occupational Safety and Health Administration (OSHA),² alternate curing agents were investigated as replacements.

The second epoxy examined was Epon 828 cured with diethyltoluenediamine (DETDA) (Ethacure 100, Ethyl Corp., Baton Rouge, LA) and salicylic acid as a catalyst. Sandia and other facilities in the DOE weapons complex have made a considerable effort to evaluate Ethacure 100 and other curing agents as a direct replacement for Agent Z. These facilities have also examined other epoxy systems.³ The physical properties of this epoxy are comparable to the physical properties of the Agent Z-cured epoxy.⁴ Unfortunately, it was subsequently discovered that the DETDA has toxicological problems similar to those found with Agent Z.⁵

The third epoxy (designated ANH2) used Epon 828 cured with hexahydrophthallic acid (HHPA) anhydride. The anhydride material was developed at SNL/NM as a replacement for the unacceptable Ethacure 100. The HHPA anhydride has none of the toxic properties associated with Ethacure 100.

Initial evaluation of the ANH2 material as a possible header encapsulant showed considerable promise.⁴

The fourth and fifth epoxies studied were based on Epon 826 resin (Shell Oil Co., Houston, TX) and Jeffamine D-230 (Texaco Chemical Co., Bellaire, TX) and Ancamine 2049 (Pacific Anchor, Chemical Corp., Los Angeles, CA) as curing agents. These epoxies are under extensive evaluation by L. Domeier of Sandia/CA as replacements for Epon 828 cured with Agent Z.⁶ The Epon 826 is similar in composition to the Epon 828; it differs only in the degree of polymerization (183 g/eq vs. 189 g/eq., respectively).

The compositions of the five epoxies studied are listed in Table 1. Alumina is added to the epoxies in a nominal ratio of 300-320 parts by weight to 100 parts by weight of epoxy, to increase the tensile strength and modulus of the encapsulants. Alumina-filled epoxies were used in all cases during this work.

Table 1. Compositions of Epoxies Evaluated in Pyrolysis Study

Ingredient	Wt. % of Ingredients
<u>Epoxy #1</u>	
Epon 828	23.81
Agent Z	4.76
Alumina	71.43
<u>Epoxy #2</u>	
Epon 828	22.4
Ethacure 100/salicylic Acid (97.47/2.53)	5.8
Alumina	71.8
<u>Epoxy #3 (ANH2)</u>	
Epon 828	11.71
HPA anhydride	9.37
NIAX 1025*	3.51
EMI 24 [#]	0.47
Alumina	74.94
<u>Epoxy #4 ("456")</u>	
Epon 826	12.50
Dow XU-71790.04	6.26
Jeffamine D-230	3.13
Ancamine 2049	3.13
Alumina	75.00
<u>Epoxy #5 ("459")</u>	
Epon 826	18.75
Jeffamine D-230	3.13
Ancamine 2049	3.13
Alumina	75.00

* Polyalkyleneoxide polyol (ARCO Chemicals, Newton Square, PA); added as a plasticizer.

2-ethyl-4-methylimidazole (Pacific Anchor, Chemical Corp., Los Angeles, CA); added as a curing catalyst.

Measurement Techniques

Gas Chromatography/Mass Spectrometry (GC/MS)

A small amount of the cured epoxy shavings were pyrolyzed using a JAI Curie-point pyrolyzer (Japan Analytical Industry Co., Japan) under a helium atmosphere. The samples were inductively heated at temperatures of 155°C, 255°C, and 445°C using ferromagnetic foils; a new sample was used for each temperature. The upper temperature for the pyrolysis experiments was established by thermogravimetric analysis of the epoxies. The analysis showed that pyrolysis was complete by 500°C in all cases. The resulting vapors were swept onto a gas chromatographic column that was ramp-heated from 50°C to 250°C to prevent condensation. The gases were then analyzed over a 45-minute period using a Perkin-Elmer gas chromatograph/mass spectrometer (Model PC8500/ITD, Norwalk, CT). Mass spectra of the outgassing products were compared with published literature data to obtain the best match.⁷⁻⁹

The gas-analysis system was calibrated by pyrolyzing a sample of polyethylene at 590°C before the epoxy samples were run. The mass spectrum showed a clear breakdown of polyethylene. A good resolution was obtained among the peaks of the decomposition products.

Thermogravimetric Analysis (TGA) TGA analysis of the epoxies was carried out using a Du Pont Model 9900. Samples of 20 mg to 50 mg were heated in ultra-pure argon (99.999%) under a flow of 50-75 cc/min from room temperature to between 700°C

and 1,000°C at a rate of 10°C/min. The resulting weight loss was then recorded. A limited number of tests were also performed under a flow of dry air.

It is important that the flow rate of gas be adequate to prevent rate limitations caused by diffusion of the gaseous reaction products from the sample into the bulk stream during pyrolysis. The flow rate was varied from 20 cc/min to 100 cc/min and a minimum value of 50 cc/min was found to be adequate to avoid diffusion limitations.

It should be noted that there is the potential for localized nonhomogeneities of the alumina filler in the epoxies because of the small sample sizes used in the TGA work. This could give rise to weight losses that are greater than theoretical under certain conditions.

Results

Thermogravimetric Analysis

The behavior of the various epoxies was studied under a flowing stream of high-purity Ar. For relative comparison, the decomposition of some epoxies was also examined under an air atmosphere.

The TGA test results for Epon 828-based epoxy cured with Agent Z (see Epoxy #1 in Table 1) and heated in flowing argon are shown in Figure 1. The major loss of weight began near 365°C and was basically complete by 500°C. The weight loss amounted to 24.3% of the sample weight at 900°C. The maximum theoretical weight loss would only be 28.57% because of the alumina filler in the epoxy.

Figure 1. Thermogravimetric Analysis of Agent-Z-Cured Epon 828 Epoxy Heated in Argon

Figure 2. Thermogravimetric Analysis of Agent-Z-Cured Epon 828 Epoxy Heated in Air

The TGA trace for the Agent Z-cured material heated in flowing air is shown in Figure 2. The onset temperature was similar to that for the sample heated in argon. However, a transition occurred at 400°C that was associated with epoxy oxidation. The oxidation process was not complete until about 550°C. The final weight loss was higher due to complete oxidation of the epoxy, which cannot occur when the material is heated in argon. The measured weight loss of 28.64% was very close to the theoretical maximum value of 28.57%.

When finely divided shavings were used in place of the small pieces in flowing air, the initiation temperature for decomposition was reduced to 250°C. The onset temperature for oxidation was reduced to 290°C, because of the higher available surface area. Thus, caution must be exercised when interpreting data where there are large differences in surface areas of the samples.

The TGA trace for the Epon 828-based epoxy cured with Ethacure 100 (see Epoxy #2, in Table 1) and heated under flowing argon is shown in Figure 3. The onset temperature for pyrolysis was the same as that for the Agent Z-cured epoxy. The overall weight loss was 26.95% at 700°C. (The maximum theoretical weight loss is 28.2%.) Pyrolysis was complete by ~ 500°C.

When heated in flowing air, the Ethacure 100-cured epoxy was completely oxidized by 550°C and showed the same type of oxidation transition as did the Agent Z-cured epoxy.

The TGA curve for pyrolysis of the AHN2 epoxy (see Epoxy #3, in Table 1) under flowing argon is shown in Figure 4. The onset temperature for pyrolysis (369°C) was

comparable to those for the Epon 828 epoxies cured with Agent Z (Figure 1) or Ethacure 100 (Figure 3). Pyrolysis was complete by 500°C and the overall weight loss was 25% at 900°C. This is very close to the maximum theoretical weight loss of 25.06%, which suggests complete decomposition and volatilization took place. (No oxidation tests were conducted with this epoxy.)

The TGA curve for pyrolysis of the so-called "456" epoxy (see Epoxy #5, in Table 1) under flowing argon is shown in Figure 5. This material is based on Epon 826, instead of Epon 828, resin. (These materials are very similar and only differ in the extent of polymerization.) The material exhibited an onset temperature of 351°C that is somewhat lower than that of the Epon 828-based epoxies studied. Pyrolysis was complete by 500°C, which is comparable to that for the Epon 828-based epoxies. The weight loss at 700°C was 23.9%, which is less than the maximum theoretical value of 25%. (No oxidation tests were conducted with this epoxy.)

The TGA curve for pyrolysis of the so-called "459" epoxy (see Epoxy #6, in Table 1) under flowing argon is shown in Figure 6. In this case, the onset temperature of decomposition was 356°C, which is slightly higher than that for the "456" epoxy. The temperature at which pyrolysis was complete, however, was the same. The weight loss at 700°C was 23.5%, which is less than the maximum theoretical value of 25%. (No oxidation tests were conducted with this epoxy.)

Structure of Epoxy Constituents.

The structure of the constituents that make up the various epoxies can have a significant effect on the nature of the decomposition products during pyrolysis. To help elucidate the source(s) of the various pyrolysis products, the molecular

10 deg. C/min; 75 cc/min Ar flow

Figure 3. Thermogravimetric Analysis of DETDA-Cured Epon 828 Epoxy Heated in Argon

10 deg. C/min; 75 cc/min Ar flow

Figure 4. Thermogravimetric Analysis of AHN2 Epoxy Heated in Argon

Figure 5. Thermogravimetric Analysis of "456" Epon 826-Based-Epoxy Heated in Argon

Figure 6. Thermogravimetric Analysis of "459" Epon 826-Based Epoxy Heated in Argon

structure of the various organics in the epoxies are listed in Appendix A. The structures of the various decomposition products are listed in Appendix B

Pyrolysis Experiments: Heating at 150°C

MDA-Cured Epoxy. A typical mass chromatogram (relative ion intensity vs. scan number) for Agent Z-cured epoxy heated at 150°C is shown in Figure 7. Most of the outgassing was associated with peaks between scans 800 and 1700. The mass spectra of the large peaks at approximately scan 1000 are consistent with the other triplet peaks associated with polymer fragmentation (e.g., scans 1120 to 1150 and 1320 to 1370).

DETDA-Cured Epoxy. The outgassing results of heating the Ethacure 100-cured epoxy at 150°C were very similar to those of Agent Z-cured epoxy.

ANH2 Epoxy. The outgassing mass chromatogram of the ANH2 epoxy was considerably different than those for the MDA-cured and DETDA-cured epoxies (see Figure 8). The ANH2 epoxy appeared to outgas only one major component. The large peak around scan 750 most closely resembles N,N, N', N' tetramethylmethanediamine.⁷⁻⁹ (See Appendix B for the structure of this material.)

Extraction of data for the mass peak based on a mass/charge (M/e) ratio of 71 is shown in Figure 9a. The corresponding mass spectrum for N,N,N',N'-tetramethylmethanediamine is shown in Figure 9b. The good match would indicate that N,N,N',N'-tetramethylmethanediamine is the major likely component of the outgassing process

at 150°C, along with other unidentified species.

456 Epoxy. The outgassing mass chromatogram for the 456 epoxy heated at 150°C is shown in Figure 10. It is similar to the mass chromatogram for the Epon 828-based epoxies, in terms of the peaks between scans 500 and 2000. There were also several other prominent peaks between scans 3300 and 4100.

459 Epoxy. The outgassing mass chromatogram for the 459 epoxy heated under the same conditions is shown in Figure 11. The mass chromatogram is very similar to that of the 456-cured epoxy except that the peaks above scan 1000 are absent.

It should be emphasized that the amount of gas that evolved at 150°C under these conditions was relatively small for all of the epoxies. Typically, signals over ~5,000 counts are considered significant, while counts <5,000 are associated with trace components. The peaks associated with the low (<5,000) counts would barely be above the normal background signal.

Pyrolysis Experiments: Heating at 255°C

MDA-Cured Epoxy. The mass chromatogram for the Agent Z-cured epoxy heated at 255°C is shown in Figure 12. The amount of outgassing, while measurable, was still not very large. The mass spectrum at 255°C is quite similar to that at 150°C (see Figure 7), which indicates that the outgassing process was similar at both temperatures. In other words, the epoxy is relatively thermally stable to 255°C.

Figure 7. Mass Chromatogram for Agent Z-Cured Epon 828 Epoxy Heated at 150°C in Helium

Figure 8. Mass Chromatogram for ANH2 Epoxy Heated at 150°C in Helium

9. Mass Spectra for Mass/Charge Ratio of 71

a From Mass Chromatogram of ANH2 Epoxy Heated at 150°C in Helium

b Mass Spectrum for N,N,N',N'-Tetramethylmethanediamine

Figure 10. Mass Chromatogram for 456 Epon 826-Based Epoxy Heated at 150°C in Helium

Figure 11. Mass Chromatogram for 459 Epon 826-Based Epoxy Heated at 150°C in Helium

Figure 12. Mass Chromatogram for Agent Z-Cured Epon 828-Based Epoxy Heated at 255°C in Helium

Extraction of data for the major peak based at a M/e ratio of 65 is shown in Figure 13a; see 13b for the corresponding mass spectrum for phenol. The good match indicates that phenol is probably the major component of the outgassing process at 255°C.

DETDA-Cured Epoxy. The corresponding mass chromatogram for the Ethacure 100-cured epoxy heated at 255°C is shown in Figure 14. Peak extraction and analysis results were quite similar to those observed for the Agent Z-cured epoxy heated under the same conditions.

ANH2 Epoxy. The mass chromatogram for the ANH2 epoxy heated at 255°C is shown

in Figure 15. The mass spectrum at 255°C shows an increase in overall outgassing, as well as an increase in outgassing of fragments of higher molecular weight between scans 2000 to 4000, relative to the mass chromatogram at 150°C (see Figure 8). The epoxy does not appear to be breaking down, but may be outgassing polymer fragments remaining as a result of incomplete polymerization during curing. (This is consistent with aging data on this material, where the tensile strength actually increased after heating at 130°C for one month. The Agent Z-cured epoxy showed a reduction in tensile strength under these same conditions.¹⁰)

13 Mass Spectra for Mass/Charge Ratio of 65

a From Mass Chromatogram for Agent Z-Cured Epon 828-Based Epoxy Heated at 255°C in Helium

b Mass Spectrum for Phenol

Scan Range: 1 - 2400 Scan: 1 Int = 407 @ 0:00 100% = 34888

Figure 14. Mass Chromatogram of DETDA-Cured -Epon 828-Based Epoxy Heated at 255°C in Helium

Scan No: 5858 Retention Time: 84:11 RIC: 6773 Mass Range: 35 - 355
Plotted: 1 to 5858 Range: 1 to 5858 100% = 631493

Figure 15. Mass Chromatogram for ANH2 Epoxy Heated at 255°C in Helium

456 Epoxy. The mass chromatogram for the 456 epoxy heated at 255°C is shown in Figure 16. While the amount of outgassing was greater than that for the sample heated at 150°C, the amount of degradation was insignificant at these temperatures. This is shown by the lack of major peaks at scans above 1500. The major outgassing product was phenol, as noted with the other epoxies under these conditions. The new peaks between scans 400 and 1200 include alkanes and polymer fragments in addition to phenol (at scan 475). These may be related to incomplete polymerization during curing.

459 Epoxy. For the mass chromatogram for the 459 epoxy heated at 255°C see Figure 17. It is quite similar to the mass chromatogram of the 456 epoxy and shows the same temperature trends in its spectra.

Pyrolysis Experiments: Heating at 455°C

MDA-Cured Epoxy. The mass chromatogram for the Agent Z-cured epoxy heated at

455°C is shown in Figure 18. The small number of peaks from scans 0 to 400 are associated with low-molecular-weight hydrocarbons. Note that there are a large number of peaks between scans 500 and 900 that were not present for the lower-temperature scans (see Figures 7 and 12). This shows that a decomposition threshold was crossed between 255°C and 455°C. This is consistent with the TGA data for this material that showed that the major weight loss occurred between 350°C and 450°C (see Figure 1).

Extraction of data for the major peak based at a M/e ratio of 94 (scan 507) is shown in Figure 19a. The corresponding mass spectrum for phenol is shown in Figure 19b. The good match indicates that phenol is the major component of pyrolysis at 455°C.

The corresponding mass-spectra data for the pyrolysis are summarized in Table 2 for the significant peaks.

Table 2. Summary of Mass-Spectra Data for Agent Z-Cured Epoxy Heated at 455°C Under Helium

Mass/Charge Ratio	Species
<70	Low-molecular-weight CH _x
77	4-ethyl-2-methylphenol
91	(1,1-dimethylethyl)-benzene
94	phenol (major) (C ₆ H ₆ O)
108	2-methylphenol (C ₇ H ₈ O)
121	4 (1-methylethyl)-phenol (C ₉ H ₁₂ O)
	3-(1-methylethyl)-phenol (C ₉ H ₁₂ O)
134	2-(2-propenyl) phenol (C ₉ H ₁₀ O)
	1,2,3,5-tetramethylbenzene (C ₁₀ H ₁₄)
	2,3-dihydro-2-methylbenzofuran (C ₉ H ₁₀ O)
164	N,N,N',N'-tetramethyl-1,4-benzenediamine (C ₁₀ H ₁₆ N ₂)

Figure 16. Mass Chromatogram for 456 Epon 826-Based Epoxy Heated at 255°C in Helium

Figure 17. Mass Chromatogram for 459 Epon 826-Based Epoxy Heated at 255°C in Helium

Scan No: 11400 Retention Time: 198:01 RIC: 350 Mass Range: 50 - 639
 Plotted: 1 to 11400 Range: 1 to 11400 100% = 1500574

Figure 18. Mass Chromatogram for Agent Z-cured Epoxy Heated at 455°C in Helium

Figure 19. Mass Spectrum for Mass/Charge Ratio of 94

- a From Mass Chromatogram for Agent Z-Cured Epon 828-Based Epoxy Heated at 455°C in Helium
- b Mass Spectrum for Phenol

During pyrolysis, the bonds in the epoxy are broken, which results in the formation of compounds with smaller molecular weights. The major decomposition product occurring under these conditions was phenol, which is associated with the large peak at scan 500 (see Figure 18). The mass-spectra data for the other decomposition products are consistent with phenol derivatives, some long-chain alcohols, and polymer fragments (substituted aromatics).

DETDA-Cured Epoxy. The mass chromatogram for the Ethacure 100-cured epoxy heated at 455°C is shown in Figure 20. Analysis of the mass spectrum showed most of the species generated during pyrolysis could be associated with M/e values of 77, 91, 94, 108, and 134. This is very similar to the data obtained for the Agent Z-cured epoxy heated under the same conditions (see Table 2). Phenol was again the major decomposition product.

ANH2 Epoxy. The outgassing mass chromatogram of the ANH2 epoxy heated at 455°C is shown in Figure 21. Analysis of the mass/charge data show that the decomposition products were very similar to those

observed during pyrolysis of the Agent Z-cured and Ethacure 100-cured epoxies. These data suggest that the Epon 828 resin, which is common to these epoxies, is more important than the curing agent with respect to pyrolysis products.

456 Epoxy. The outgassing mass chromatogram of the 456 epoxy heated at 455°C is shown in Figure 22. Major decomposition is evident by the large increase in the ion current for the major peaks at scans <600 and the appearance of new peaks at scans >1500. A thermal decomposition threshold is crossed between 255°C and 455°C. This is consistent with the TGA trace for this material (see Figure 5). As for the other epoxies, the major decomposition species were phenol (at scan 475), along with phenol derivatives, some long-chain alcohols, and various polymer fragments.

459 Epoxy. The outgassing mass chromatogram of the 459 epoxy heated at 455°C is shown in Figure 23. It exhibits many of the same features of the mass chromatogram for the 456 epoxy, but with a higher concentration of peaks associated with polymer fragments at scans >1500.

Scan Range: 1 - 1800 Scan: 1 Int = 314 100% = 476071

Figure 20. Mass Chromatogram for 456 Epon 826-Based Epoxy Heated at 455°C in Helium

Scan No: 4935 Retention Time: 82:16 RIC: 70639 Mass Range: 35 - 504
Plotted: 1 to 4935 Range: 1 to 4935 100% = 1203666

Figure 21. Mass Chromatogram for ANH2 Epoxy Heated at 455°C in Helium

Scan No: 9000 Retention Time: 150:01 RIC: 14 Mass Range: 74 - 277
Plotted: 1 to 9000 Range: 1 to 9000 100% = 58470

Figure 22. Mass Chromatogram for 456 Epon 826-Based Epoxy Heated at 455°C in Helium

Scan No: 9000 Retention Time: 150:01 RIC: 1226 Mass Range: 35 - 348
Plotted: 1 to 9000 Range: 1 to 9000 100% = 63015

Figure 23. Mass Chromatogram for 459 Epon 826-Based Epoxy Heated at 455°C in Helium

Discussion

Pinellas Data

The species reported by Mauldin for the same Agent Z-cured and Ethacure 100-cured Epon 828 epoxies heated at 200°C and 250°C are summarized in Table 3. (Except for phenol, the ranking of species is not necessarily in order of abundance.)

The data generated in the Pinellas study were obtained under prolonged heating (one to two hours). The data in the present study were generated after heating for only 4 s, to avoid degradation of the outgassed compounds. The same types of organics listed below were observed over the same temperature range for both the Pinellas study and the present study:

- phenol
- substituted phenols
- various substituted aromatics.

Origin of Outgassing Species

The composition of the gases generated during heating of the various epoxies did not change dramatically as the curing agent was varied, except for the AHN2 epoxy--and that appeared to be associated with incomplete curing. This indicates that the bulk of the

decomposition products are associated with the Epon 828 and Epon 826 resins which were used for all three epoxies; i.e., the curing agent did not contribute significantly to the major pyrolysis reactions.

This becomes somewhat clearer when one examines the chemical structures of the various ingredients used in the formulation of the epoxies (Appendix A). The only difference between Epon 828 and Epon 826 resins is in the degree of polymerization (i.e., the value of n in the formula shown in Appendix A). Both have a high degree of aromatic character. The phenol and various substituted phenols could readily be derived from fragmentation of the basic polymer structure.

In the case of the amine-type curing agents, MDA and DETDA are also aromatic in character. This contrasts to the aliphatic nature of the Jeffamine and the cycloaliphatic structure of Ancamine curing amines. The HHPA anhydride curing agent, in comparison, contains carboxylic constituents instead of amine groups that react during curing.

The final polymerized material will be somewhat different for the various curing agents and resins. The outgassing data, however, suggest that the structure of the base resin dominates the pyrolysis reactions.

Table 3. Summary of Species Identified During Heating of Agent Z-Cured and DETDA-Cured Epon 828 Epoxies at Pinellas Plant¹

Curing Agent	Temperature, °C	Species
MDA	200/1 h	phenol
DETD	200/1h	phenol
MDA	250/2 h	phenol 2-propenol N,N-dimethyl-benzeneamine, 4-(1-methylethyl) phenol 4,4'-(1-methyl ethylidene) bisphenol aromatic hydrocarbons
DETD	250/2 h	phenol benzene methyl benzene 2-methyl phenol 2-ethyl phenol 2-(2-propenyl) phenol 4-(1-methyl-ethyl) phenol 1-(1,1-dimethyl ethyl) 3-ethyl-5-methyl benzene bisphenol A aromatic hydrocarbons

Environmental/Safety Aspects

The high aromatic content of the gases generated during pyrolysis of all the epoxies would suggest that they are very likely to be carcinogens or suspect carcinogens. Consequently, all necessary precautions should be taken while testing thermal batteries that employ these materials as encapsulants. These precautions will prevent or minimize exposure of test personnel to such gases should battery rupture occur. This can be achieved by testing the batteries in "boom

boxes" that are vented under negative pressure to a hood or other suitable ventilation system.

Alternatively, the "boom box" or test fixture can be connected to a negative-pressure system (e.g., a vacuum cleaner) that vents to the atmosphere after passing through a bed of activated charcoal and a HEPA filter. The efficacy of such a system should be verified prior to use under actual test conditions and with the concurrence of the appropriate personnel from industrial hygiene or its equivalent.

Conclusions

Outgassing studies have been conducted with five different potential encapsulants for thermal-battery headers. The epoxies were based on Epon 828 and 826 resins and were cured with MDA, DETDA, HHPA anhydride, and mixtures of Jeffamine and Anca-mine. Very little outgassing occurs at a temperature up to 255°C, which indicates the epoxies are basically thermally stable up to this temperature. The primary compound observed for all epoxies under these conditions is phenol. Some fragments from uncured epoxy were observed for the ANH2 epoxy.

The GC/MS data indicate that significant pyrolysis begins at temperatures between 350°C and 450°C for all the epoxies examined. These data are corroborated by the TGA data. Pyrolysis is complete near 500°C. Of all the epoxies studied, only the ANH2 material shows complete decomposition and volatilization during pyrolysis. The remaining epoxies produce residual char. When heated in air, the Agent Z-cured and Ethacure 100-cured epoxies show incipient oxidation near 400°C, with oxidation being complete by 550°C.

At the highest temperature of 455°C in the study, major pyrolysis of the epoxies occurs. The primary decomposition products are:

- phenol
- substituted phenols
- long-chain alcohols
- various substituted aromatics.

Because of the toxic nature of the pyrolysis products, personnel exposure to such materials should be minimized to the extent possible in the event of a thermal runaway

and venting of the thermal battery during testing.

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Appendix A. Structures of Epoxy Constituents

Bis A Epoxy

Basic structure of Epon 826 and Epon 828, differing only in n .
 XU-71790 is a bis A epoxy containing 40% acrylic modifiers.

DETDA
(Ethacure 100)

MDA
(Shell Z)

m-PDA

NIAX 1025

EMI 24

2-ethyl-4-methylimidazole

HHPA

hexahydrophthalic acid anhydride

Jeffamine D-230

Ancamine 2049

Appendix B. Structure of Pyrolysis Products

benzene (C_6H_6)

toluene (C_7H_8)

1,2,3,5-tetramethylbenzene ($C_{10}H_{10}$)

(1,1-dimethylethyl)-benzene ($C_{10}H_{14}$)

2,3-dihydro-2-methylbenzofuran ($C_9H_{10}O$)

N,N,N',N'-tetramethyl-1,4-benzenediamine
($C_{10}H_{16}N_2$)

phenol (C_6H_5OH)

2-methylphenol (C_7H_8O)

4-ethyl-2-methylphenol ($C_9H_{12}O$)

4-(1-methylethyl)-phenol ($C_9H_{12}O$)

3-(1-methylethyl)-phenol ($C_9H_{12}O$)

2-(2-propenyl)-phenol ($C_9H_{10}O$)

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