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LOW DENSITY EPOXY ENCAPSULANTS

PDO 6984764, Final Report

J. M. Walker, Project Leader

Project Team:
J. M. Conway
H. M. McIlroy
W. E. Richardson
J. W. Steele

Published August 1976

MASTER

Prepared for the United States Energy
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Bendix Kansas City Division

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Technical Communications **Bendix** **Kansas City Division**

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Prepared by J. M. Walker, D/814, under PDO 6984764

The resin, catalyst, and filler of an epoxy-hollow glass microsphere encapsulant were evaluated to solve problems associated with encapsulated electronic assemblies and an alternate source of hollow glass microspheres was selected. Specific problems related to the use of this encapsulant are discussed. The results of attempts to modify the blowing agent of an epoxy foam are also included.

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A prime contractor for the United States Energy Research and Development Administration
Contract Number E(29-1)-613 USERDA

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SUMMARY

This investigation was initiated to improve the epoxy resin-hollow glass microsphere encapsulant, solve problems associated with encapsulated electronic assemblies, and develop a backup material for Ablefoam 5 (Ablestick Corporation).

In order to determine where improvements were needed in the epoxy resin-hollow glass microsphere encapsulant, the resin, catalyst, and filler were evaluated using the acceptance tests called out by their respective Materials Standards.

The resin and catalyst supplied by manufacturers were checked to Material Standard 2140045 for the resin and MS 4604020 for the catalyst. Other tests, including gel time, were also performed. Analysis of the test data obtained on the resin indicated that MS 2140045 is still selective and capable of screening out unacceptable material from the various suppliers. MS 4604020 was revised to exclude some suppliers since they could not meet the material requirements and to include the use of gas chromatography in analyzing the catalyst's components. Some modifications in the allowable composition of the catalyst were also made.

In conjunction with the analysis of Type B40A glass bubbles (GMB) from the 3M Company both Type I and Type II glass microballoons (GMB) from Emerson & Cuming (E&C) were analyzed as a reference. Many of the tests were based on MS 6090009 and Processing Standard 9927003. These standards are intended primarily for use with the E&C GMB but were used for the 3M bubbles since very little difference in behavior was expected. From the tests on the Type B40A GMB as a free flowing powder it was observed that the filler was uniformly smaller, had a lower bulk density and alkalinity, and was substantially freer of broken and unblown particles than either type of E&C GMB. Also the Type B40A GMB exhibited no measurable tendency to form insoluble agglomerates in the presence of moisture. Primarily because of the reduced particle size and relative immunity to moisture, Materials Standard 6090015 was written especially for the 3M Type B40A GMB.

A 75/25 resin/GMB formulation was chosen for evaluation since it corresponded to a 50 percent by volume filler loading and because it was the same formulation used for the E&C Type II GMB. The viscosity of the new mix also paralleled the Type II mix.

A complete set of physical properties: mechanical, electrical, and thermal was obtained to provide design information and a

comparison with available data on E&C GMB. These data indicate that the 3M GMB may be slightly better for this particular application than the E&C GMB but does not reflect on the overall quality of either material.

The problem solving phase of the study consisted of checking the cure cycle, exotherm, reduction of voids, resin-filler separation, and thermal shock behavior for the GMB encapsulant. Either a 16-hour 150°F (66°C) cure in the mold followed by a 4-hour 150°F (66°C) post cure after demolding or 20 hours at 150°F (66°C) in the mold was shown to provide complete cure.

The exotherm of the encapsulant was shown to be mass dependent. In masses of approximately 2500 grams the exotherm temperature reached 260°F (127°C) and, if prolonged, could damage thermally sensitive electronic components. The tests indicate that exotherm can be minimized by controlling the encapsulant mass and by delaying the oven cure until after the initial exotherm has subsided.

The three principal sources of voids are air bubbles that become trapped under components or printed circuit boards, outgassing from components and coatings, and shrinkage. The data show that these voids can be reduced by designing assemblies to eliminate mechanical traps, maintaining uniform mold temperature in all phases of the encapsulation process, minimizing the amount of encapsulant in mold reservoirs, vacuum filling of the mold, and pressurized cure.

Resin-filler separation is caused by the low density GMB floating in the higher density resin. In the old encapsulant the problem was obscured by the broken and unblown particles that settled out of the mix. The resin rich layers are harmful because they create areas of localized stress during thermal cycling and can damage leads and solder joints. By delaying the cure for 2 hours at room temperature it was possible to reduce the resin rich layer to acceptable levels.

Thermal shock testing consisted of evaluating the existing thermal shock tests and trying to develop one that would quantize the thermal shock resistance of various encapsulants. Tests were performed using the Quant hollow cylinder,[1] Navy hex bar (Mil-I-16923F), Olyphant and Sato washer tests,[2,3] and the Miron wedge test.[4] None were successful in this particular application although they were successful when used on unfilled resin. A test was developed by Bendix Kansas City that should have provided the desired quantization; however, the thermal shock failures observed using this test were random in nature and not sufficiently reproducible.

A low density, blown epoxy has been developed by modifying the Capoxy I foam system developed at Bendix Kansas City. Designated Frefoam II, this new foam may prove to be an acceptable alternative to Ablefoam 5 in electronic applications.

DISCUSSION

SCOPE AND PURPOSE

This work was done under PDO 6984764, Low Density Encapsulation Material, the objectives of which were to evaluate low density materials used for encapsulating electronic assemblies, determine alternatives to existing materials, and to study specific problems associated with low density encapsulants. The purpose of this investigation was threefold, improve or upgrade the present epoxy resin-hollow glass microsphere encapsulant, develop a backup material for Ablefoam 5, and seek solutions to the problems commonly associated with encapsulated electronic assemblies. The first phase of the investigation included reevaluating the resin, catalyst, and filler used in the epoxy resin-hollow glass microspheres encapsulant and obtaining a new source of the hollow glass microsphere filler. The second phase consisted of an in-depth analysis of the problems that plague encapsulated systems such as shrinkage, air voids, and cracks due to thermal cycling. The improved resin-glass microspheres system developed in the first phase was used in this portion of the project. The final portion of the investigation consisted of modifying an existing epoxy foam premix developed by Bendix Kansas City so that a second source of foam encapsulant would be available.

ACTIVITY

Improved (Low Density) Epoxy-Hollow Glass Microsphere Encapsulant

Fourteen years ago, Sandia Laboratory, Albuquerque, developed a low density encapsulant consisting of a mixture of hollow glass microspheres (GMB) in an amine catalyzed epoxy resin matrix. The encapsulant was designed to protect delicate electrical assemblies from external interferences such as thermal and mechanical shock and vibration. The system performed well and has been used extensively. However, it has become increasingly difficult to process the GMB-epoxy material. Many of the current processing problems have been attributed to changes in the resin, catalyst, and filler that make up the potting compound. The most obvious changes have occurred in the filler, changes which have caused alterations in the resin-filler mix ratio due to widely divergent filler densities. Before total responsibility could be assigned to the filler, all three materials were completely reevaluated according to their respective materials standards.

Epoxy Resin Evaluation

The general purpose epoxy resin used in making the epoxy-GMB encapsulant is defined by MS 2140045 and can be any one of four: Araldite 6010 (Ciba Products), Epi Rez 510 Special 8E (Celanese Resin), Epon 828 (Shell Chemical), or ERL 2774 (Union Carbide). The other three resins covered by the specification were not used at Bendix because of several requirements, not related to design intent, that apply only to Bendix and its suppliers and subcontractors. One of the three, DER 331 (Dow Chemical) was included in this evaluation as a check on the special Bendix requirements. Of the five resins selected for study only the Epon 828 and Epi Rez 510 were purchased to MS 2140045 requirements so it was anticipated that these two would conform to that standard in every respect whereas the other three might not. Three tests were performed on each resin using a single lot of catalyst from Jefferson Chemical Company, reactivity (exotherm as a function of time after catalyst addition), gel time, and pot life viscosity. In MS 2140045, reactivity is defined as the time elapsed from the combination of hardener and resin until the maximum exothermic temperature is reached. The required reactivity value in this case is 100 to 200 minutes. Analysis of the test data reveals two exotherm peaks instead of one. The first peak is the highest, reaching 225° to 237°F (107° to 114.2°C) in only 5.9 to 7.1 minutes. The second peak reaches 190° to 206°F (88° to 96.6°C) in 107 to 153 minutes. The second peak in all probability is the one specified by the materials standard because of the time interval and despite the lower peak temperature. All five resins fit easily into the 100 to 200 minute reactivity requirement although they tend toward the low side of the range.

Pot life viscosity values are obtained by measuring the viscosity of catalyzed resin that has been held in a constant temperature bath for a specified period of time. For these resins, the requirement is 1400 to 4000 centipoise (1.4 to 4.0 Pa·s) after 60 minutes and is generally indicative of the amount of processing time available for a material. Since the GMB filler will increase the viscosity of the mixture substantially, values on the low side of this range would seem most desirable. Only Epi Rez 510 and Epon 828 had acceptable viscosities. DER 331 and ERL 2774 were too fluid and Araldite 6010 was not fluid enough. These failures in no way reflect on the quality of the resins involved but merely reinforce the value of pot life as a test. Those three resins, had they been purchased according to the materials standard and pentagon M requirements, should have passed this test.

Gel time is the time required for a catalyzed material to gel. Gel times for each resin were obtained by using a Tecam gelation timer (Techne Incorporated) equipped with a 0.875-inch-diameter (22.2 mm) disposable glass rod. The plunger is moved up and down in the catalyzed resin which is held at constant temperature until the material has gelled sufficiently to support it. At this point, the timing clock stops automatically. Gel time relates to pot life since it reflects the viscosity of the catalyzed resin. For these resins gelation time also relates to reactivity since all five gel within 10 minutes after the maximum exotherm temperature is reached. Gel time is not a test required by the materials standard. It was used to help establish the validity of the other two tests. The test data indicate any resin listed, if purchased to MS 2140045 and meeting the Bendix requirements, would be acceptable. A slight decrease in reactivity and viscosity may have occurred but these changes are not sufficient to result in widely divergent behavior by the cured material.

Catalyst Evaluation

Since the resin had remained reasonably stable, the next step was to evaluate the catalyst, diethanolamine (DEA). As with the resin, the purpose was to compare past and present performance. Issue P of MS 4604020 listed six sources of DEA: Union Carbide Corporation, Jefferson Chemical Company, Dow Chemical Company, Allied Chemical Corporation, Olin-Mathieson Chemical Corporation, and Furane Plastics. Of the six only DEA from Allied Chemical Corporation was not tested. Since DEA from Jefferson was currently being used in production areas and in the laboratory, samples from four different lots of their material were analyzed. As a result, eight different samples of material were evaluated for monoethanolamine (MEA), DEA, triethanolamine (TEA), and water content.

The minimum allowable diethanolamine content at that time was 97 percent by weight and the maximum water content was 0.20 percent by weight. The MEA and TEA are naturally occurring impurities. DEA content was obtained by a wet chemistry technique developed at Bendix. However, since Issue P was written, Bendix had obtained gas chromatography (GC) equipment and the eight samples were tested using the more recent technology. The wet method was also used as a check. The results are given in Table 1. The investigation was essential since the results obtained using GC clearly indicated that all lots of the Jefferson DEA could not meet the requirements of the materials standard while the wet method results indicated acceptable material.

Wet chemical test methods determined total alkalinity, total primary amines, total tertiary amines, and total secondary amines by difference. Consequently, the wet methods are unable to determine purity or the exact percentage of any individual component that may or may not be present. Even with the gas chromatograph, direct analysis is difficult because of the strong hydrogen bonding in the ethanolamines. Analysis of the DEA by

Table 1. Analysis of DEA Components

Trial	Catalyst Manufacturer	Lot Number	Method	MEA (pbw)	DEA (pbw)	TEA (pbw)	H_2O (pbw)
1	Jefferson	OZ25	GC*	5.36	92.59	1.13	0.92
2	Jefferson	1H-473 CHS-467	GC	2.88	96.65	0.29	0.18
3	Jefferson	1H-473 CHS-467	Wet**	0.16	99.14	0.52	
4	Jefferson	OZ50	GC	4.07	94.88	0.61	0.44
5	Jefferson	OZ50	Wet	2.45	96.04	1.07	
6	Furane	IF42	GC	2.93	96.25	0.68	0.09
7	Furane		GC	1.11	97.79	0.78	0.33
8	Furane		Wet	1.58	96.84	1.25	
9	Union Carbide		GC	0.03	99.27	0.34	0.36
10	Union Carbide		Wet	0.24	98.66	0.74	
11	Dow	TBO 4201-D12B	GC	0.50	98.08	0.77	0.65
12	Dow	TBO 4201-D12B	Wet	0.00	98.07	1.29	
13	Olin		GC	0.20	99.67	0.00	0.13
14		MS 4604020 Issue P	Wet		97.00		0.20

*Gas Chromatography

**Wet Chemistry

GC involved the conversion of the hydroxylamines to their trifluoroacetal (TFA) derivatives by reaction with trifluoroacetic anhydride (TFAA). The major advantage of the GC is that if a peak appears at the same time as the standard mix the identity of the component is certain whereas the wet methods are nonselective and respond to any primary, secondary, or tertiary amine. As a result of this information and the GC data, the decision was made to remove Jefferson DEA from the production area until further information could be received. The Jefferson material did not meet the specification but the effect of the failure on the filled epoxy was not known. Using Epi Rez 510 as the resin, reactivity information was obtained on the various catalysts. Then pure samples of MEA and TEA were obtained from Jefferson and added in varying quantities to the Union Carbide DEA since it has the highest DEA content of all the samples tested. Figure 1 represents the reactivity curves obtained from the pure materials.

No clear-cut distinction could be made between the catalysts from the reactivity data obtained. None of the reactivities were out of specification in any manner although they all tended toward the low side of the acceptable range. Addition of various concentrations of MEA and TEA did have a marked effect but only when much larger quantities than that present in the questionable Jefferson DEA were used. Increasing the amount of MEA shortens the time to first peak, increases the first peak temperature, increases the time to second peak, decreases the second peak temperature, and shortens the time to gelation.

Excess TEA up to the 10 percent level has little effect on the first peak time and temperature. The second peak time is considerably shortened, though, and the second peak temperature appears to increase. The relationship between the MEA and TEA as impurities and the exotherm temperature can be better shown by Figure 1. It is important to remember, however, that reactivity data are based on 100 gram batch sizes and probably cannot be transposed to apply to larger sample sizes. The information is useful because it indicates the importance of having some control over the purity of the DEA. As a result of the various tests and the recognized acceptability of the gas chromatograph, the minimum allowable level of impurities was decreased.

Filler Evaluation

Both the catalyst and resin evaluations may be regarded as preliminary to the major function of this portion of the study. Before the microsphere work could be performed it was necessary to establish the uniformity and reliability of the resin and catalyst. In

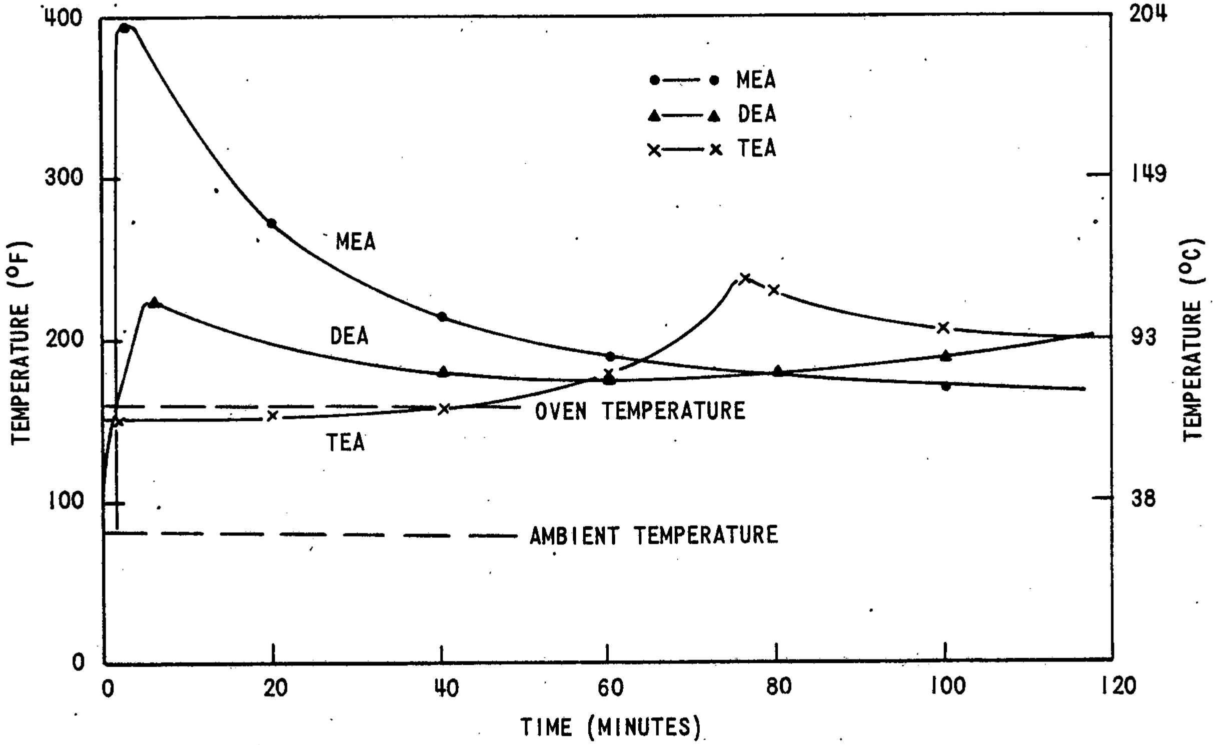


Figure 1. Reactivity for Pure MEA, DEA, and TEA in Epoxy Resin

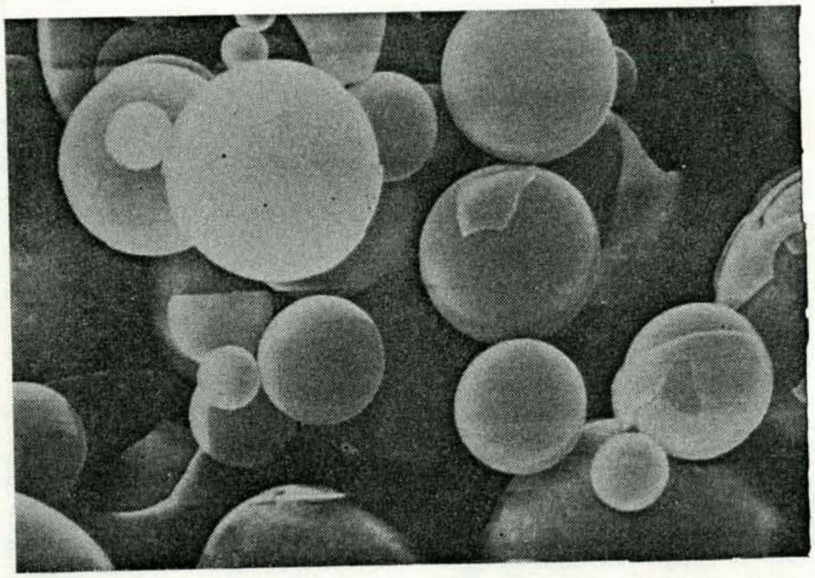
this manner the basic soundness of both materials standards was also reinforced. The changes made in the DEA specification were the result of advanced technology, unavailable when the specification was last revised and should be considered not as errors, but as a logical step in maintaining the accuracy and quality of the materials standards.

With examination of the resin and catalyst virtually complete the final step was to compare the existing filler, E&C Types I and II GMB, with any that might be suitable substitutes. Selected for intensive study were type B40A glass bubbles from 3M Company which are also called GMB. These GMB were selected because they had the highest average particle density available, they exhibited very little tendency to float or settle during cure in a resin matrix, and a 50 percent by volume loading required the same resin/GMB/catalyst ratio of 75/25/9 as the E&C Type II. With the same resin/GMB ratio a direct substitution of 3M GMB could be made in production with very little difficulty. Using MS 6090009, which directly applied to the E&C GMB as a guide, the following tests were performed as a preliminary comparison: scanning electron photographs, sieve analysis, water content, particle density by toluene displacement, micromerograph before and after tumbling, alkalinity (Process Specification 9981001), and ratio of floaters to sinkers.

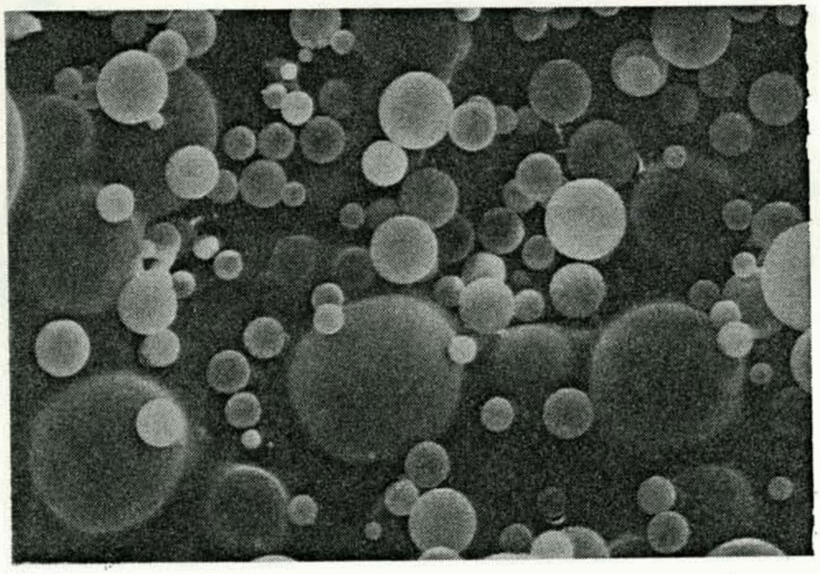
Scanning electron photographs were taken to provide a visual inspection of the GMB. Figure 2 shows two of the pictures that were taken. Both pictures were taken at 300 power magnification and from them it is possible to compare the relative size and quality of the GMB. The 3M GMB are smaller and appear to have somewhat fewer broken and unblown GMB. Table 2 shows the results from the other tests. The size differential was a problem with respect to Materials Standard 6090000 which states that "no less than 20 percent nor more than 60 percent by weight of filler shall pass through a 200 mesh sieve." The larger E&C GMB meet this requirement, but virtually all of the 3M GMB are smaller than 200 mesh. In addition, the material standard gives an allowable particle density range of 390 to 440 kg/m^3 for Type II GMB and 440 to 500 kg/m^3 for Type I GMB. The 3M particle density range is specified by 3M as 350 to 400 kg/m^3 which is lower overall than either allowed range. At this point it was decided that in the event a 3M material was selected a new material standard would be required.

Both the 3M and E&C GMB meet the material standard requirement of 0.2 percent or less water content (Table 2) and it might be expected that both would respond equally to moisture. Unfortunately this is not the case since the E&C GMB are hydrophillic and tend to absorb moisture on exposure to the atmosphere and form insoluble agglomerates. To prevent this the E&C GMB must be packed with desiccant in two layers of polyethylene. In contrast, exposure to moisture has little or no effect on the pourability of the 3M GMB and the previously mentioned precautions seem unnecessary. Excessive alkalinity was postulated as a possible cause of the unexpected difference in moisture response. An alkalinity maximum of 2000 milliequivalents per pound (4.63 meq/g) had originally been written into the specifications. However, subsequent revisions had eliminated the alkalinity requirement. From the alkalinity data in Table 2 it is apparent that the difference in alkalinity between 3M and E&C GMB is substantial.

A comparison of the production methods of 3M and E&C provide some insight into the wide difference in alkalinity. Emerson and Cuming prepare an unfused raw batch mixture, basically sodium silicate and boric acid, incorporating a blowing agent. Heating this mixture triggers a simultaneous glass formation and expansion. Alkalinity becomes a problem because of the excess of unreacted sodium present. Minnesota Mining does not have this difficulty because they start with preformed glass particles and modify them to contain the necessary ingredients for expansion (blowing) during heating. These preformed glass particles can be neutralized and the sodium eliminated. In addition to reduced alkalinity, 3M predicts an increased wall strength since their process allows them to use high strength glass. This prediction is valid when samples of 3M and E&C GMB are inspected for broken and unblown balloons. Minnesota Mining's GMB are also treated with a proprietary adhesion promoter that increases the bonding between resin and GMB.



EMERSON & CUMING GMB, TYPE II (300X)



3M GMB, TYPE B40A (300X)

Figure 2. Two Types of GMB Illustrating the Difference in Particle Size and Number of Imperfect Bubbles

Table 2. Analysis of Hollow Glass Microspheres

GMB	Percent Retained on 60 Mesh Screen	Percent Through 200 Mesh Screen	Water Content (Percent)	Alkalinity (meq/g)*	Particle Density (g/cm^3)	Floaters (Percent)
B40A	0.00	81.7	0.08	0.11	0.360	97.6
E&C I	0.03	32.3	0.09	4.50	0.455	78.0
E&C II	0.03	24.1	0.03	4.10	0.410	78.0

*Milliequivalent per gram

The number of broken and unblown GMB, shown in the electron photographs of Figure 2, are quantitatively evaluated by means of the ratio of floaters to sinkers given in Table 2. Floaters are the perfectly formed GMB while the sinkers are the broken or unblown GMB and occasional impurities. Both before and after tumbling, the 3M samples were 96 to 99 percent floaters while the E&C samples were only 78 percent floaters.

It has been previously noted that E&C GMB tended to stratify during shipping and storage. It was necessary therefore to determine the extent of stratification present in 3M GMB. Micromerographs were obtained for tumbled B40A and E&C Type I and II GMB. From the particle size distribution it was observed that 50 percent by weight of the B40A GMB have a Stokes diameter of 49 microns (μm) or less with an overall range of 6.5 to 130 microns. For Type I and II material the 50 percent mark came at 71 and 78 microns respectively and the ranges were 4.5 to over 200 and 8 to 210 microns.

Processing Parameters

The next series of tests was designed to test both the formulation and the GMB. The tests were working viscosity, reactivity of the filled epoxy, and physical properties of the cured encapsulants. All three are areas of concern. The working viscosity of the GMB-resin system is important because the material must remain fluid enough to pour for at least 30 minutes. This requirement has been a major problem for mixes containing E&C Type I GMB. Pot life viscosity was easily tested using the unfilled resin and catalyst. But adding a filler makes this test nearly impossible since a consistent reading cannot be obtained. Inconsistent viscometer readings result when the spindle rotates in a nearly filler-free well of resin. The readings obtained are not a true reflection of viscosity. After the various methods for obtaining the viscosity were examined a suitable solution was obtained. Ideally the viscometer should be disposable and highly reproducible. Zahn cups and disposable Gardner viscosity apparatus were evaluated but the orifices of the Gardner cups were too small to be used with the high viscosity system and the Zahn cups were not disposable.

Semco tubes (Semco Sales and Service, Incorporated) were selected because, being plastic, they were completely disposable, cheap, and came with a screw-in conical tip which could be cut off at any desirable diameter. The tips were removed just past the screw threads to give a fairly reliable 0.350 inch (0.889 cm) diameter. The material was prepared using a 2000 gram batch size per Process Standard 9927003 except that the mix was not returned to the oven after catalyst addition.

One hundred gram samples were poured at appropriate time intervals into Semco tubes that had their tips sealed with masking tape. The tubes had also been preheated to 150°F (66°C). Thermocouples were used to monitor the temperature of the material in the mixing bowl and to obtain the initial temperature of the 100 grams of GMB mix in the Semco tube. After the GMB mixture had been poured into the tube and the temperature recorded the Semco tube was positioned over a polyethylene cup on a tared balance. When the tape covering the orifice was removed a timer was started.

After 5 minutes the weight of the material that had flowed through the orifice was recorded. The results of this test are presented in Figure 3. It can be seen from the graphs that 30 minutes after catalyst addition the E&C Type II and the 3M B40A GMB are more fluid than the E&C Type I after only 10 minutes. It was also noted that the lines drawn through the curves are nearly parallel. In addition, at 10 minutes virtually 85 percent of the B40A filled material had flowed through the orifice. At 20 and 30 minutes the percentages were 65 and 55 respectively. This data would appear to indicate little if any problems with viscosity over a 30-minute pot life.

Once it was determined that the 3M GMB met the more important features of the existing material standard for E&C GMB, it was necessary to determine the maximum exotherm of the material. Table 3 contains exotherm data obtained from the materials standard procedure for reactivity except that filled material was used. The reactivity procedure specified 100 gram samples and 160°F (71°C) cures so it is useful primarily as a reference. The resin and catalyst used with each type of GMB were Epi Rez 510 and Jefferson DEA, so if the exotherm data from the unfilled material is compared with that of the filled material it is possible to note any changes resulting from the presence of the various fillers. Using average values it can be seen that filler addition increases the first peak temperature and delays the occurrence of that peak. This is expected because of the insulating properties inherent in the filler. The time to the second peak and the temperature rise were seemingly unaffected by filler addition when B40A material was used. However, the use of E&C GMB of either type shortened the time to the second peak and increased the second peak temperature by about 14°F (8°C). Another interesting fact is that in some of the reactivities obtained for Type I and II a second peak was not apparent. This erratic behavior did not develop in the 3M GMB and may be peculiar to the E&C GMB. Additional testing of exotherm as a function of mass is discussed in the second section of this report.

Physical Properties of Cured Material

The final step before requesting general acceptance of the 3M Type B40A GMB was to completely characterize the mechanical, electrical, and thermal properties of the selected formulation. Tables 4 through 9 present these properties as averaged values and compares them with data on Type I GMB obtained from the

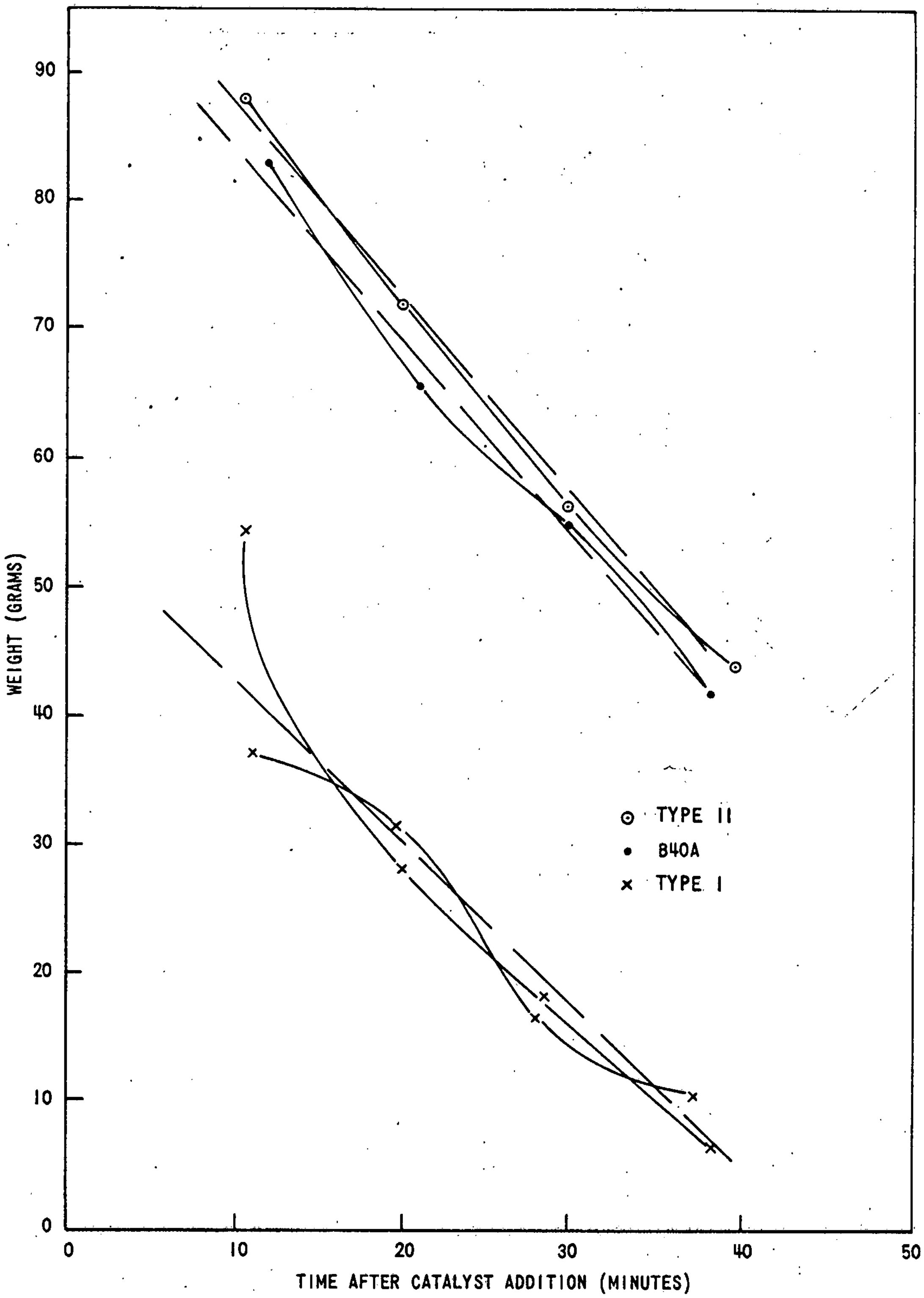


Figure 3. Weight of Material Flowed Through a Semco Tube as a Function of Time in Minutes After Catalyst Addition

Table 3. Reactivity and Gel Time for Filled Resins

		Reactivity						
Type GMB	GMB (pbw)	First Peak Time (min)	First Peak Temperature (°F)	(°C)	Second Peak Time (min)	Second Peak Temperature (°F)	(°C)	Gel Time (min)
I	30	9.5	236.8	114.1	83.0	203.8	95.3	84.6
II	25	11.6	233.2	111.9	84.2	203.8	95.3	110.3
Resin only	0	5.98	230.1	110.0	116.6	189.9	88.0	122.5
B40A	25	7.8	233.8	112.3	113.8	191.3	88.7	127.9

Table 4. Tensile Properties After Cure for 24 Hours at 150°F (66°C)

	Process Specification	
Variable	9927003 Type I	9927085 B40A
Maximum Stress in psi (MPa)	4,660 (32.1)	5,590 (38.5)
Strain At Maximum Stress (Percent)	1.14	1.23
Yield Stress in psi (MPa)	No yield	No yield
Yield Strain (Percent)	No yield	No yield
Elastic Modulus in psi (MPa)	490,000 (3,380)	477,000 (3,290)

encapsulating resins properties chart prepared by A. J. Quant and C. W. Hatcher of Sandia Laboratories, Albuquerque. These tests indicate that the 3M GMB are not radically different from the E&C GMB. They vary slightly but this is to be expected since 3M GMB are made by a completely different process and are coated with an adhesion promoter. This would in part, account for the increased mechanical properties. The electrical properties are also slightly improved. Since GMB formulations are used as insulators, low dielectric constant and dissipation factor values are desirable, whereas, high volume resistivities are expected. In all three instances the 3M GMB appear slightly superior.

Some of the differences in the electrical properties may be attributed to the GMB but consideration must be given to changes in the test methods. Dielectric constant and dissipation factor tests are now being performed using a Balsbaugh Test Cell (Model LD-3 Balsbaugh Laboratories) instead of the micrometer sample holder previously used. Specimen size was also changed from 2-inch-diameter (5.08 cm) by 0.125-inch-thick (0.317 cm) discs to 3.25 by 3.25 by 0.125-inch (8.26 by 8.26 by 0.317 cm) plates. In

Table 5. Compressive Properties After Cure for 24 Hours at 150°F (66°C)

	Process Specification	
Variable	9927003 Type I	9927085 B40A
Maximum Stress in psi (MPa)	10,600 (73.1)	11,960 (82.5)
Strain At Maximum Stress (Percent)	3.36	3.70
Yield Stress psi (MPa)	10,600	No yield
Yield Strain (Percent)	3.36	No yield
Rupture Stress in psi (MPa)	9,020 (62.2)	11,960 (82.5)
Rupture Strain (Percent)	4.66	3.70
Elastic Modulus in psi (MPa)	420,000 (2,900)	481,000 (3,320)

addition, the fluid normally used in dielectric strength testing, Intertine by Monsanto, is no longer available and Dow Corning 200 has replaced it. According to ASTM D-149, results in one medium cannot be compared with results in another. A dielectric strength of 279 volts per mil was obtained for the E&C Type I GMB using the DC 200 fluid. This indicates that the 3M GMB have slightly higher dielectric strengths and that testing in DC 200 imparts lower overall strength values.

Only in volume resistivity is the difference between the two materials so large as to preclude experimental errors. Apparently the 3M GMB provides superior insulation ability. Thermal properties are nearly identical and no clear cut superiority can be projected. Only in moisture absorption is there a wide difference indicating a better moisture resistance for the 3M Type B40A GMB filled material.

Table 6. Flexural Properties After Cure for 24 Hours at 150°F (66°C)

	Process Specification	
Variable	9927003 Type I	9927085 B40A
Maximum Fiber Stress in psi (MPa)	5,850 (40.3)	7,064 (48.7)
Deflection At Maximum Fiber Stress in./in. (mm/mm)	0.29 (7.37)	0.18 (4.57)
Rupture Stress in psi (MPa)	5,850 (40.3)	7,064 (48.7)
Rupture Strain in./in. (mm/mm)	0.29 (7.37)	0.18 (4.57)
Elastic Modulus in psi (MPa)	440,000 (3,030)	440,000 (3,030)

Specific Problems With Encapsulated Assemblies

Once the selectivity of the resin and catalyst specifications had been re-established and an improved filler had been located the next step was to investigate specific, chronic problems involving encapsulated electronic assemblies. These problem areas include cure time, exotherm, voids, resin-filler separation, and thermal shock. Some are peculiar to the epoxy-GMB material but others are shared by all encapsulants.

Cure Cycle

Although the cure cycle of an epoxy-GMB-DEA encapsulant has been well established and is not a problem area in the true sense, attempts to modify the cycle by shortening the time have been made. Initial heat distortion data indicated that 24 hours at 150°F (66°C) is an acceptable cure for the 3M Type B40A GMB filled resin as it has been for the E&C GMB. However, if the cure could be shortened to 16 or even 20 hours a considerable savings in mold turn-around-time would result.

Table 7. Volume Resistivity and Dielectric Strength After Cure for 24 Hours at 150°F (66°C)

Variable	Process Specification 9927003 Type I	 9927085 B40A
	Volume Resistivity	
Ambient	1.50 TΩ•m	1.84 TΩ•m
100°F (37.8°C)	0.13 TΩ•m	1.63 TΩ•m
150°F (66°C)	6.2 GΩ•m	382 GΩ•m
200°F (93°C)	0.041 MΩ•m	10.3 MΩ•m
250°F (121°C)	3.0 MΩ•m	475 MΩ•m
300°F (149°C)	1.9 MΩ•m	79 MΩ•m
350°F (177°C)		45 MΩ•m
	Dielectric Strength	
Short Time		
0.025 in. (3.2 mm)	465 V/mil (18.3 V/mm)	371.4 V/mil (14.6 V/mm)

The three cure cycles selected for investigation were 16, 20, and 24 hours at 150°F (66°C). The reference cycle was 24 hours at 150°F since it is the current cure cycle for epoxy-GMB cured with DEA. Sixteen and 20 hours were chosen as cure times because they are convenient time intervals for use in the production area.

Several properties were evaluated at various cure times; these included the tensile properties of maximum stress and strain at maximum stress, stress and strain at yield, and elastic modulus in accordance with ASTM D-638; the compressive properties of maximum stress and strain at maximum stress, stress and strain at yield, stress and strain at rupture, and elastic modulus in accordance with ASTM D-695; and the heat distortion temperature (HDT) in accordance with ASTM D-648.

Table 8. Dielectric Constant and Dissipation Factor After Cure for 24 Hours at 150°F (66°C)

	Process Specification	
Variable	9927003 Type I	9927085 B40A
	Dielectric Constant	
0.1kHz	3.53	2.92
1kHz	3.30	2.87
10kHz	3.10	2.83
0.1MHz	3.07	2.69
MHz	2.89	2.62
	Dissipation Factor	
0.1kHz	0.080	0.013
1kHz	0.036	0.012
10kHz	0.028	0.017
0.1MHz	0.030	0.025
MHz	0.032	0.031

Fifteen specimens were prepared for each set of properties tested. In addition, two different pallet lots of 3M's type B40A GMB were used to make the specimens. The tensile specimens were molded to conform to Sandia's Standard Test Specimen Number 196-B (Sandia Laboratories, Standard Test Specimens, SC-4540C (M) July 1965). Both the top and bottom surface were machined to eliminate any potential resin-layer effects due to molding. The compressive specimens (Number 6) and HDT specimens (Number 50) were machined from 6 by 4 by 0.5 inch (15 by 10 by 1.3 cm) slabs.

Averaged data for the tensile, compressive, and HDT tests are given in Tables 10, 11, and 12. In the tensile testing no yield point was observed so only maximum or ultimate stress and strain were recorded. A similar situation exists in the compressive test results since maximum and rupture stress occurred at the same point and no yield was apparent.

Table 9. Thermal and Miscellaneous Properties After Cure for 24 Hours at 150°F (66°C)

Property	9927003 Type I	9927085 B40A
Heat Distortion Temperature (°C)*	78	77
Coefficient of Thermal Expansion (in/in/°C) (cm/cm/°C)	0.000034** 0.000040***	0.000033** 0.000034***
$\frac{\text{BTU} \cdot \text{in}}{\text{ft}^2 \cdot \text{hr} \cdot {}^\circ\text{F}}$ (W/m · K)	1.1 0.158	0.91 0.132
Heat Resistance in Percent of Weight Loss	0.06	0.04
Thermal Shock†	Passed	Passed
Glass Transition Temperature (°C)	76	81
Specific Gravity	0.87	0.79
Moisture Absorption in Percent of Weight Gain	2.49	0.54

*At 264 psi (1.82 MPa)
**At -65°F (-53.9°C) to ambient
***At ambient to 165°F (74°C)
†Hollow cylinder, SCR-417

From the tensile and compressive test data it can be seen that stress, strain, and modulus values are relatively unchanged during the sixteenth to twenty-fourth hours of cure. In fact it appears that there is more variation in results caused by using different pallet lots of GMB than there is from shortening the cure time by one-third. However, a change in mechanical properties was not anticipated and the data were intended primarily as a check. Any obvious discrepancies in mechanical properties could also have been the result of processing problems or specimen preparation.

Table 10. Tensile Properties of Filled Resin After Various Cure Cycles

Cure Time (Hours)	GMB	Elastic Modulus		Ultimate Stress		Strain at Ultimate (Percent)
		(psi)	(GPa)	(psi)	(MPa)	
24	P-6793-7	500,000	3.45	5,600	38.6	1.17
	P-6793-7	486,000	3.35	5,620	38.7	1.20
	P-7249-1	472,000	3.25	5,660	39.9	1.24
20	P-6793-7	503,000	3.47	5,370	37.0	1.09
	P-7249-1	490,000	3.38	5,720	39.4	1.26
	P-7249-1	489,000	3.37	5,440	37.5	1.21
16	P-6793-7	502,000	3.46	5,820	40.1	1.22
	P-7249-1	480,000	3.31	5,860	40.4	1.32
	P-7249-1	493,000	3.40	5,770	39.8	1.31

Table 11. Compressive Properties of Filled Resin After Various Cure Cycles

Cure Time (Hours)	GMB	Elastic Modulus		Ultimate Stress		Strain at Rupture (Percent)
		(psi)	(GPa)	(psi)	(MPa)	
24	P-6793-7	510,000	3.52	13,200	91.0	3.98
	P-6793-7	477,000	3.29	11,700	80.6	3.32
	P-7249-1	471,000	3.25	11,800	81.4	3.48
20	P-6793-7	490,000	3.38	13,800	95.2	4.15
	P-7294-1	485,000	3.34	12,600	86.9	3.45
	P-7249-1	472,000	3.25	12,600	86.9	3.61
16	P-6793-7	495,000	3.41	13,800	95.2	4.10
	P-7249-1	485,000	3.34	12,700	87.6	3.48
	P-7249-1	485,000	3.34	12,600	86.9	3.41

Table 12. Heat Distortion Temperature of Filled Resin at 264 Psi (1.8 MPa)

GMB	24 Hour Cure (°F)	(°C)	20 Hour Cure (°F)	(°C)	16 Hour Cure (°F)	(°C)
P-6793-7	174	79.0				
P-6793-7	176	80.0	175	79.5	170	76.7
P-7249-1	174	79.0	175	79.5	171	77.5
P-7249-1			175	79.5	174	79.0

The most important test of extent of cure is heat distortion temperature (HDT). HDT or deflection temperature is an indicator of the extent of cross-linking present in a cured material. For epoxy-GMB a minimum of 170°F (77°C) has been established. Nonetheless it is considered desirable that actual HDT exceed this value. Fully cured (24 hours) epoxy-GMB typically exhibits an average HDT of 175°F (79.5°C). The data in Table 12 reflects this but also shows that the HDT reaches a plateau between 16 and 20 hours of cure. This would seem to indicate that 20 hours at 150°F (66°C) is an adequate cure. While the minimum average HDT is attained after 16 hours, closer examination reveals that some values were slightly below minimum. Therefore a 16-hour cure would result in some uncertainty. One solution would be to cure for 16 hours, remove the part from the mold, and post cure for 4 additional hours to increase the HDT. The exact effects of this cure on dimensional stability have not been analyzed. However additional stress buildup due to cooling and reheating the material should be considered when a post cure is used. Therefore, even though the HDT at 16 hours approximates the minimum acceptable value and an additional safety factor can be added by a 4-hour, 150°F (66°C) post cure, the 20-hour cure is the most acceptable alternative.

Even though shortening the cure cycle to 20 hours represents a savings of 12 percent over the current cycle such a change should not be made without careful consideration of the individual needs of each assembly.

Exotherm

The reactivity data obtained on the filled and unfilled catalyzed resin provided a limited insight into the exotherm of the system. The data was limited because the quantity of material involved was 100 grams and because the pint (473 cm^3) cans used allowed heat to escape freely. As a result larger specimens were prepared using one-half pint, pint, and quart size metal paint cans and an 8- by 8- by 4-inch (20 by 20 by 10 cm) aluminum mold. The metal cans were filled to a depth equal to their diameter which corresponded to 200, 330, and 680 grams respectively. The aluminum mold was chosen as the most severe case and contained approximately 2500 grams. Figure 4 shows typical exotherm data. It was difficult to position the thermocouples in the exact center of mass so some irregularities are present but this data is representative of actual measurements taken from mold parts. As the mass increases, the double peak disappears altogether and only one peak, intermediate in time and magnified in intensity, remains. At the normal mix temperature of 150°F (65°C) the viscosity of the catalyzed epoxy-GMB is too high for it to flow properly. Exotherm thus provides a more workable material by reducing the viscosity. Increasing the temperature also increases the reaction rate and the subsequent increase in viscosity due to cross-linking (gelation) can surpass the viscosity reduction resulting from the increased temperature. High exotherms about 200°F (93°C) can also harm thermally sensitive electronic components if prolonged. One solution is to control the mass of encapsulant used in an assembly. This is not a total answer because of the variety of encapsulated assemblies. Another, better alternative is to combine control of the encapsulant mass with control of the external temperature. Putting the catalyzed, epoxy-GMB into an oven increases the thermal energy input into the reaction and increases the exotherm and the reaction rate. If the material is allowed to exotherm without adding additional heat the maximum exotherm can be reduced.

Voids

Another chronic problem with encapsulants are voids caused primarily by entrapped air, component outgassing, and cure shrinkage of the encapsulant. Voids on the exterior of a unit are unsightly but can be reworked in most cases. Interior voids are more serious. In certain environments the gases within the void could ionize, become conductive, and short the electronic assembly.

The viscosity of a freshly mixed epoxy-GMB encapsulant is sufficiently low that the air bubbles introduced during mixing or the pouring operation can be removed by evacuating the mixture at 1 to 3 mm Hg for 1 to 5 minutes after the initial foam rise collapses. Although empirically established, this was verified by calculating the terminal velocity of a bubble rising through a fluid filled with spheres of unequal diameter (Stokes Law) and by experimentation. However components and horizontal printed circuit boards can act as mechanical traps. This problem can be minimized by proper design of the assembly to be encapsulated, but not entirely eliminated.

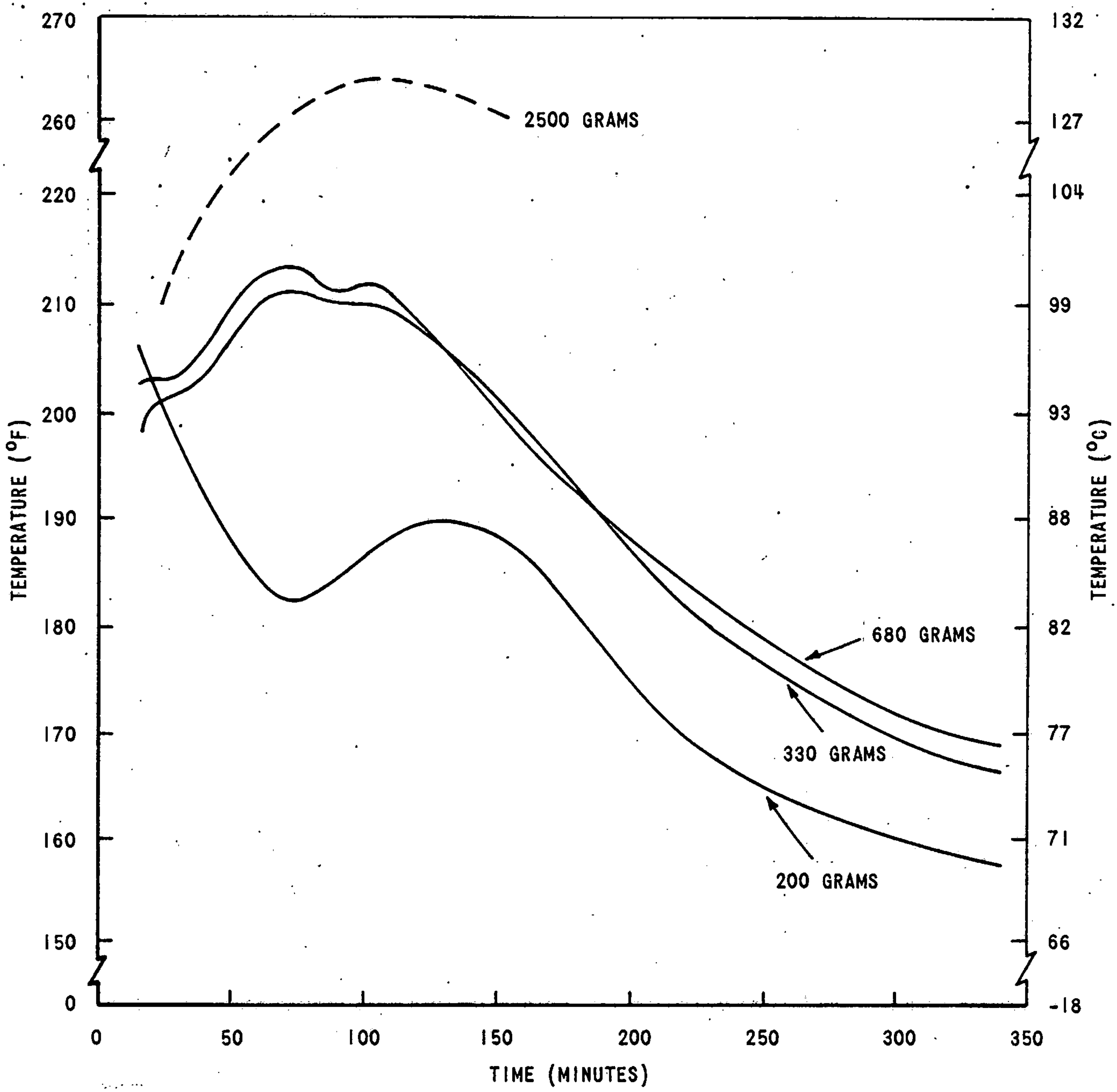


Figure 4. Exotherm Data for 3M Type B40A GMB

Related to air voids is the problem of component outgassing. Included in component outgassing is the problem of volatiles in the various coatings used inside an assembly. In order to assess the magnitude of the problem, attempts were made to fill, with catalyzed resin, an inverted test tube suspended into a larger tube. Two fill and two cure techniques were used. The tube assembly was either vacuum filled or filled and then evacuated. The cure was either in a forced convection oven or in an autoclave pressurized to 125 psig (861 kPa). The technique that provides the maximum void reduction consisted of the vacuum fill followed by a pressure cure.

In combination with vacuum filling the concept of replacing the air with a reactive gas that would interact with the resin was considered. It was not pursued because the more suitable gases were highly toxic and would have required special handling equipment and procedures.

The third cause of voids, shrinkage of the encapsulant away from a mold surface, is a slightly different problem from the other two. These voids which normally occur along mold parting lines or inserts are a result of the natural shrinkage of a curing epoxy (Figure 5). Shrinkage can be distinguished from voids caused by trapped bubbles because the shrink voids lack the glossy surface of air bubbles. Also shrink voids are not randomly located but normally occur in a specific pattern. Shrink voids are usually caused by thermal gradients within a curing assembly and can be minimized by reducing hot spots. This is partially accomplished by uniform mold temperature prior to encapsulation. In addition, since the reaction is exothermic, temperature can build in areas where there is a large mass of catalyzed resin such as the mold reservoir. If cure is initiated within the assembly material is pulled from the reservoir to accommodate the natural shrinkage of the encapsulant during cure. If, however, cure is initiated in the reservoir the reverse is true and shrink voids increase. Therefore it is important to minimize reservoir size in addition to controlling mold temperature.

To summarize, voids can be reduced, if not eliminated by designing assemblies to eliminate mechanical traps; minimizing thermal gradients between the mold and potting compound, particularly between the potting compound near the mold surface and that near the center of mass; vacuum filling the mold; and pressurized curing the encapsulated assembly.

Resin-Filler Separation

When the initial work was done on the improved epoxy-GMB-DEA formulation, checks on the density distribution of the encapsulant were performed using samples cut from 6- by 0.5- by 9-inch (15 by 1.3 by 23 cm) slabs. At that time no undesirable density

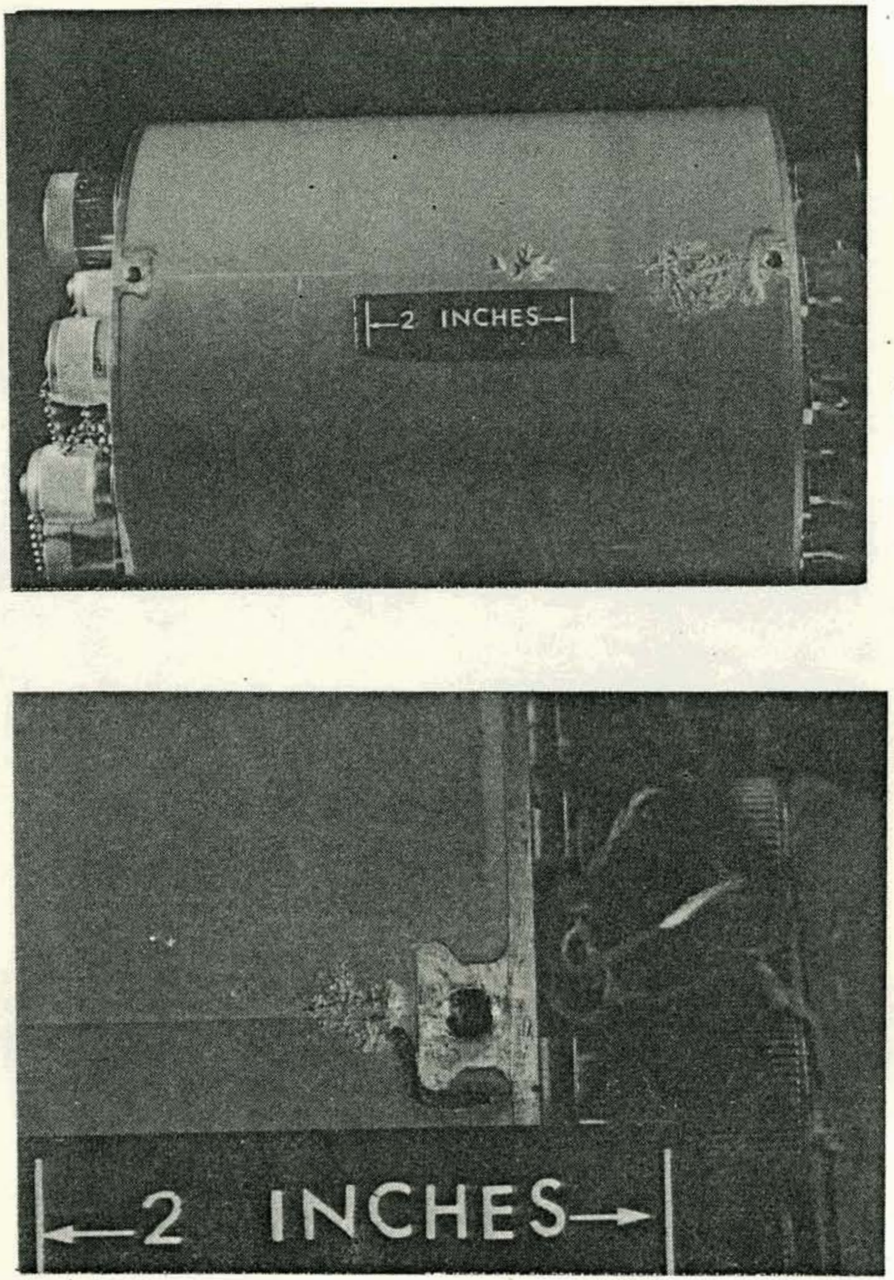


Figure 5. Voids Caused by Shrinkage

variations were observed. It was noted, however, that the GMB tended to float and leave a small layer of clear, cured resin at the bottom of the mold. This separation occurs in most low density fillers and, as a result, the bottom 0.125 inch (0.318 cm) of each slab is removed before density samples are cut. In test specimens this resin rich layer can be easily removed but in an electronic assembly this same separation can occur on each horizontal surface.

The problem with resin/filler separation is that the resin layer has undesirably high thermal expansion properties compared to the bulk encapsulant and is in intimate contact with materials having low coefficients of thermal expansion such as printed circuit board (PCB). This creates areas of high stress concentration and may cause cracks in encapsulated units. The separation arises because the lower density GMB have a tendency to migrate to the top of the mix while the higher density resin tends to settle on the bottom.

If horizontal surfaces such as PCBs are present within the assembly the buoyant GMB are trapped against the bottom surface of the PCBs while the resin rests on top. While this effect was present in encapsulated assemblies using Emerson & Cuming GMB, it was diminished by the presence of a high percentage of broken GMB that would accumulate with the resin on the horizontal surfaces. The 3M GMB with their larger percentage of high quality balloons or floaters paradoxically aggravated the filler separation problem. Three illustrations (Figures 6, 7, and 8) show the problems of resin filler separations with the 3M GMB. All the figures are dummy assemblies having 3 layers of PCBs, with a hole drilled in the center board. All units were potted as specified by MS 9927085.

Figure 6 represents a dummy unit encapsulated according to MS 9927085 with no delay between evacuation and cure. Figures 7 and 8 represent 30 minutes and 2 hours delays respectively at room temperature before cure.

Following cure, a diagonal slice was taken through the 4.5 inch (114 mm) cubical dummy units and machined to a thickness of 0.10 inch (2.54 mm). To obtain the photographs for Figures 6, 7, and 8 the machined samples were photographed with a light source behind the specimen.

The 3M GMB system in general is shown to be almost devoid of sinkers or broken GMB. A layer of what appeared to be pure resin of approximately 0.20 inches (5 mm) in depth occurred on the top of each board. Beneath the PCBs there is a dark area, again due to the presence of a GMB rich area. The specimens made with no delay and 30 minutes delay before cure (Figures 6 and 7) show the resin flowing off the PCB edges and particularly through the

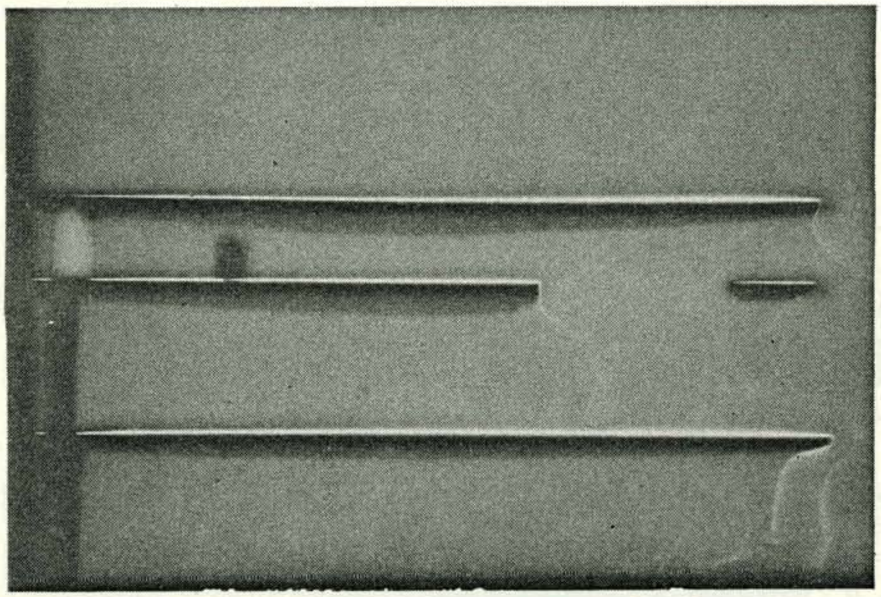


Figure 6. Cross Section, X-Ray of Dummy Unit with 3M GMB Standard Process

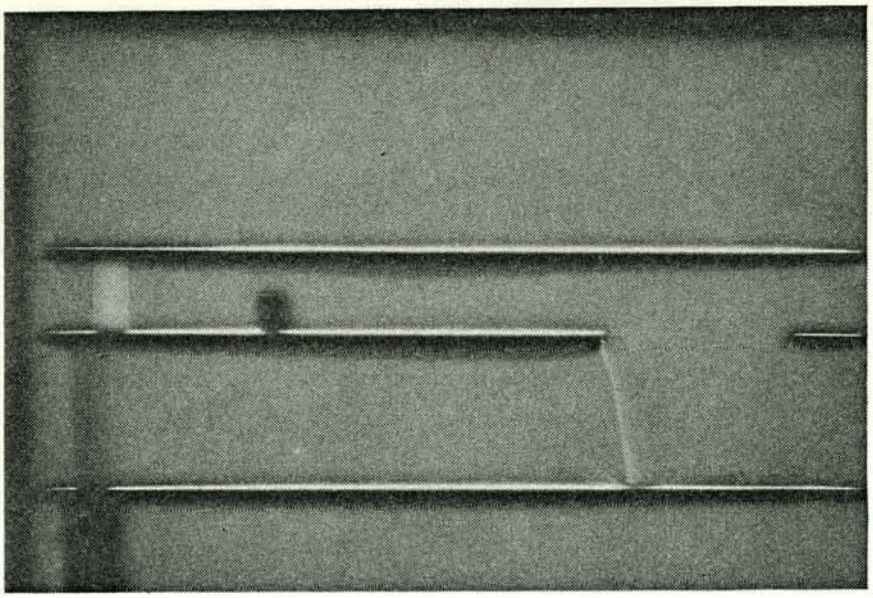


Figure 7. Cross Section, X-Ray of Dummy Unit with 3M GMB 30 Minute Delayed Cure

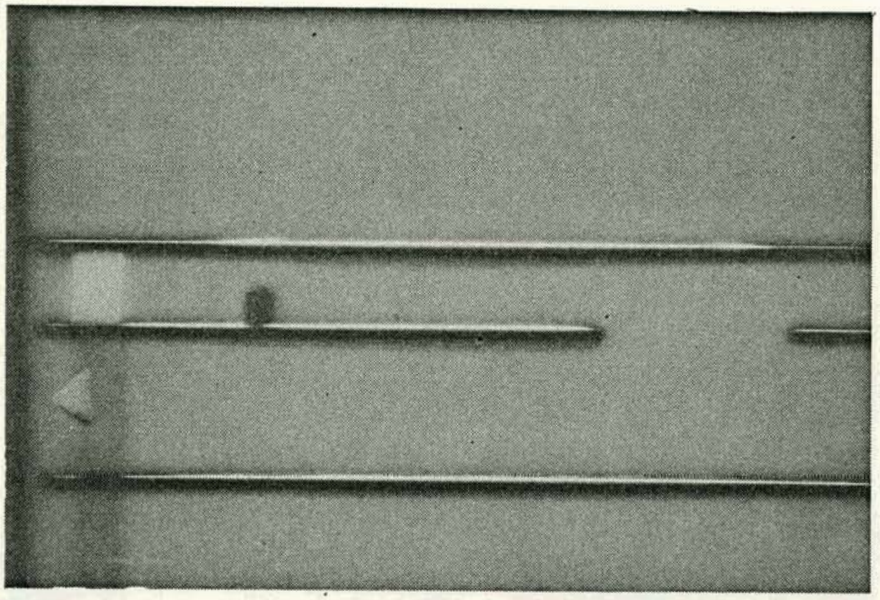


Figure 8. Cross Section, X-Ray of Dummy Unit with 3M GMB 2 Hour Delayed Cure

hole and down to the PCB beneath. The 3M GMB system section which underwent the 2-hour room temperature delay prior to cure (Figure 8) was free of any evidence of resin flow from the top of the boards. To diminish the effects of resin-filler separation, a 2-hour delay cure was incorporated into the encapsulation process using 3M GMB which also serves to reduce exotherm.

Thermal Shock

All of the electrical assemblies manufactured by Bendix Kansas City are subjected to some type of thermal cycling. The cycling can result from the exotherm and cure of the encapsulant, environmental conditioning, or the design requirements of the final assembly. Thermal cycling generates internal stresses within the assembly because of the diverse materials with their different thermal expansion coefficients (CTE). Coupled with thermally induced stresses are those developed within the encapsulant when it is restrained from shrinking during cure by the components within the assembly. Cracking can result when these stresses exceed the strength of the encapsulant. Other indications of excessive stress include deformation of the encapsulant and bond failure between the components and the encapsulant. These failures can cause solder joint failure, pull leads from components, break fragile components, and permit moisture and other corrosive environments to penetrate the unit.

There were two tests originally developed to determine the thermal shock resistance; the "Nut and Bolt" Test and the Quant hollow cylinder test. Both tests were based on the difference between the CTE of a steel insert and the encapsulant. The Quant hollow cylinder test was the more severe test and only the epoxy-GMB formulations could pass. This test was tried on the new epoxy-GMB formulation using 3M GMB with mixed results. Investigation of these results indicated that pour depth was critical. A difference in depth of as little as 0.125 inch (0.3 cm) could determine success or failure. In addition the test was nonspecific. There was no way to determine the relative stress resistance of an encapsulant. Consequently a number of other thermal shock tests were evaluated to increase the severity as well as quantize the test. In order to observe the cracks, most of the tests were performed on catalyzed-unfilled epoxy and then on the GMB filled epoxy. The thermal shock tests included the Navy hex bar test (Mil-I-16923F), the Olyphant and Sato washer tests[2,3] and the Miron wedge test. Although the specimen encapsulated varied in size and shape all were essentially similar to the Quant hollow cylinder and the results were equally contradictory. Although the unfilled epoxy specimens cracked easily none of the specimens prepared failed either the hex bar test or the washer tests.

The Miron wedge test was developed by the 3M Company specifically for this type of problem. The insert is wedge-shaped with 4 holes ranging in size from 0.250 (6 mm) to 1 inch (25 mm) in diameter. The 0.5 (12 mm) diameter hole corresponds roughly to the Olyphant washer tests also developed by 3M Company. The severity of the test can be controlled by the thickness of the wedge. The thermal shock strength of various materials were rated on the basis of how many holes starting from the smallest produced fractures. In theory the stresses in the resin inside the holes do not depend upon the diameter of the hole. In practice the deformation of the resin at the surface above the hole causes the failure to occur at the small hole first. The wedge test offers a graduated scale of hole sizes and wedge thickness that allows number values to be assigned to a failure.

A number of specimens were poured using the Miron wedge as the insert. The first specimens were unfilled Epon 828 resin catalyzed with DEA and tested at -40°C. Cracks due to thermal shock on the resin did occur. A catalyzed mixture of GMB-epoxy was then tested and the first instance of thermal shock failure was recorded. The crack, however, occurred in the hole having the largest diameter which was contrary to the previous data reported by the inventor of the test method. Because of this and the expense and difficulty experienced in preparing test specimens, effort was directed toward other possible thermal shock tests.

What was desired was a severe thermal shock test of simple design that used test specimens that could be machined from the density and ash content slabs poured in the production area. This led to the development of a ring and tapered mandrel test setup. The test fixture is a tapered mandrel made of a material having a low CTE such as steel or ceramic. A locking taper is machined onto the mandrel. Test rings are machined out of production test slabs to such a size that the ring can be slipped onto the mandrel to a predetermined stress by using a force gage or by measuring ring expansion. The ring and tapered mandrel are then thermally shocked to a temperature, such as -40°F (-40°C). Theoretically, as the ring and test mandrel are cooled, large stresses are developed in the test ring since its high CTE causes it to shrink tightly onto the mandrel which has a lower CTE. Eventually a temperature should be reached which produces stresses in the test ring that exceeds its tensile strength and fracture occurs. Since the CTEs of the encapsulant and the mandrel are known, as well as specimen dimensions, the stresses required to break test specimens can be calculated. The method has the additional advantages that it is of simple design, that specimens are machined from slabs poured with production parts, that many tests can be run at once, and that the testing fixtures are not destroyed during a test.

Both steel and ceramic mandrels were used. The steel mandrels were 18 inches (46 cm) long with a 0.002 in/in (cm/cm) locking taper and a diameter range of 0.620 to 0.656 inches (1.57 to 1.67 cm). The ceramic mandrels were 13 inches (33 cm) long with a diameter range of 0.624 to 0.650 (1.59 to 1.65 cm). The test rings were 0.50 inches (1.27 cm) high, had an inner diameter of 0.624 inches (1.59 cm) and a wall thickness of about 0.08 inches (0.20 cm). Varying amounts of mechanical prestressing from 0 to 200 lbs-force (0 to 890 newtons) were also evaluated in conjunction with thermal stressing from 200°F to -100°F (93 to -73°C). No combination of these variables could produce consistent thermal cracking failures. Only excess mechanical stress produced consistent failures. At this point the tests were terminated. Apparently there is a key to thermal cracking but the exact casual relationship between stress and cracking was not determined.

Investigation of a Backup Encapsulant for Ablefoam 5

In addition to improving the GMB-epoxy low density encapsulant, attempts were made to find a suitable back-up encapsulant for Ablefoam 5.

Initial efforts in this area involved using the Capoxyfoam I system developed at Bendix Kansas City to reduce formulation work on the basic epoxy foam premix. By doing this, the endeavor would be reduced primarily to evaluating various blowing agents and surfactants. Experimentation with the basic resins, curing agents and processing could be minimized if not eliminated.

The preliminary formulation work involved the introduction of various low boiling organic liquids into the Capoxyfoam I system. The basic Capoxyfoam I formulation is given in Table 13. Fabrication of this type of foam premix consists of blending the foam constituents with the liquid blowing agent and then pouring the foam premix into a mold and curing for 4 hours at 170°F (77°C).

An evaluation of the organic liquids employed and their respective foams is presented in Table 14. Petroleum ether was found to be the most suitable blowing agent in this evaluation, yielding a completely blown epoxy foam with uniform density.

As evidenced by the weights of the cylindrical specimens cut from each foam block the average overall density varies less than 1.04 percent for the Capoxyfoam I formulation using petroleum ether. Compressive strengths for 20 lb/ft^3 (320 kg/m^3) foam specimens averaged 609 psi (4.2 MPa) and 295 psi (2.0 MPa) at room temperature and 200°F (93°C), respectively.

Attempts were made to increase the relative compressive strength by employing additional curing agents and activators. The use of such agents as the BF_3 piperidine complex, 2,4-lutidine, and Merginamide L-425 (Stepan Chemical Company) indicated no substantial increase in the compressive strengths.

Formulation activity also included the use of glass microballoons in the foam system. Concentration of the microballoons were approximately 25 percent by weight of the total epoxy resin. The foams appeared to be of uniform density with an average variance less than 1.5 percent, and their respective compressive strengths were increased by approximately 30 percent.

Further evaluation of the petroleum ether blown epoxy foams included examination of the thermal and electrical properties. The values of the Capoxyfoam I - petroleum ether cured foam system appear to be within the expected range for epoxy foams of this nature. Thermal gravimetric analysis determined that initial weight loss occurs at 350°C (662°F). The volume resistivity was 157 teraohms/cm when tested in accordance with ASTM D-257. The dielectric constant was 1.5 and the dissipation factor was 0.0119 when tested at 1 MHz in accordance with ASTM D-150.

One property of prime concern in using petroleum ether as the active blowing agent is the open-to-closed cell content of the cured foam. Using a helium and set pychnometer technique, the total void content of the Capoxyfoam I-petroleum ether foam system was 73.4 percent. The open cell and closed cell void contents were 20.22 percent and 53.18 percent, respectively. These values are meaningful when compared to those of the Capoxyfoam I system using ammonium carbonate as the blowing agent.

Table 13. Capoxyfoam I Formulation

Components	Materials	Weight (Grams)
Resin	DER 431 (Dow Chemical Company)	100
	EPON 828 (Shell Chemical Company)	100
	Phenyl Glycidyl Ether	2
	L-5320 (Union Carbide Corporation)	4
Curing Agent	Epon Z (Shell Chemical Company)	40
	Nadic Methyl Anhydride (Allied Chemical Corporation)	8
	Maleic Anhydride	2
Blowing Agent	NH_4CO_2-Ammonium Carbonate	26

As can be seen from the data in Table 15, using petroleum ether in the Capoxyfoam I system has resulted in increasing the open cell content nearly four-fold. Attempts were also made to mold various dummy configuration units with the petroleum ether foam. Examination of foamed units indicated that the foam effectively flowed into small spaces of close cross-sectional tolerance. However, the extreme flammability of petroleum ether made it desirable to evaluate other blowing agents. After considering all available nonflammable blowing agents it was decided to introduce a Freon compound (E. I. du Pont de Nemours & Company) into the foam system.

Initially Freon 11 (trichloromonofluoromethane) was employed as the blowing agent. However the boiling point of Freon 11 is only 74.8°F (23°C) and mixing with the foam premix caused premature foaming due to the volatilization of the Freon. Consequently Freon 113 (trichlorotrifluoroethane) was selected as the active blowing agent because its boiling point is 117.6°F (47°C). It was determined by examining density gradients, relative compressive strength values, and general foam appearance that the optimum concentration of Freon 113 was approximately 13 phr (parts per hundred parts by weight of resin). Amounts less than 13 phr caused incomplete mold fill, and amounts greater than 13 phr did not appreciably increase the quality of the foam specimens. The new formulation was identical to that given in Table 13 except that Freon 113 was substituted for ammonium carbonate. The foam was given the name Frefoam I.

Table 14. Evaluation of Organic Liquids Employed as Blowing Agents in the Capoxyfoam I Formulation

Organic Blowing Agent	Boiling Point (°C)	Percent Mold Fill	Voids	Remarks
Petroleum ether	36.9 to 47.3	100	Few	No dimensional distortion. Uniform cell size.
Chloroform	61.3	50	Many	Resin settles out.
Heptane	98	65	Large	Voids near top of foam.
Carbon Tetrachloride	76.8	65	Large	Voids near top of foam. Resin settles out.
Methyl ethyl ketone	79.6	65	Large	Voids near top of foam. Resin settles out.
Methanol	64.6	75	Large	Voids near top of foam.
Isopropanol	82.3			Little blowing action.
Acetone	56.5	75	Many	Some surface distortion.
1,2-dichloroethane	83.6			Little blowing action.
Benzene	80	50	Many	Resin settles out.
Dichloromethane	40.1	85	Large	Voids near top of foam.
1,4-dioxane	101.5			No blowing action.
Ethanol	78.5	50		Voids near top of foam.
Freon, 113	47.6	75	Many	Some surface distortion.

Table 15. Analysis of Void Content

Content (Percent)	Capoxyfoam I Petroleum Ether	Capoxyfoam I Ammonium Carbonate
Total Voids	73.40	72.06
Open Cell Voids	20.22	5.03
Closed Cell Voids	53.18	67.03

After mixing, the Frefoam I is poured into a Semco tube, capped, and quickly frozen. The quick-freezing process essentially halts the possible chemical reactions between the foam components. When required, the frozen foam package is allowed to thaw and the premix is then injected into the desired mold.

Most of the foam specimens initially developed lacked dimensional stability. These foams had a density of approximately 18.6 pounds per cubic foot (298 kg/m^3), and were cured at 170°F for 4 hours. At room temperature and 200°F (93°C) the compressive strength values averaged 325.6 psi (2.24 MPa) and 115.7 psi (0.798 MPa) respectively.

When one-cubic-inch cylindrical specimens of the rigid foam were exposed to 200°F the interior cell matrix swelled and caused a 10 percent increase in the diameter of the specimen. It was hypothesized that residual Freon trapped within the closed cell network of the cured foam began to diffuse outward when the specimens were heated above the cure temperature. At these temperatures, the Freon may have a plasticizing effect upon the foam causing the cell matrix to swell.

To confirm this hypothesis a test was performed using a foam specimen cured at 170°F (77°C). The foam sample, enclosed in a pyrolysis unit, was heated to 200°F (93°C) and the gases diffusing out of the foam were collected and analyzed using gas chromatography. The preliminary results indicated that Freon 113 vapors were passing out of the foam matrix. As a result further attempts to increase the compressive strength and decrease the variations in dimensional stability involved modifications of the cure cycle.

Preheating the molds to 120°F (49°C) before cure caused a 20 percent increase in compressive strength values for samples tested at 200°F (93°C). Increasing the cure time to 8 hours had little effect in increasing compressive strengths.

The best results were obtained by curing the Frefoam I system at 200°F (93°C). Compressive strength values for specimens tested at 200°F (93°C) were shown to have increased 100 percent. In addition there was little evidence of interior swelling or density gradient variations. The higher cure temperatures appeared to enable more of the residual Freon to diffuse out of the cure foam; and increase the dimensional stability of the foam.

Despite the increase in dimensional stability and compressive strength properties, further improvements were required. The primary problem with the Frefoam I was the retention of excessive amounts of Freon 113 due to the closed cell content.

It was anticipated that the reduction of Freon from 13 phr to 6.5 phr (Frefoam II) would help to alleviate this problem. Even with the lower amount of blowing agent, the foam appeared to fill all mold spaces completely and still possess a uniform cell structure. It was noted that the average skin thickness of the Frefoam I cured specimens was 0.125 inch while the skin of the Frefoam II specimens was only 0.0625 inch in thickness.

Measurements made to determine the dimensional behavior of Frefoam I and II cured samples subjected to a post cure environment of 200°F (93°C) are shown in Table 16. The foams are initially cured at 200°F (93°C) for 4 hours and all specimens possessed a density of between 20.0 to 21.50 pounds per cubic foot. In addition to those foams cured at 200°F, several Frefoam II samples were cured at 165°F.

As seen in the table, the Frefoam II samples possess the greater dimensional stability. The dimensional changes for those Frefoam II samples cured at 165°F (74°C) suggest that the higher cure temperature directly influences the dimensional characteristics of the foam specimens. Samples left at room temperature following initial cure exhibited only a minimal change.

Next a set of compressive specimens was prepared to check the existence of a relationship between the concentration of Freon in the premix and the compressive strength of the cured foam. Average compressive strength values for the Frefoam I samples cured at 200°F (93°C) were 485 psi (3.3 MPa) and 250 psi (1.7 MPa) at room temperature and 200°F (93°C), respectively. Under equivalent conditions, the Frefoam II sample exhibited values of 595 psi (4.1 MPa) and 340 psi (2.3 MPa). Again, the Frefoam II system appears to be the superior foam formulation.

Because the Frefoam II formulation possessed many of the properties required of an encapsulant foam, it was tested on a "B" deck dummy mold unit. The foam flowed quite easily into spaces and gaps as small as 0.03 inch (0.76 mm). Complete mold fill was noted in every instance. There were some randomly distributed voids but these were a direct result of improper venting of the mold.

Table 16. Dimensional Stability of Frefoam I and II

Material	Initial Cure Temperature	Dimensional Change in Percent Length at 200°F Post Cure					
		1 (Hour)	2 (Hours)	4 (Hours)	8 (Hours)	24 (Hours)	36 (Hours)
Frefoam I	200	0.9	1.7	1.9	1.9	2.0	2.0
Frefoam II	165	0.9	1.4	1.3	1.4	1.4	1.4
Frefoam II	200	0.4	0.6	0.6	0.7	0.7	0.7

ACCOMPLISHMENTS

An acceptable alternative to Emerson & Cuming (E&C) glass microballoons used as a filler was located. The new material was Type B40A glass bubbles from 3M Company. Tests on the 3M Type B40A material indicate that as both a free flowing powder and as a filler it is equal, and in some cases slightly superior, to the material currently in use.

Alternate cure cycles were developed for the epoxy-GMB-DEA encapsulant that cut the existing cure time by 4 hours.

The exotherm of the encapsulant was monitored and shown to be mass dependent. Minimizing this exotherm was accomplished by controlling the encapsulant mass and by allowing the encapsulant to exotherm before the unit was put into an oven to cure.

After studying the three sources of voids, entrapped air, component outgassing, and shrink, a series of operations were recommended for minimizing the problems. The operations include designing assemblies to eliminate mechanical traps, maintaining uniform mold temperature throughout the cycle, minimizing the material in mold reservoirs, vacuum filling of the mold, and pressurized cure of the encapsulated assembly.

The switch to 3M GMB magnified the problem of resin-filler separation which had been partially concealed by the broken and unblown balloons found in the E&C GMB. The effects of the resin rich layer were minimized by a 2 hour, room temperature delay between filling the mold and curing the encapsulant.

Evaluation of the various thermal shock tests used to determine the thermal shock resistance of catalyzed resins indicates that these tests are not sufficiently severe to be used on epoxy-GMB encapsulant. Attempts to develop a severe, quantizable test suggest that the relationship between cracks and thermal and mechanical stress is complicated by the creep exhibited by the epoxy-GMB encapsulant.

A low density blown epoxy foam was developed as a potential backup for Ablefoam 5. The backup foam has been designated Frefoam II and may be comparable to Ablefoam 5 in most physical properties and processing characteristics.

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