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BDX-613-195 (Rev.)

RIGID EPOXY FOAM ENCAPSULATION

Final Report

F. C. Ayres, Project Leader

Project Team:
H. M. McIlroy
W. E. Richardson

Internal Distribution November 1971

Released June 1974

MASTER

Prepared for the
United States Atomic Energy Commission
Under Contract Number AT(29-1)-613 USAEC

Bendix Kansas City Division

DISCLAIMER

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Department 841

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Technical Communications
Bendix
Kansas City Division

MASTER

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ABSTRACT

The production capability to encapsulate electronic component assemblies of a major assembly, using a one-component rigid epoxy foam, was achieved. A complete characterization of the material properties was determined, and a potential back-up epoxy foam for the single source proprietary material was developed.

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SUMMARY

A complete characterization of the properties of Ablefoam 5 (Ablestick Adhesive Company, Gardena, California) was compiled, defining mechanical, electrical, thermal, and environmental properties. The effects of various processing and testing parameters on the properties of this material were determined and a formulation variation study was made.

Using Ablefoam 5, the production encapsulation processes and tooling required for fabrication of electronic components of a major assembly were developed and are currently being used.

A potential back-up epoxy foam, Capoxyfoam I, was developed by Bendix. Capoxyfoam I has successfully encapsulated the electronic component assemblies, employing existing production tooling. The only modification of the existing encapsulation process necessary was the addition of a mold preheat. Capoxyfoam I possesses a higher closed cell content and contains slightly more blowing agent (ammonium carbonate) than does Ablefoam 5. However, these differences have no significant effect on either the electrical and physical properties or the processability of the material.

Additional development work is in progress to evaluate the use of non-ammonium carbonate blowing agents.

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BACKGROUND

During the development of the assembly, the design agency, Sandia Laboratories, Albuquerque (SLA), demonstrated the feasibility of using an epoxy foam encapsulant to structurally support and isolate electrical components. In January 1968, following an investigative survey, Ablefoam 5 was selected to meet the encapsulation requirements. This was the first application of an epoxy foam at Bendix Kansas City. Since very little was known about the properties, processability, and reliability of this material, development studies were promptly initiated.

It was first necessary to determine if the material would meet the electronic component encapsulation requirements, then to develop the processes and tooling needed to build a quality product in scheduled quantities. Concurrently an investigation began to determine the properties of the basic material and to study the effect various processing parameters have on the material; repeatability and reliability controls were dependent upon these evaluations.

No commercial product was found which would substitute for Ablefoam 5. To prevent subjecting parts schedules to single source control, the design agency asked Bendix to conduct formulation studies to find a suitable back-up foam material.

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INVESTIGATION OF ABLEFOAM PROPERTIES

MATERIAL

The rigid epoxy foam system investigated (Ablefoam 5, BKC Material Specification 2140587) is known to be a blend of aromatic and aliphatic epoxy resins, amine curing agents, and a solid blowing agent that decomposes when heated. Since the epoxy resins are premixed with the curing and blowing agents, the one-component system must be continuously maintained at minus 60°F or colder to prevent premature reaction. When stored at minus 60°F the shelf life is at least six months.

The premixed material is normally packaged in polyethylene cartridges. At room temperature the frozen premix will thaw to an extrudable temperature within 1 hour. The liquid premix has a work life of approximately 1 hour after thawing.

According to the manufacturer, this material was developed specifically as an encapsulating foam for electronic components. The material has been molded successfully in this application in foam densities of between 10 and 30 pounds per cubic foot. When molded at low densities or in open molds, the cell structure is undesirable. At high densities or in thick cross-sections of foam the exotherm temperatures developed may be detrimental or prohibitive.

Whenever possible, specimens were tested by standard ASTM procedures. In some cases other accepted test methods were employed, particularly for the determination of thermal properties of the foam system. Listed in Table 1 are the properties tested, testing method, and specimen size.

MECHANICAL PROPERTIES

Compressive Strength

Compressive strength is a convenient test of the mechanical strength of a foam. Throughout this characterization study on epoxy foam, the compressive strength was determined using either one cubic inch cylinders or one-inch cubes. Since this foam system is basically an epoxy polymer using an amine curing agent, the exotherm temperature developed is significant and must be considered in this molding application. Evaluation of actual exotherm data is discussed below. Since thick cross-sections cannot be molded from the material, the compressive test specimens were not homogeneous foam samples cut from the center of

Table 1. Test Methods for Characterization of Epoxy Foam

Property	Test Method	Specimen Size
Mechanical		
Compressive Strength	ASTM D-695	1 by 1 by 1 inch
Tensile Strength	ASTM D-1623	1 by 1 by 1 inch Type B
Shear Strength	ASTM D-732	2 by 2 by 1/4 inch
Flexure Strength	ASTM D-790	5 by 1/2 by 1/2 inch
Thermal		
Thermal Expansion	ASTM D-696	0.45-inch diameter by 4 inches
Thermogravimetric Analysis (TGA)	15°C/minimum temperature rise/nitrogen atmosphere	
Thermomechanical Analyzer (TMA)	10°C/minimum temperature rise/5 gram penetration	
Differential Thermal Analysis (DTA)	15°C/minimum temperature rise/nitrogen atmosphere	
Thermal Conductivity	ASTM C-177	8-inch diameter by 0.25-inch thick
Electrical		
Dielectric Strength	ASTM D-149	4 by 4 by 0.1 inch
Volume Resistivity	ASTM D-257	4 by 4 by 0.1 inch
Dielectric Constant	ASTM-D-150	2-inch diameter by 0.1 inch
Dissipation Factor	ASTM D-150	2-inch diameter by 0.1 inch

a larger molded block, as is most data listed for rigid urethane foams. Part of the samples were taken from molded 6 by 6 by 1 test blocks, and part were taken from 1.129-diameter by 8-inch-long cylinders.*

The test cubes cut from the 6 by 6 by 1 block had molded skin on two faces. Thus the two standard test directions (perpendicular and parallel to platen travel) have more significant effect on compressive strengths. Borrowing from the terminology of sandwich structure, edge testing is parallel-to-foam rise with the two skin faces carrying most of the load. In flat testing, the molded skin surfaces are on the platens and the lower density center portion is loaded perpendicular to foam rise. A typical foam block is shown in Figure 1.

The cylindrical test specimens are machined from 1.129 diameter by 8-inch-long molded cylinders. Figure 2 shows the molded cylinder and location of test specimens. These cylindrical test specimens have molded skin around the periphery of the specimen and can be compression-loaded in only one direction.

That the test specimens have high density skins on two faces significantly alters the strength, depending upon the direction of testing. Figure 3 shows a typical stress-strain relationship for the Ablefoam 5 molded to a density of 22 lb/ft^3 and cured 4 hours at 165°F. Normally, both the edge and flat tests have the same compressive moduli of approximately 30,000 psi at room temperature. At 200°F the modulus drops to about 12,000 psi. The flat specimens exhibit a yield point at between 2 and 5 percent strain while the edge specimens do not reach an ultimate before 10 percent strain. The compressive strength is typically 1000 psi for edgewise at 77°F, 600 psi flatwise at 77°F, and 300 psi flatwise at 200°F.

The specimens machined from the molded cylinder have a similar stress-strain relationship. However, the cylinders do tend to have higher compressive strengths at a particular density because of the density distribution within the test specimen. Compressive strength values for specimens tested at room temperature are about 1200 psi, while at 200°F the value is about 450 psi.

As with other types of rigid polymeric foam materials, the strength is a function of the density. Figure 4 is a log-log plot of density versus strengths for foam cured 4 hours at 165°F. These curves allow the prediction of strength from density measurements, and are used to normalize test data to a particular chosen density. The curves for room temperature strengths have slopes of 1.7 and 1.9.

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* All foam block and specimen dimensions are in inches throughout this report.

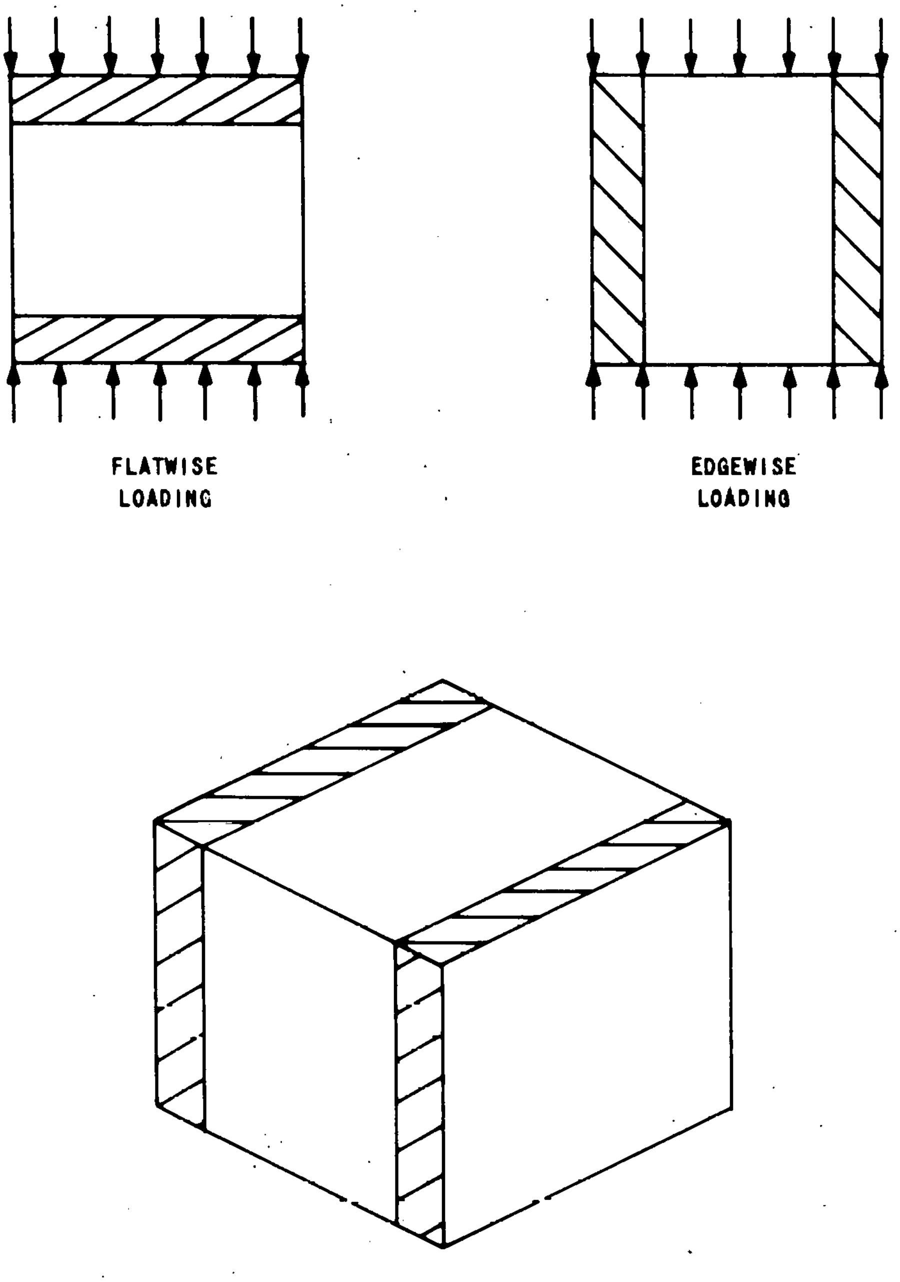

Figure 1. Typical Foam Test Specimen

Figure 5 is a log-log plot of curves for compressive modulus versus density. The slope for the room temperature tests is about 1.65 with intercepts of 2 to 3. The 200°F test has a slope of about 1.2 with an intercept of 3. The data scatter is much greater for the 200°F tests than for the room temperature tests.

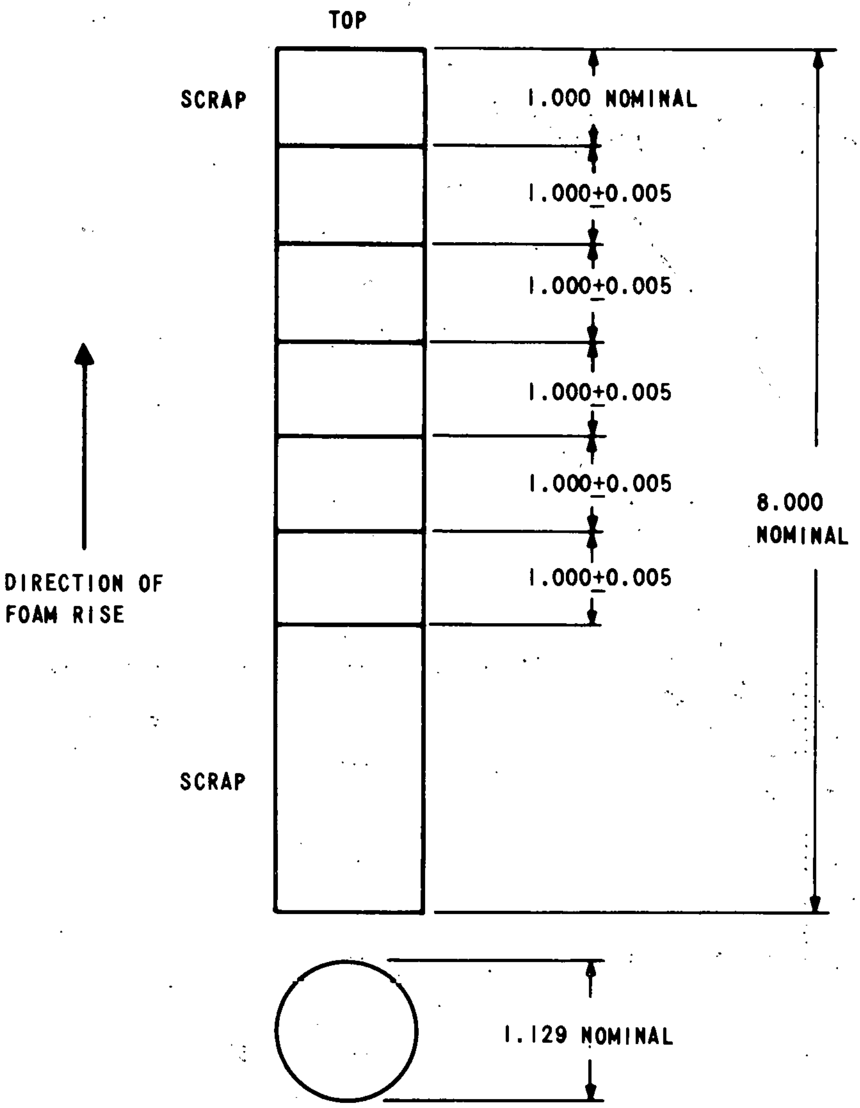

Figure 2. Molding for Cylindrical Test Specimens

Figures 4 and 5 (depicting the effect of density on compressive strength) are drawn from data collected on the 1-inch cubes machined from the standard 6 by 6 by 1 test block. The cylindrical test specimens exhibit a similar effect, but the individual test values at a particular density are greater for the cylinder than the 1-inch cubes. This greater measured strength is due to the density variation within the test specimen.

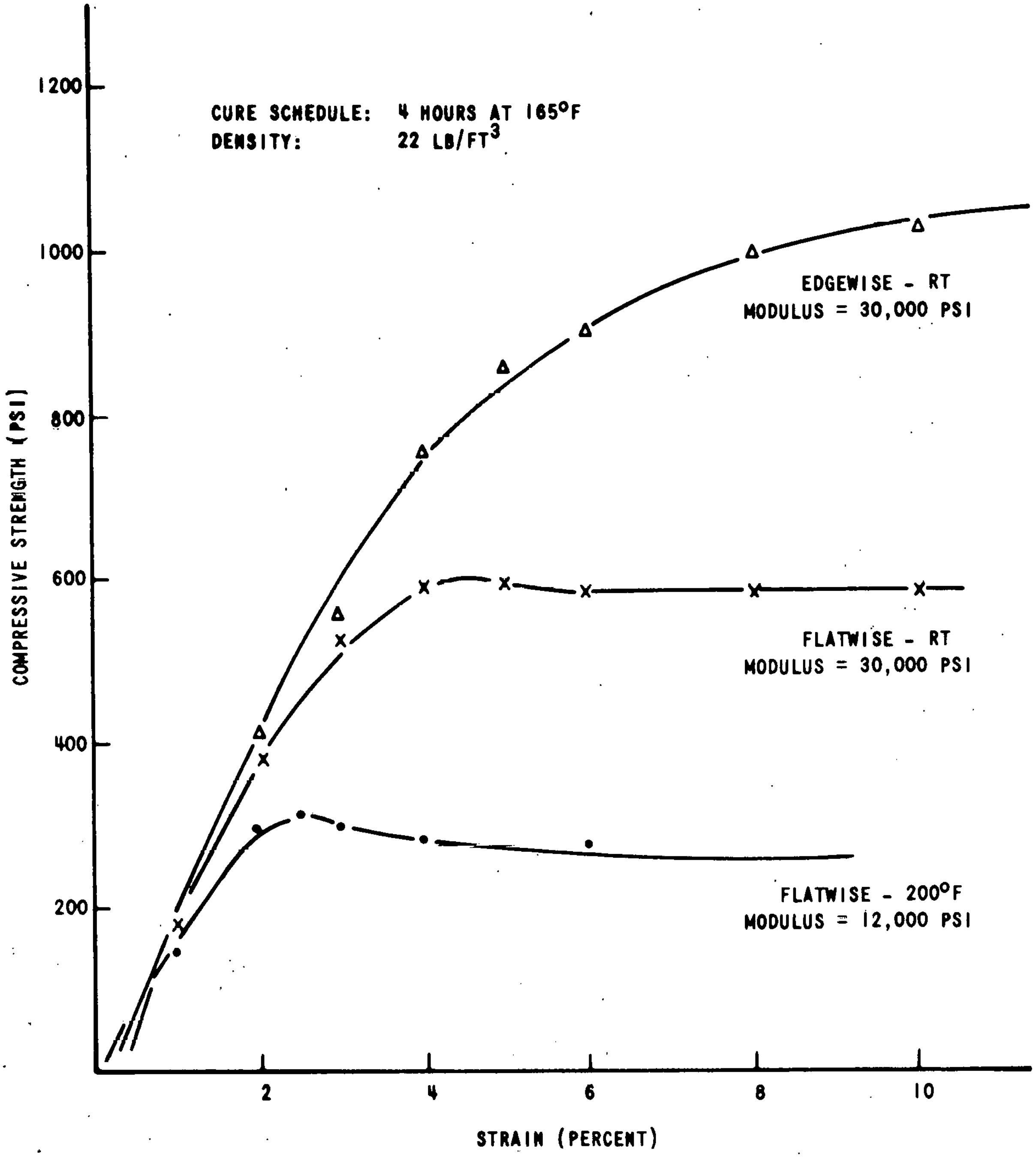

Figure 3. Compressive Stress-Strain Curves for Epoxy Foam

An in-depth study of this density variation or skin effect was made by Mr. R. D. Hermansen (Organization 5513 of Sandia) during the Round Robin Testing of Ablefoam. (See Page 51.)

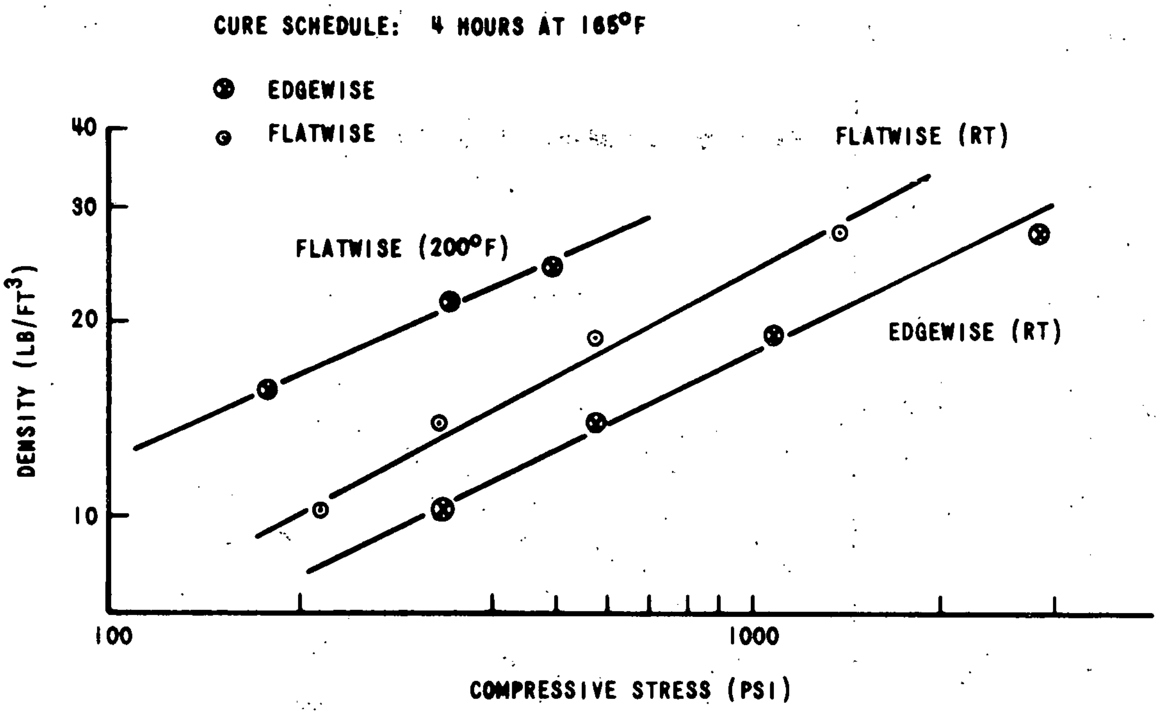

Figure 4. Density Versus Strength Graph

Tensile Strength

The tensile strength of Ablefoam 5 was tested per ASTM 1623, using 1-inch cubes bonded to aluminum blocks. The tests were performed at room temperature, 165°F, and 200°F at molded densities of 10, 20, and 30 lb/ft^3. Part of the specimens were tested perpendicular-to-rise and part parallel-to-rise. A summary of the test data is listed in Table 2. While these data are from two different lots tested at different times, the data may not be a complete picture of the Ablefoam population; for instance, the test values for the 30-lb/ft^3 foam samples are the same as the 20-lb/ft^3 samples. However, these data do indicate that the tensile strength does increase with higher densities and does decrease with higher test temperatures.

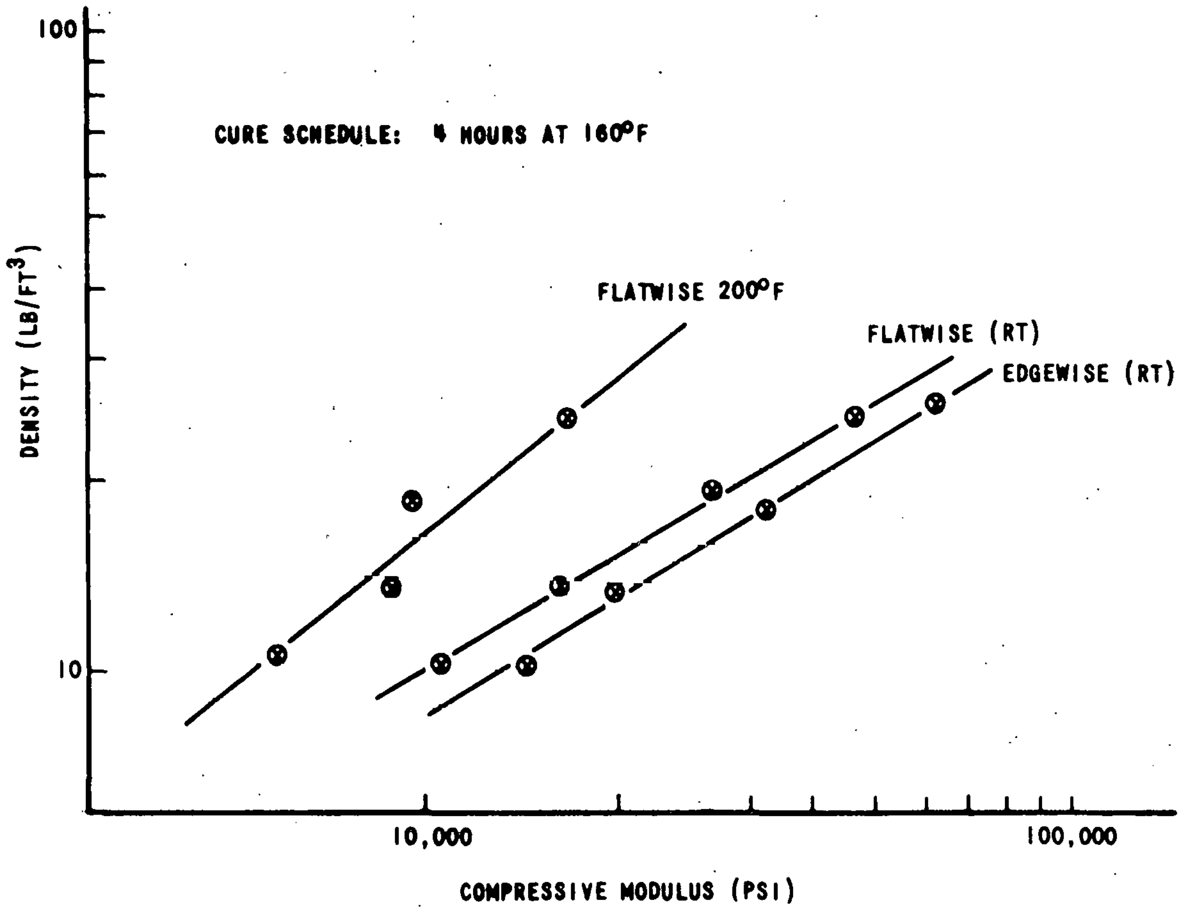

Figure 5. Density Versus Compressive Modulus Graph

Shear Strength

Limited data has been collected on the shear strength of Ablefoam 5 tested per ASTM D-732 using 2 by 2 by 1/4 test specimens. The shear strength was determined as a function of density for specimens cured at 165°F for 4 hours and tested at temperatures of 75 and 200°F. As shown in Figure 6, the shear strength varies from 650 psi at 25 lb/ft^3 to about 200 psi at 10 lb/ft^3. The shear strength is, of course, reduced when the test temperature is increased to 200°F. At 200°F the shear strength is about 500 psi at 25 lb/ft^3 and 150 psi at 10 lb/ft^3.

Flexural Strength

Flexural strength data as a function of density, cure temperature, and test temperature were collected on one set of test specimens. The standard

Table 2. Tensile Strength of Ablefoam 5

Foam Density (lb/ft^3)	Test Temp. (°F)	Test Orientation	Average Tensile Strength (psi)
10	75	*	186
10	75	**	145
20	75	*	373
20	75	**	400
30	75	*	326
30	75	**	392
22	75	**	460
22	165	**	385
22	200	**	265

* Parallel to rise
** Perpendicular to rise

ASTM D-790 test method with 5 by 1/2 by 1/2 samples was used. As noted in Table 3, the actual test specimen density differs considerably from the overall density of the test block. All of these specimens were machined from the interior of a standard 6 by 6 by 1 test block. This difference in block and test specimen density reflects the density distribution within the molded block.

For test blocks cured at 165°F and tested at 75°F, the flexural strength ranged from 380 psi at 15 lb/ft^3 to 900 psi at 26 lb/ft^3. When tested at 200°F the values dropped to about 216 psi at 15 lb/ft^3 and 575 psi at 26 lb/ft^3. Increasing the cure temperature from 165°F to 200°F does increase the flexural strength.

ELECTRICAL PROPERTIES

The electrical properties of Ablefoam 5 compare favorably with other polymeric materials used to package electronic equipment. However, the electrical properties of cellular materials are difficult to measure and the data scatters may be significant. Also, since the individual test specimens were machined from 6 by 6 by 1 blocks the density differences are important and must be considered.

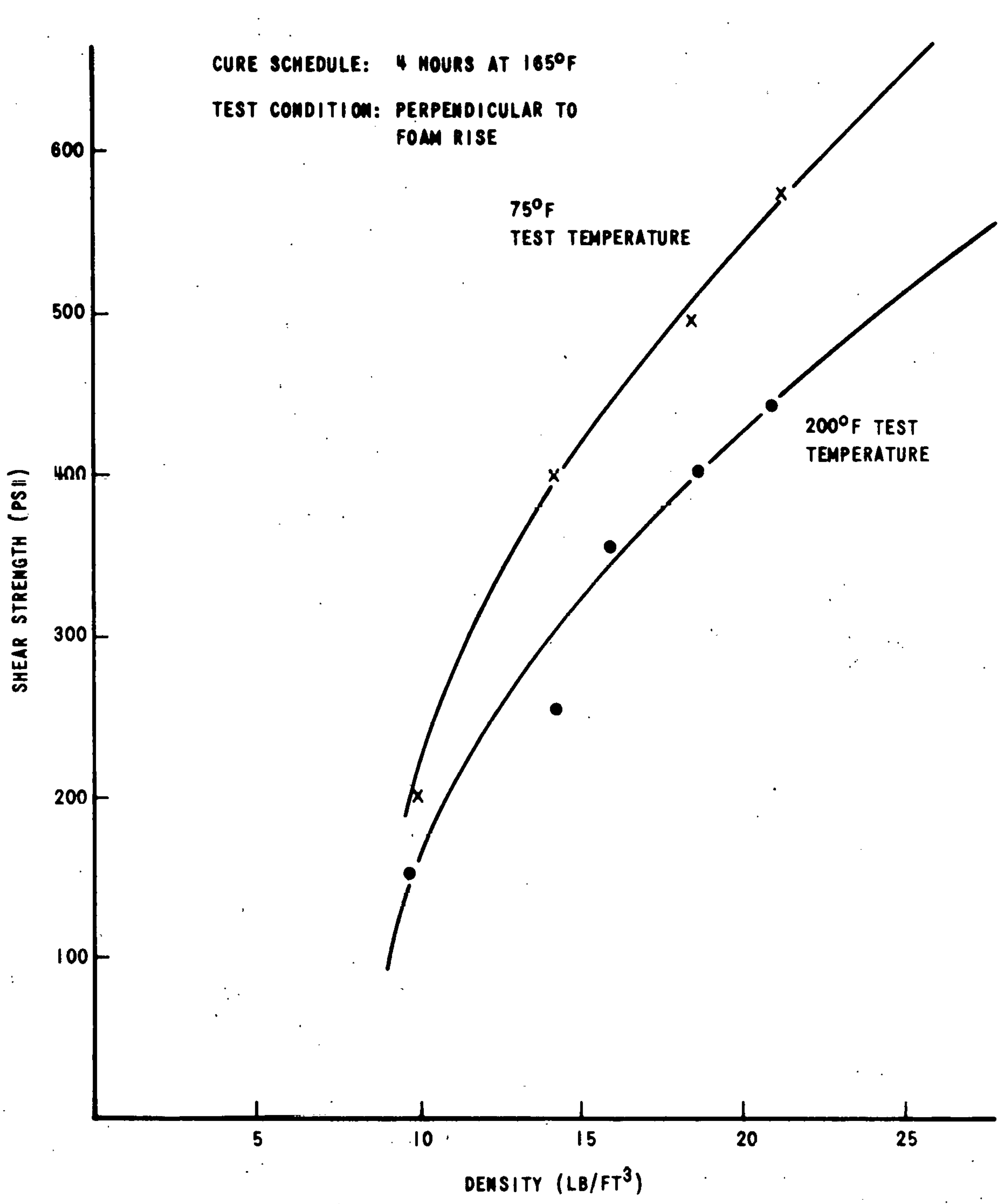

Figure 6. Shear Strength Versus Density Graph

Table 3. Flexure Strength of Epoxy Foam*

Density (lb/ft^3)		Cure Temp (°F)	Test Temp (°F)	Flexural Strength (psi)
Block	Specimen			
15	10.0	165	75	381
22	13.9	165	75	657
26	17.3	165	75	907
15	10.0	165	200	216
22	14.6	165	200	445
26	16.8	165	200	575
15	12.2	200	75	475
22	18.4	200	75	955
26	20.7	200	75	1156
15	12.4	200	200	362
22	16.8	200	200	645
26	10.7	200	200	864

* Tested perpendicular-to-foam rise

To determine dielectric strengths, the 4 by 4 by 0.1 specimens were machined from the standard 6 by 6 by 1 test blocks and tested per ASTM-D 149. The dielectric strength of solid epoxy in comparable thickness is 425 volts per mil. Tested values of the epoxy foam are shown in Figure 7 and are about 50 to 70 volts per mil over a density range of 10 to 15 lb/ft^3. Contrary to expected results, the dielectric strength decreased with increasing density.

In another series of test data, the dielectric strength values were fairly constant at 84 to 88 volts per mil for densities of 18 to 26 lb/ft^3. While the available data are not consistent, all the test values seem to be in the range of 50 to 90 volts per mil over the entire density range of Ablefoam 5.

The volume resistivity was also determined from specimens machined from 6 by 6 by 1 test blocks. The standard ASTM-D 257 test method with 4 by 4 by 0.1 test specimens was used. Typical resistivity values of 10^{13} ohm-centimeters (ohm-cm) have been reported in the literature for epoxy foams. Figure 8 is a plot of volume resistivity versus test temperature for the one-component epoxy foam system; values in the order of 10^{13} to

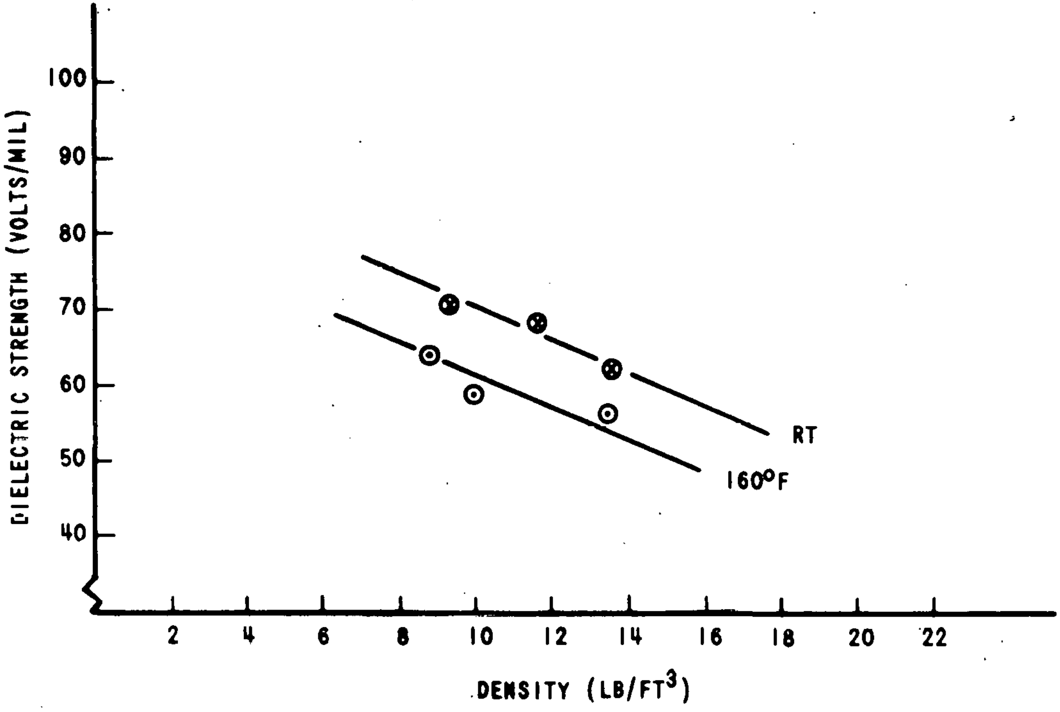

Figure 7. Dielectric Strength Versus Density Graph

to 10^{10} ohm-cm over a temperature range of 75 to 350°F were measured. Volume resistivity measurements are difficult to run, and repeatable results are not always obtained. However, these data are consistent with data for other cellular materials.

The dielectric constant and dissipation factors were tested in accordance with ASTM D-150 using 2-inch-diameter by 0.1-inch-thick specimens. Once again, the test specimens were machined from 6 by 6 by 1 molded test blocks. The test values for dielectric constant as a function of density and frequency are depicted in Figure 9 and the corresponding dissipation factors are shown in Figure 10. The dielectric constant does tend to increase with higher densities and to decrease slightly with higher frequencies. The values at room temperature ranged from about 1.4 at 10 lb/ft^3 to about 2.4 at 30 lb/ft^3 when tested at 10^2Hz. At 10^6Hz, under similar conditions, the test values ranged from 1.3 at 10 lb/ft^3 to 2.0 at 30 lb/ft^3. The companion dissipation factor ranged from about 0.01 to 0.03 over a density range of 13 to 30 lb/ft^3 at low frequencies. Increasing the test frequency tended to increase the dissipation factor.

A more recent series of tests shows the dielectric constant to be more independent of density and frequency. In this series the values ranged from 1.4 at 18 lb/ft^3 to 1.6 at 26 lb/ft^3 as tested at low frequency (10^2Hz).

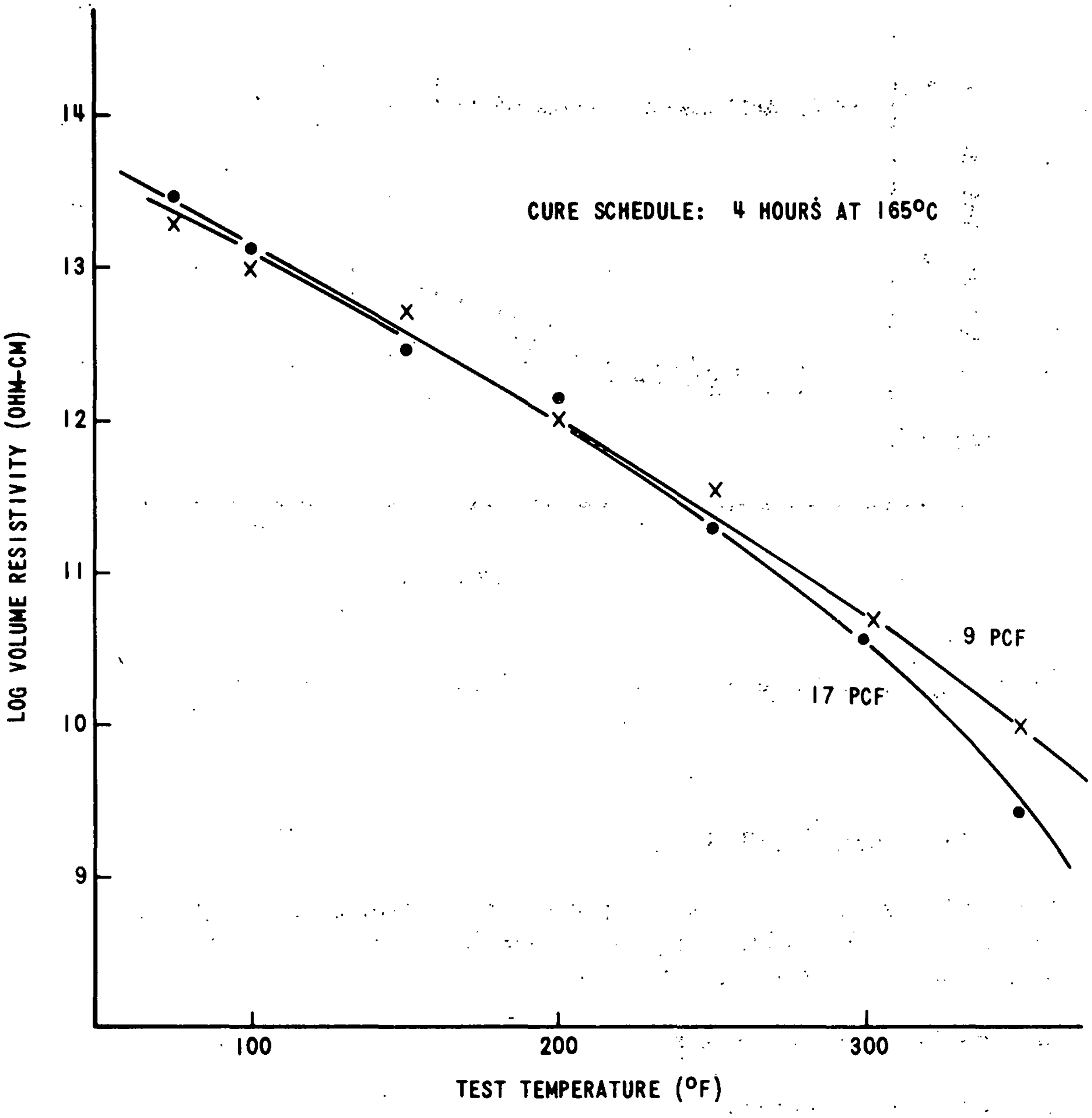

Figure 8. Volume Resistivity Versus Test Temperature Graph

At a higher frequency (10^6Hz) the test values were 1.3 at 18 lb/ft^3 and 1.5 at 26 lb/ft^3 for a solid epoxy resin, a typical value for dielectric constant is 3.8, and 0.003 to 0.03 for the dissipation factor when tested at 10^3Hz and 25°C (77°F).

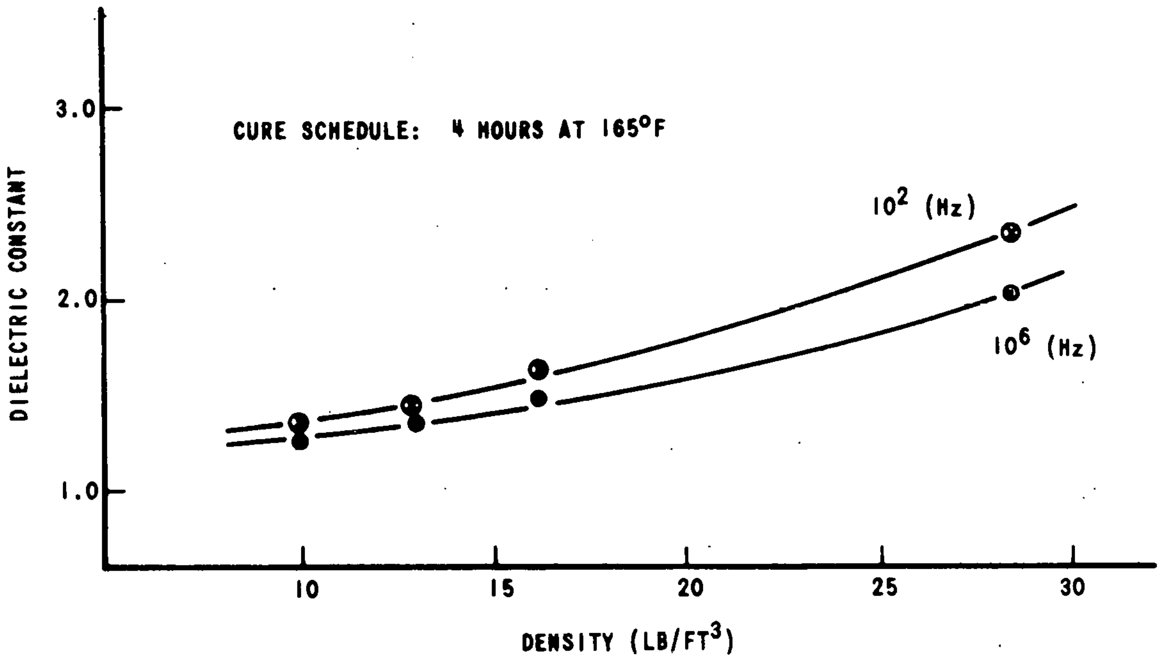

Figure 9. Dielectric Constant Versus Density Graph

THERMAL PROPERTIES

The behavior of polymeric materials used to package electronic components under thermal cycling is important. These thermal properties of Ablefoam 5 have been evaluated:

- Coefficient of thermal expansion;
- Thermal conductivity;
- Thermogravimetric analysis (TGA);
- Differential thermal analysis (DTA); and
- Thermomechanical analysis (TMA).

Other thermal properties, such as exotherm temperatures and effect of thermal cycling, are discussed below.

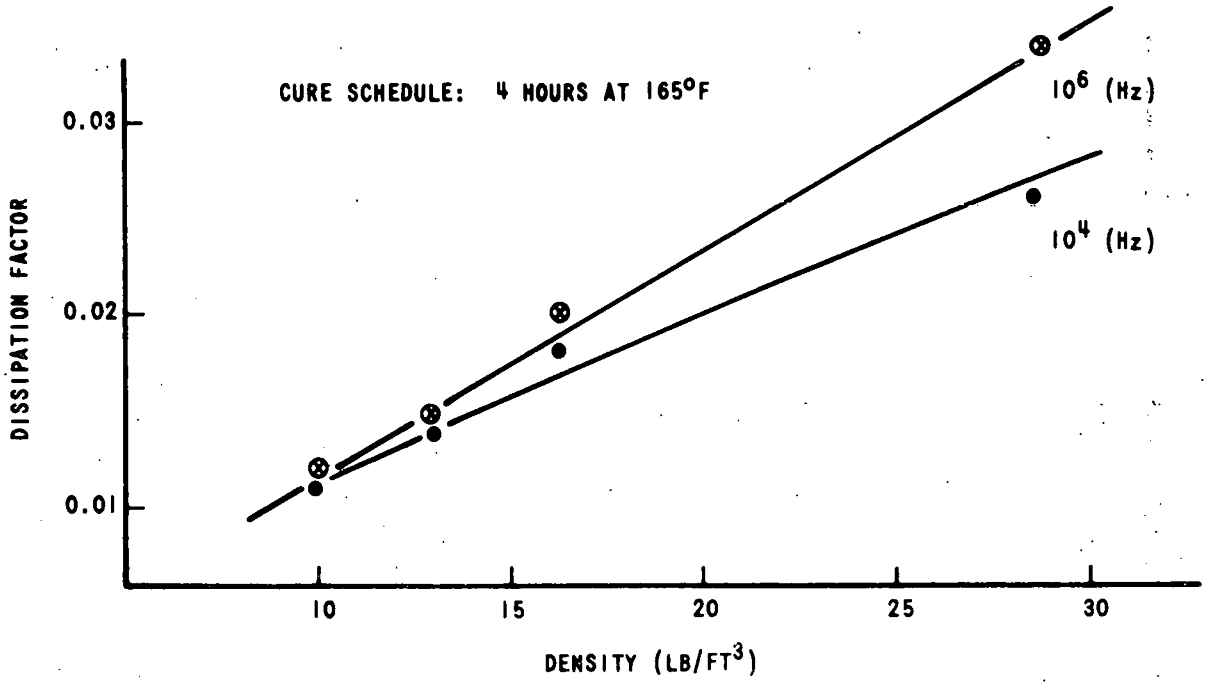

Figure 10. Dissipation Factor Versus Density Graph

Coefficient of Thermal Expansion

A quartz tube dilatometer in a horizontal position, with 0.45-diameter by 4-inch-long test specimens (ASTM D-696), was used to measure the thermal expansion of the epoxy foam.

With this apparatus, the maximum test temperature was 165°F. The samples tended to deform at temperatures greater than 165°F and gave erroneous results. In the range of -65°F to 165°F, linear thermal expansion for densities of 17 to 32 lb/ft^3 was 21 to 28 for 10^6 in./in./°F.

Thermal conductivity was tested in accordance with ASTM C-177 using 8-inch diameter and 1/4-inch thick samples. Thermal conductivity was measured as a function of density and test temperature. No difference in conductivity was noted between two lots of material. Figure 11 is a plot of thermal conductivity versus density for specimens cured at 165°F for 4 hours. The conductivity varied from 0.279 at 12 lb/ft^3 to about 0.469 at 28 lb/ft^3. At 22 lb/ft^3 the value is about 0.400 BTU-in./hr-ft^2-°F. The thermal conductivity was measured at slightly below room temperature (60-70°F) and at 160 to 170°F. The testing equipment was allowed to stabilize at any temperature within these ranges. For the samples tested, the conductivity at 165°F is about 5 to 10 percent greater than at 65°F.

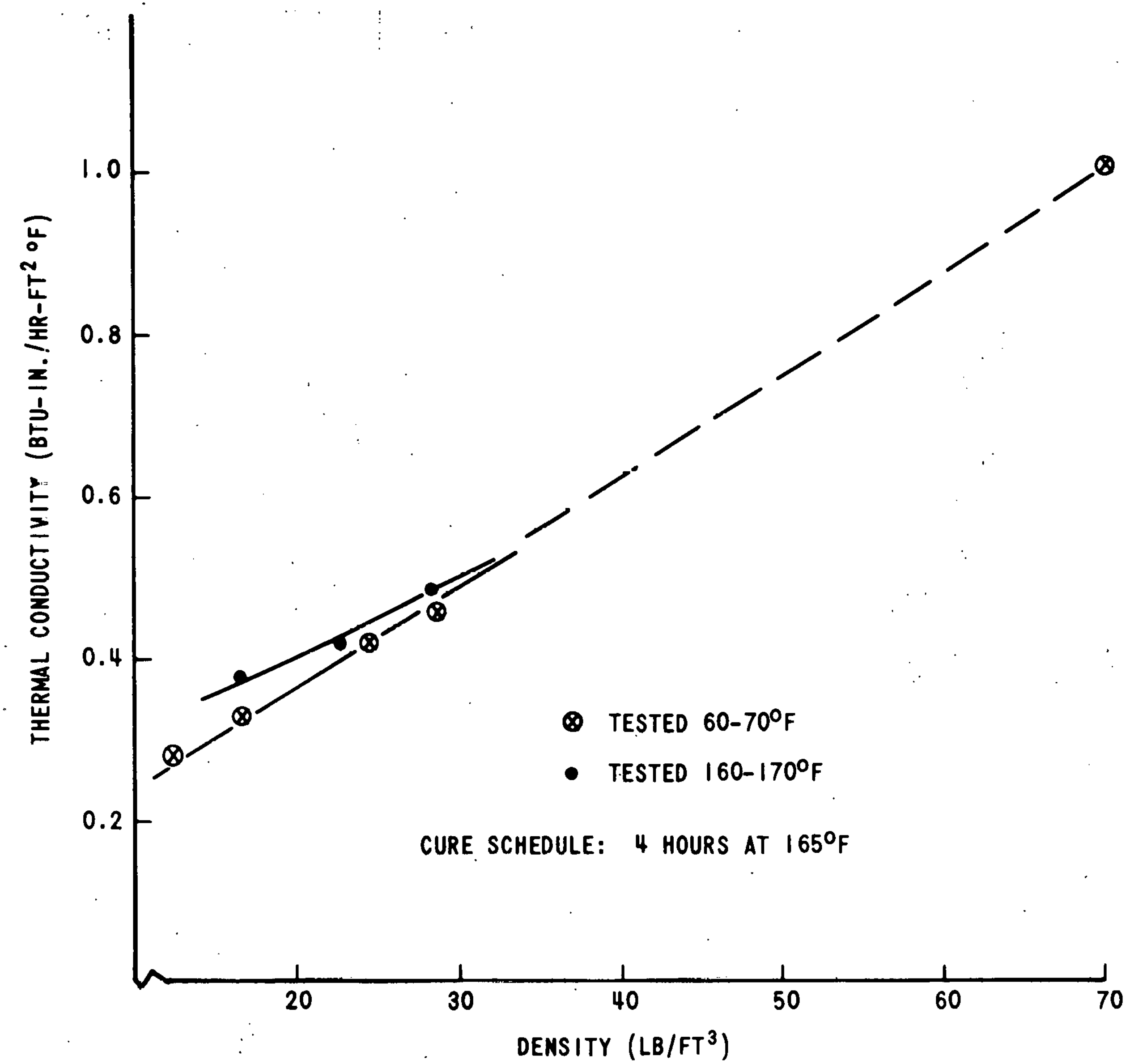

Figure 11. Thermal Conductivity Versus Density Graph

This difference between 165°F and 65°F test values diminishes as the density increases. A sample of the liquid epoxy premix was allowed to cure at room temperature without any foaming. The thermal conductivity of this sample was 1.03 BTU-in./hr-ft^2-°F which is the limiting value of Ablefoam 5. Typical values for thermal conductivity for cast epoxies range from 1 to 9 BTU-in./hr-ft^2-°F.

Thermogravimetric Analysis (TGA) tests have been made on samples of unfoamed solid epoxy cured at room temperature as well as samples cured at 165 and 325°F. Foam densities of 11 and 22 lb/ft^3 were investigated. The thermograms for all samples show a weight loss commencing at 220°C to 250°C (425 to 480°F) and having the same general shape. From this limited data, it was shown that the percent residue increased with density and with cure temperature. A typical curve is shown in Figure 12.

Differential Thermal Analysis (DTA) data was collected on samples cured the same as for the TGA. The DTA of the unfoamed epoxy cured at room temperature is interesting. This trace shows an endotherm at 50°C (120°F) followed immediately by a broad exotherm, as shown in Figure 13. The endotherm is the decomposition of the solid blowing agent followed by additional curing of the epoxy resin. The initial decomposition exotherm starts at about 260°C (500°F).

Thermomechanical Analysis (TMA) was used to determine the glass transition temperatures (Tg) of samples cured at 165, 250, and 325°F for 2, 4, and 8 hours. These results are given in Table 4. The results indicate that the Tg is increased markedly by increasing the cure temperature from 165 to 325°F. Increasing the cure time also increases the Tg. In this case the fact that the Tg does increase with both cure time and cure temperature means that the standard cure of 4 hours at 165°F is a minimum cure.

Table 4. Glass Transition Temperatures (Tg) of Epoxy Foam

Cure Condition		Glass Transition Temp	
Temp (°F)	Time (hr)	(°C)	(°F)
165	4	101	214
165	4	113	235
165	4	110	230
165	4	103	217
250	2	124	255
250	4	138	280
250	4	137	279
250	8	140	284
325	2	133	271
325	4	140	284
325	8	160	320

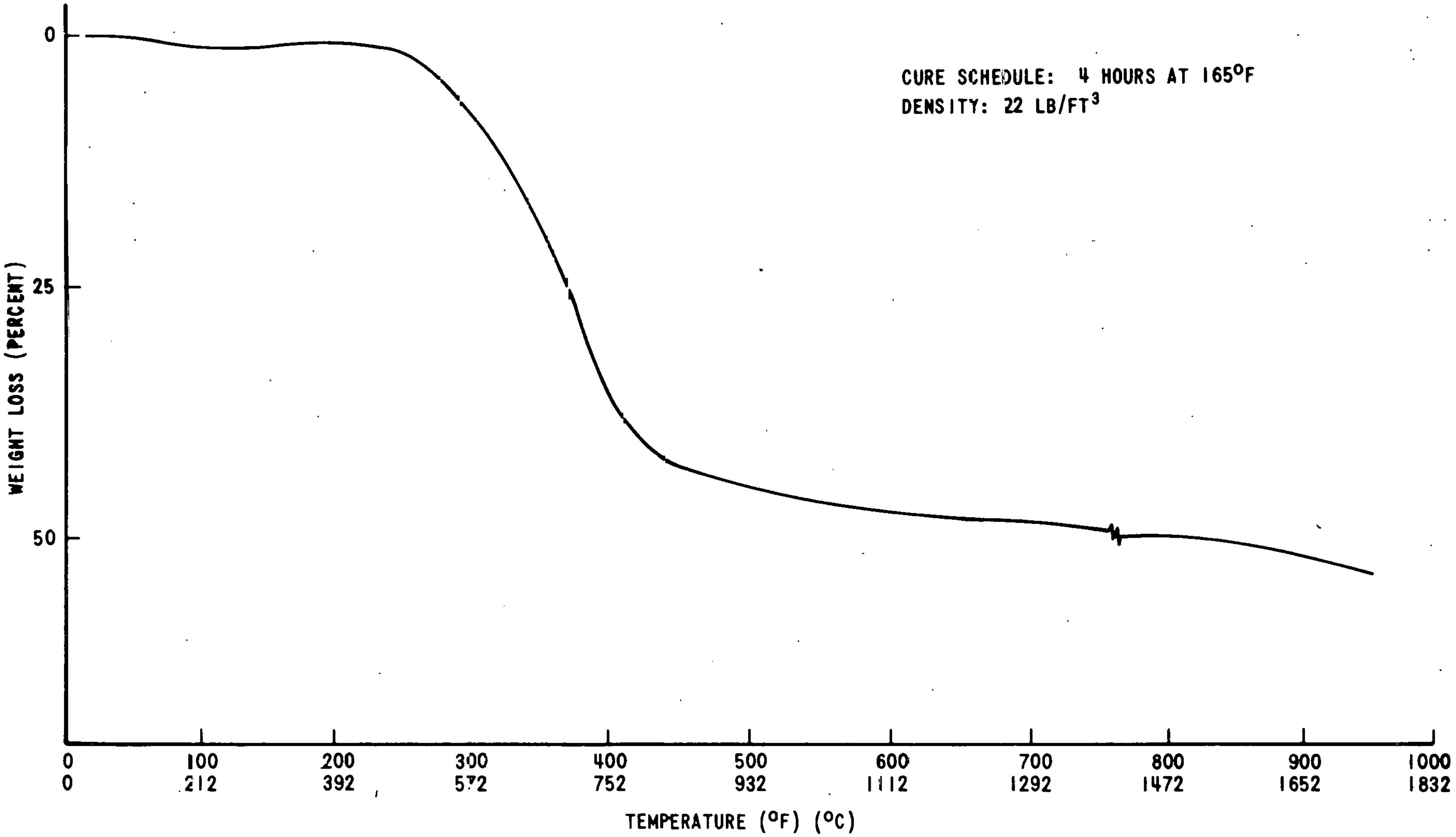

Figure 12. Typical Thermogravimetric Analysis Curve of Epoxy Foam

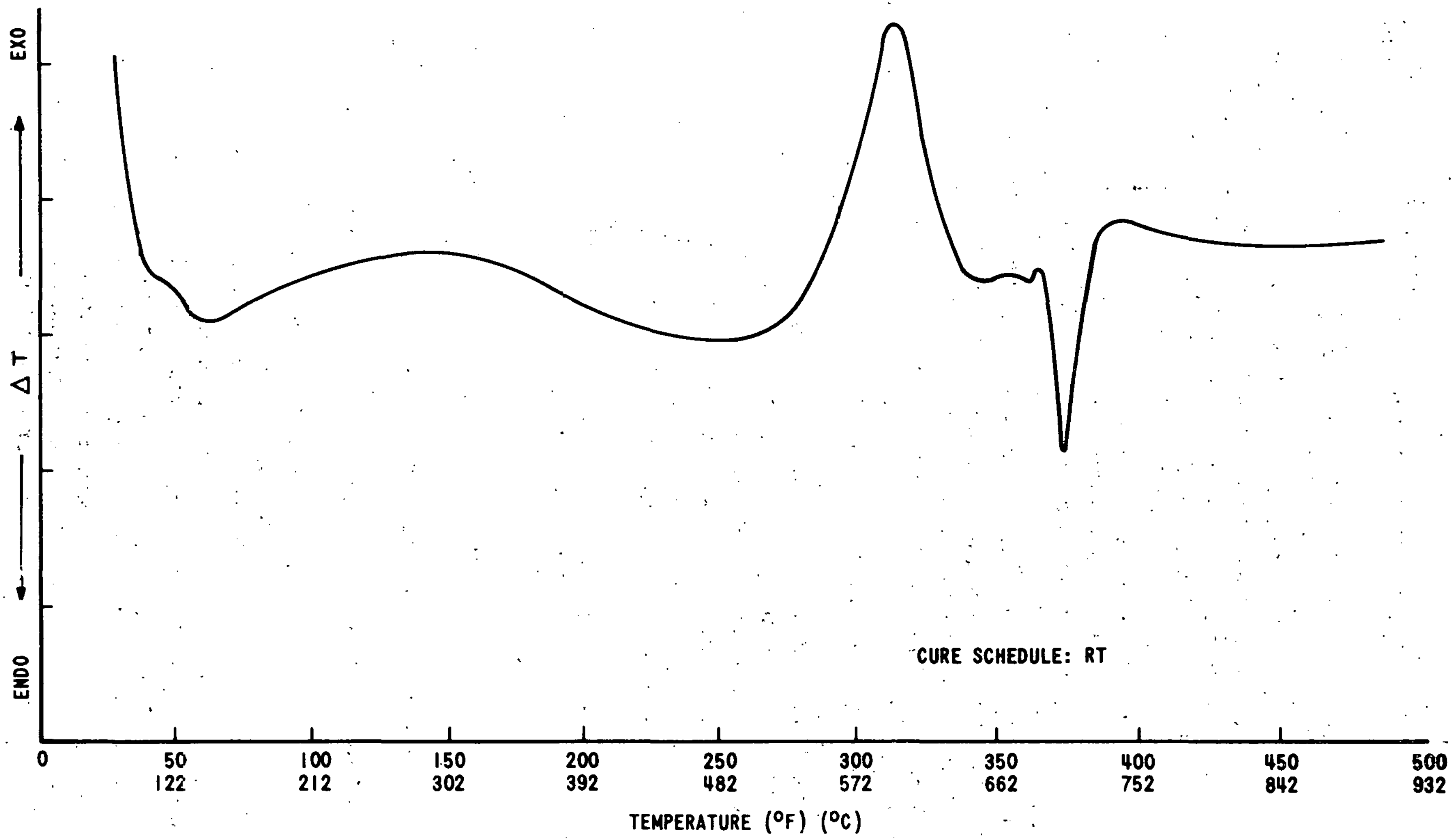

Figure 13. Typical Differential Thermal Analysis Curve of Unfoamed Epoxy

ENVIRONMENTAL PROPERTIES

Moisture absorption tests have been made by both Sandia and BKC to determine the effect of relative humidity on weight and dimensional stability. Relative humidities (RH) of 50 percent, 30 percent, 10 percent, and desiccant storage, have been investigated. The blocks tested at 30 and 50 percent relative humidity were first conditioned at 165°F and 5 mm Hg for 15 hours, followed by 30 days in desiccant storage. This conditioning before testing was to insure dry, stable blocks; the gases evolved during cure were replaced with dry air. Thus, when exposed to higher RH, the weight change was due to absorbed water. The primary reason the blocks were tested at 10 percent RH and desiccated storage was to simulate conditions in the production area to determine the effect of postcure on stabilization time. Test blocks were cured at 165°F for 4 hours and then postcured, out of the mold, for an additional 24 hours at 165°F. Other blocks were simply cured for 4 hours at 165°F. Part of the blocks from each cure condition were stored at both 10 percent RH and in desiccant. Thus, in addition to moisture absorption, the weight change was due to diffusion of gas into and out of the polymer.

The gases that expand the foam are the thermal decomposition products of ammonium carbonate. The theoretical decomposition products are ammonia, carbon dioxide, and water. Once the polymer has been expanded and cured, these gases diffuse into the atmosphere and air diffuses into the polymer. To determine the change in weight because of gas diffusion, several assumptions must made.

- Assume 2 to 3 percent blowing agent. While the actual blowing agent content is proprietary, it is believed to be about 2 to 3 percent dry weight.

- Assume that all decomposition products leave the polymer.

- Assume a polymer specific gravity of 1.2.

- Assume a foam density of 22 lb/ft^3 = 210 grams in a 6 by 6 by 1 mold.

Based upon these assumptions, approximately 0.5 grams of air would fill the voids in the foam under standard Kansas City conditions of 740 mm Hg and 70°F. About 4 to 6 grams of gas would be evolved for a weight change of 3.5 to 5.5 grams. Thus the weight change because of gas diffusion is 1.74 to 2.75 percent. However, this percentage is reduced by an undetermined amount of chemical reaction and by gas loss during foaming and cure. The ammonia that is evolved is reactive and can form a chemical bond with the epoxide group; this amount is being determined by SLA. Also, part of the gases escape from the polymer during foam rise and before the blocks can be demolded and weighed; this amount of weight loss is also unknown.

As mentioned above, a series of test blocks was prepared to determine the weight stabilization time for this epoxy foam. Weight measurements were taken for six weeks, using an analytical balance. The weights of the blocks were still decreasing for both the standard and the postcured blocks, but the rate of change was so low that measurements were stopped. All of the blocks postcured 24 hours at 165°F had a weight loss of between 0.1 and 0.2 percent for both desiccant and 19 percent RH storage. No significant difference in weight loss was noted between the test blocks stored in desiccant and the blocks stored at 10 percent RH. However, there was a slight difference in the weight loss of the blocks with the standard cure. The standard blocks with no postcure stored in desiccant had an average weight loss of 0.8 percent, while the 10 percent RH blocks had a weight loss of about 0.5 percent.

A typical weight loss versus time curve is shown in Figure 14. Based on the assumptions made above, the weight change because of gas loss should be about 2 percent of the total weight. This would mean that a large part of the gas evolved is lost during cure (including the reaction of the ammonia) or that the basic assumption of 3 percent blowing agent is too high. Blocks postcured 24 hours at 165°F increase in weight before any measured weight loss. This increase in weight prior to weight loss can be explained by differences in diffusion rates and gas pressure inside the foam. Thus the driving force, because of pressure gradient, is from the atmosphere to inside the foam. Air will move in until the total pressures are equal and then the gases will move in and out until the partial pressures of the gases are equal.

The weight and dimensional changes were measured on standard 6 by 6 by 1 test blocks that had been conditioned with heat and vacuum to ensure dry stable blocks. Figures 15 and 16 are plots of weight change versus time for 22 lb/ft^3 foam cured 4 hours at 165°F and preconditioned to remove water and evolved gases. The blocks at 50 percent RH were weighed for eight weeks and equilibrium was never really achieved. The weight change is a function of density, with 22 lb/ft^3 foam gaining about 2 to 2.2 percent by weight. The blocks at 30 percent RH were tested for only four weeks. The 22 lb/ft^3 blocks had started to level off at about 0.1 to 0.12 percent weight gain, but the 15 lb/ft^3 blocks were still picking up weight; after four weeks the 15 lb/ft^3 blocks had gained about 0.5 percent by weight, with an estimated equilibrium value of 0.8 percent.

Figures 17 and 18 are plots of percent dimensional change versus time at 50 and 30 percent RH. Once again, equilibrium was not achieved; the blocks were still growing after eight weeks at 50 percent RH. At the 50 percent RH level, the 22 lb/ft^3 blocks changed about 0.1 to 0.15 percent, while at 30 percent RH the change in length was about 0.3 percent. At 30 percent RH the data was quite scattered and the 0.01 percent change for the 22 lb/ft^3 block is just an indication that the block dimension did

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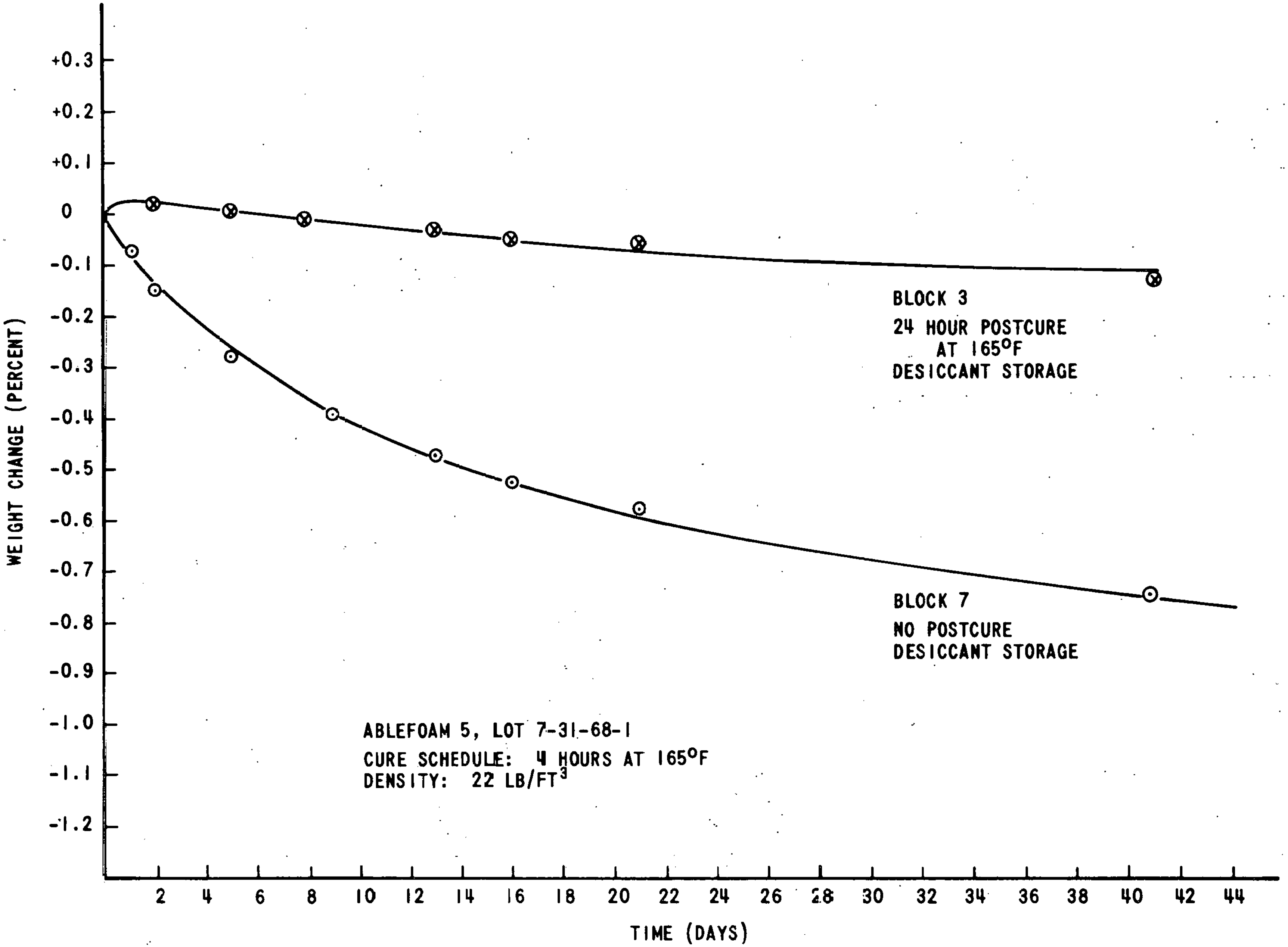

Figure 14. Typical Weight Loss Versus Time Cure Graph

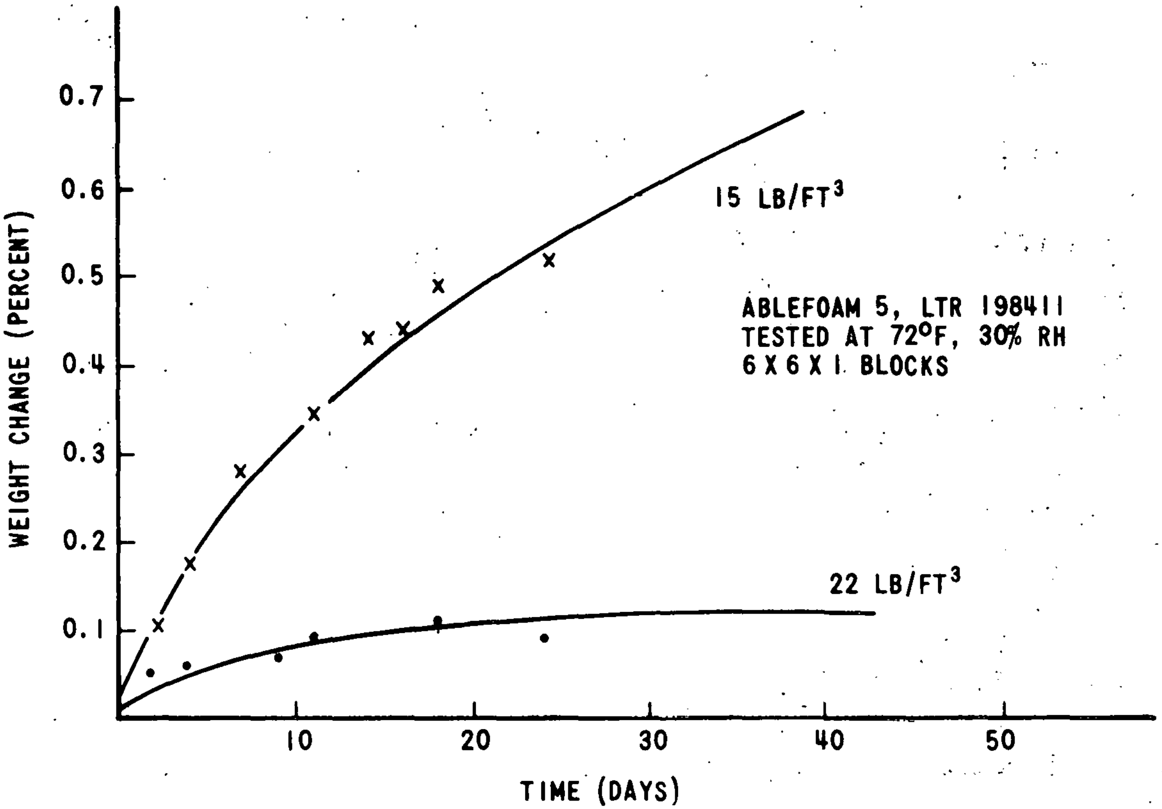

Figure 15. Plot of Weight Change Versus Time, at 30 Percent Relative Humidity

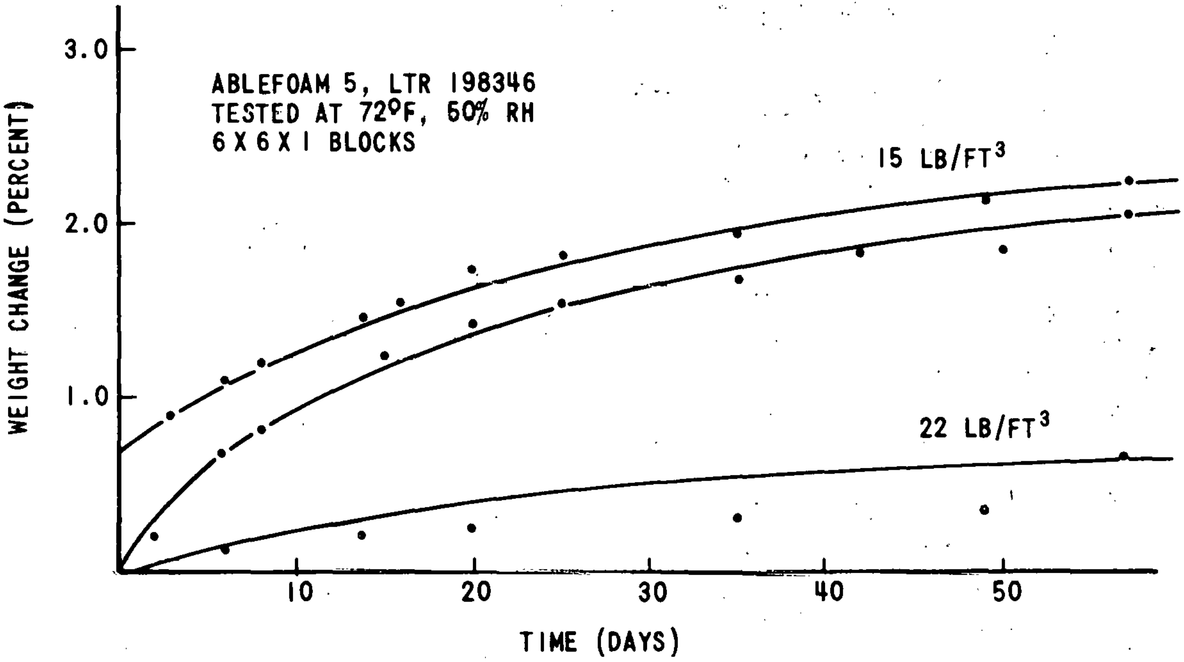

Figure 16. Plot of Weight Change Versus Time, at 50 Percent Relative Hunidity

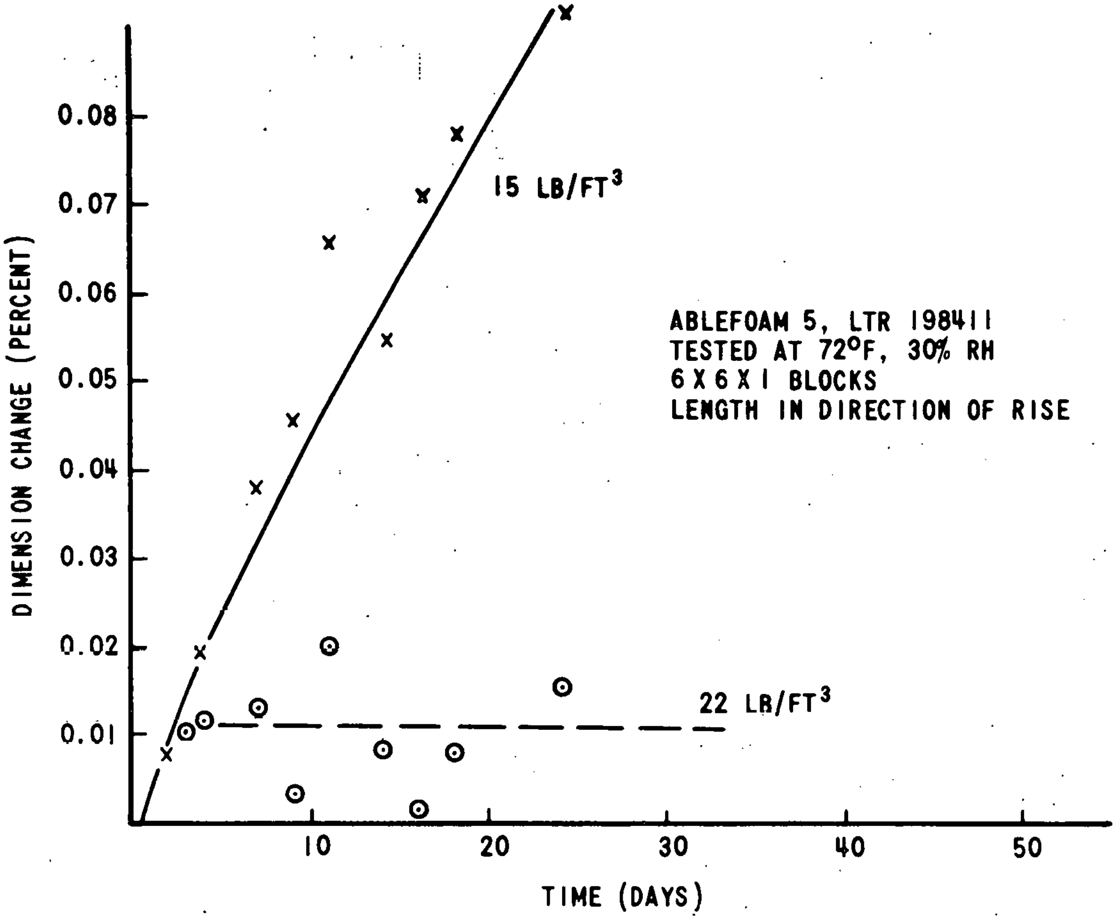

Figure 17. Plot of Percent Dimensional Change Versus Time, at 30 Percent Relative Humidity

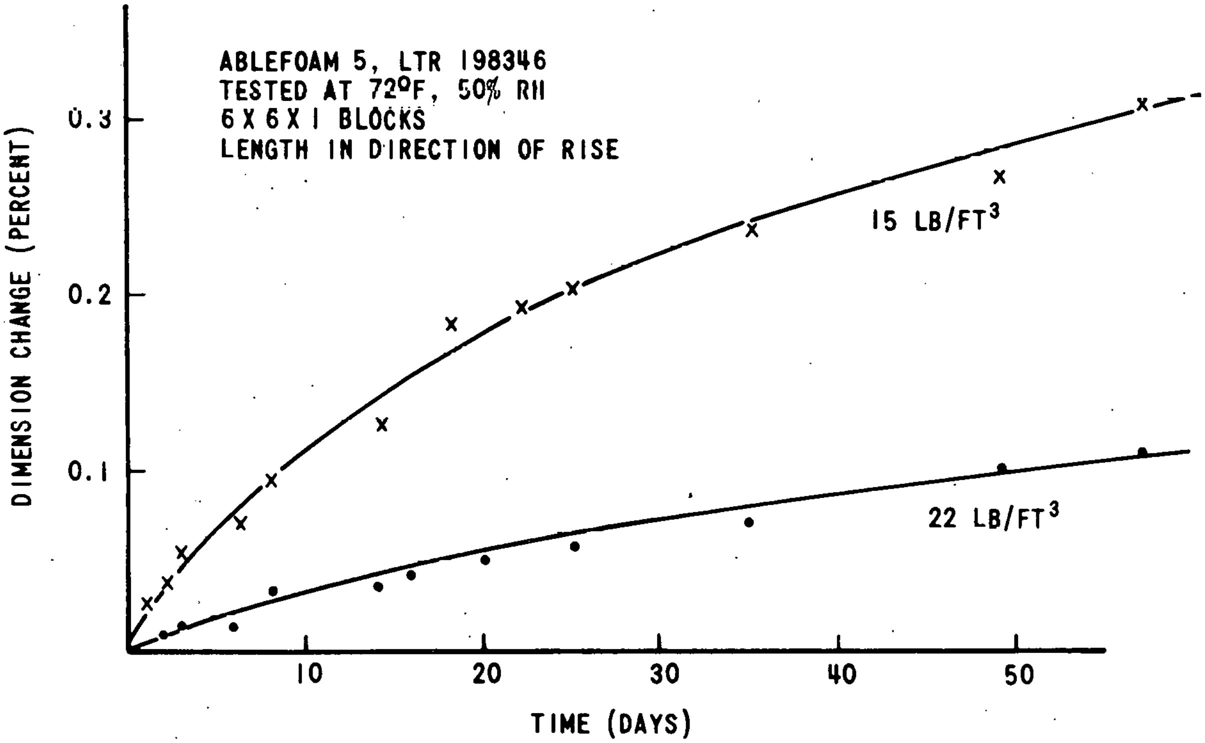

Figure 18. Plot of Percent Dimensional Change Versus Time, at 50 Percent Relative Humidity

change. The 15 lb/ft^3 blocks changed considerably more than the 22 lb/ft^3 blocks, but equilibrium was not reached.

Thermal Stability

The thermal stability of cured foam was measured on a series of nine blocks. Basically these data show that to assure dimensionally stable parts, the cure temperature of the foam should not be exceeded during use. Test blocks were made at 22 lb/ft^3 and cured at 140, 160, and 200°F. Samples from each cure temperature were then heated to 140, 160, and 200°F, measured, and then allowed to cool. Two heating, measuring, and cooling cycles were made. The height, width, and thickness of each block was measured using a gage block technique with dial indicators. The foam is fairly isotropic and the changes in dimensions are essentially the same for the three directions. Therefore, only the changes in the height dimensions are listed in Table 5. Due to the thermal expansion of the foam, the blocks were all larger (had positive change) when measured at the test temperature. In all cases the higher cure temperatures lead to lower expansion rates. This may be attributed to higher degree of cure or greater cross link density. After the blocks were allowed to cool to room temperature, the original dimension (prior to the temperature cycle) was not obtained. If the test temperature was less than the cure temperature, there was no significant change in the block dimension. When the blocks were tested at their cure temperatures, two of the blocks decreased slightly and one increased in size slightly. However, when the blocks were measured after being exposed to a temperature greater than the original cure temperature, all blocks increased in size. This residual growth amounted to nearly 3 percent for the 140°F cured block and tested at 200°F. This residual growth is significant and must be considered.

Table 5. Change in Height Dimensions, Thermal Stability Test

Block No.	Cure Temp (°F)	Test Temp (°F)	Change At Test Temp (%)	Change After Cool (%)
1	140	140	0.27	0.035
2	160	140	0.21	0.008
3	200	140	0.19	0.005
4	140	160	0.28	0.060
5	160	160	0.20	0.041
6	200	160	0.14	0.063
7	140	200	3.20	2.71
8	160	200	1.42	0.890
9	200	200	0.24	0.021

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MATERIAL VARIATION STUDIES

ROUND ROBIN PHYSICAL TESTS

Bendix, Sandia, Ablestik Adhesive Company and Testfab Engineering Company in Albuquerque were unable to agree on or correlate each other's test data. These apparent discrepancies in test values resulted in a round robin physical testing program among the four laboratories.

These variations have been attributed to several factors, including batches, units, testing, and processing differences. The deviations in test results have been great enough to cause rejection of material by one agency and yet the material would be accepted by another agency.

To discover reasons for differences in test results and to develop standard processing and testing procedures, a test program was designed by Sandia. The final report was published in January 1970 by R. D. Hermansen of Sandia.

Basically the test program was an evaluation of two lots of Ablefoam 5 (Lots 4-9-69-1 and 4-9-69-2) by four testing agencies (Ablestik Adhesive Company, Sandia Corporation, Testfab Engineering Company and Bendix Corporation) with two types of test specimens (block and cylinder). The Testfab Engineering Company is an independent fabrication and testing company in Albuquerque working under contract to Sandia. Each agency manufactured a series of blocks and cylinders from Lots 1 and 2 and each agency distributed parts from each lot to each of the other agencies for testing. Thus each agency tested representative samples manufactured at each agency.

All the test data has been analyzed by the Statistical Quality Control group at BKC. This complete analysis is included in the October 6, 1969 quarterly report on this project.

The most important result is that the variations in lots and test agencies are not significant. However, the variation in production agencies and between units is definitely significant. During the testing at Ablestik Adhesive Company, R. L. Buckner of Sandia noticed that the Ablestik 200°F test was different from the 200°F testing of the other agencies. The Ablestik test setup was not capable of maintaining the specimen temperature at 200 ± 5°F as required by MS2140587. These obvious differences in testing were still not as significant as the differences in production facilities and between units.

Inspection of the test data indicates that the strengths of the specimens made at Bendix are generally higher than the strength of specimens made at the other facilities, but the scatter or variation within a test unit was greater for Bendix than the other facilities. A statistical analysis verifies this observation; Table 6 is a summary of the data presented in the statistical analysis. Using Bendix and Testfab as examples and a 95 percent confidence level, the blocks made at Bendix from Lot 1 - regardless of where they were tested - had a density variation of ± 3.3 lb/ft^3 (1.106 x 3), while the blocks made at Testfab had a density variation of 2.3 lb/ft^3 (0.773 x 3). The strength (RT flatwise) on these same blocks had a variation of ± 345 psi for Bendix and ± 69 psi for Testfab.

The cylinder specimens are more uniform than the blocks. The density of the cylinders made from both Lots 1 and 2 could be expected to vary by about ±1.0 to 1.2 lb/ft^3 for Bendix and about ± 0.6 to 0.7 lb/ft^3 for Testfab. The compressive strength varies from ± 93 to 136 lb/ft^3 for Bendix and ± 85 psi to 162 psi for Testfab.

As predicted by the statistical analysis of the test data, the place of manufacture of test specimens and the differences between test results are the major sources of variation in the test data. Essentially the same process was used to foam and cure the blocks and cylinders, regardless of the manufacturing agency. The main differences are:

- Atmospheric pressure during foaming and cure;
- Humidity of atmosphere during thaw of cartridge;
- Type of oven used to cure specimens.

A series of tests was run to determine the effect of atmospheric pressure on density distribution and compressive strength. A vacuum oven was used to cure 6 by 6 by 1 blocks at 165°F and pressures of 500, 600, 650, 700 and 740 mm Hg. The 740 mm Hg is the standard Kansas City atmospheric pressure and Albuquerque is about 650 mm Hg. The testing was not as successful as planned since the oven temperature varied from 160°F to 200°F. For the first series of test blocks, the temperature controller on the oven was manually changed to maintain the oven temperature at 165°F. The temperature still cycled up to 185°F and the cure temperatures were different for each test pressure. To keep the cure cycles as constant as possible, the controller was set and the temperature allowed to vary. As mentioned above, the temperature peaked at about 200°F, but this was consistent for all test blocks. Room temperature physical tests, both edgewise and flatwise, were made. The results are listed in Table 7 and shown in Figure 19. These data show no significant difference in strength due to atmospheric pressure during foaming and cure. The data do show some differences, but the changing cure temperatures could have as much effect as the pressure.

Table 6. Standard Deviation Comparisons

Variable	Ablestik	Bendix	Sandia	Testfab
Lot 1				
Block Density	0.890	1.106	0.974	0.773
Block Strength RT (Flat)	94.562	115.204	52.297	23.151
Block Strength RT (Edge)	38.962	52.650	22.238	30.887
Block Strength 200°F (Flat)	65.932	87.504	45.000	23.558
Cylinder Density RT	0.244	-------	0.237	0.208
Cylinder Density 200°F	0.201	0.412	0.239	0.261
Cylinder Strength RT	26.439	-------	39.064	26.249
Cylinder Strength 200°F	33.265	45.453	56.347	54.092
Lot 2				
Block Density	1.453	1.433	0.494	0.560
Block Strength RT (Flat)	92.033	101.814	40.212	27.313
Block Strength RT (Edge)	58.412	65.154	57.229	34.928
Block Strength 200°F (Flat)	61.335	93.563	26.223	19.209
Cylinder Density RT	0.212	0.357	0.173	0.222
Cylinder Density 200°F	0.190	0.335	0.228	0.213
Cylinder Strength RT	26.926	38.079	23.728	28.461
Cylinder Strength 200°F	32.634	31.177	15.199	38.987

Table 7. Effect of Atmospheric Pressure on Compressive Strength

Test Pressure (mm Hg)	Block Density (lb/ft^3)	Strength, Flat (psi)	Strength, Edge (psi)	Edge/Flat Ratio
500	22.18	683	1050	1.54
600	22.0	659	1061	1.60
650	21.75	747	1071	1.43
700	21.92	712	1050	1.48
740	21.75	702	1030	1.47

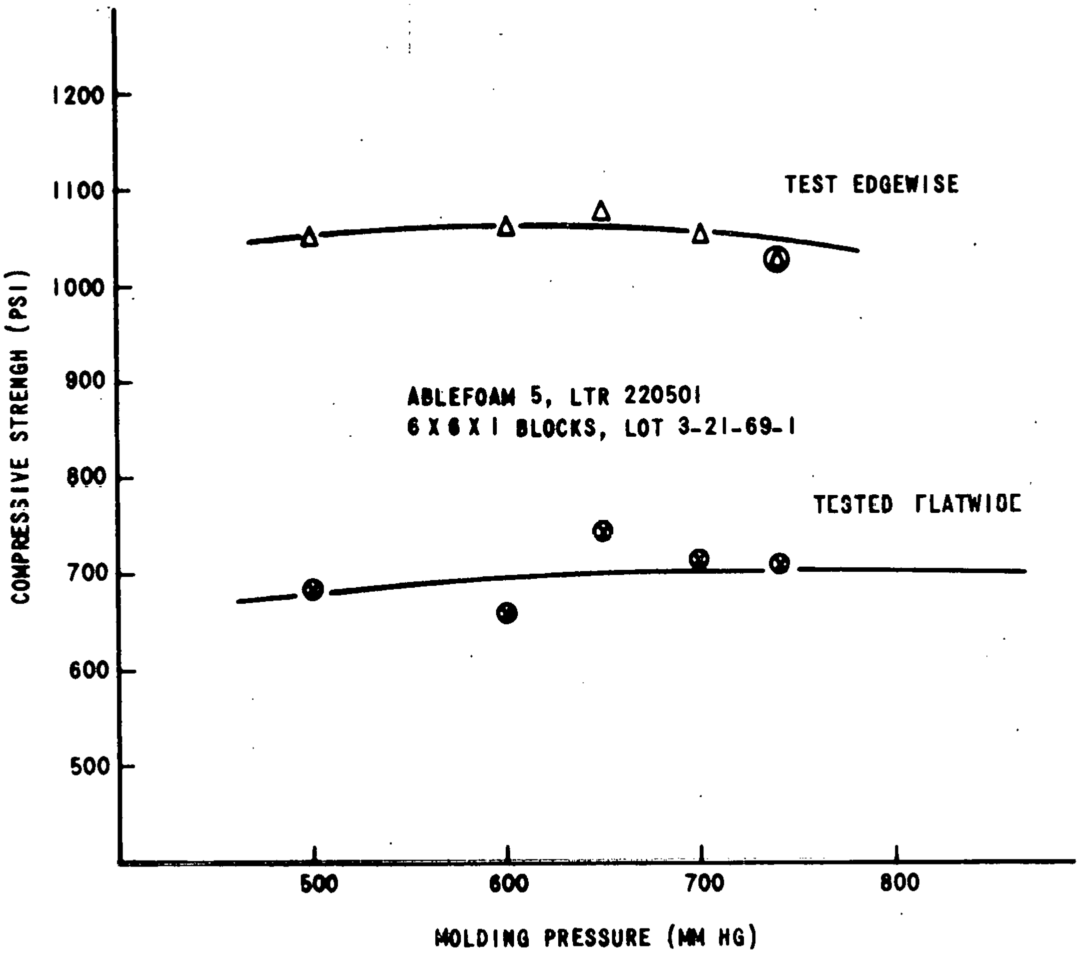

Figure 19. Strength Versus Pressure Graph, of Ablefoam 5 Blocks

The relative humidity of the atmosphere during thaw of the Ablefoam-filled cartridge could change the thaw time. At high relative humidities moisture in the air will condense and freeze on the sides of the cartridge, thus adding heat to the cartridge. However, the ice would change the thermal conductivity of the cartridge. The difference in thaw times due to relative humidity has not been measured but the difference should be small. Earlier tests have shown that the thaw time does not significantly affect the compressive strength.

A far more important variable is the air flow rate and heating rate of the oven used during cure. The test blocks prepared by Bendix were cured in any of five ovens while Testfab used only one oven. As discussed above, the density distribution and thus the strength distribution are quite different for Bendix and Testfab. Radiographs or X-ray photographs were made of representative blocks and cylinders from each manufacturing agency. The radiographs of the Bendix and Ablestik blocks were noticeably different from the Sandia and Testfab blocks. The Sandia and Testfab blocks tended to be more uniform with fewer high density streaks than Bendix and Ablestik. Testfab later foamed and cured a block in an oven with a higher heat rate than the oven used previously. The radiograph of this block was streaked and had a similar appearance to the Bendix and Ablestik blocks.

A test series was run to determine the effect of mold heating rate and air flow rate of the oven. Three 6 by 6 by 1 molds with wall thicknesses of 3/4, 1 and 1-1/4 were used to test the effect of wall thickness on exotherm temperature, as well as density distribution and strength. The standard molds with 1-inch thick walls were used to determine the effect of variation in oven air flow rates on strength. The results are listed in Table 8.

The wall thickness of the mold does make a difference in the peak exotherm temperature during cure; the thicker-walled molds have lower exotherm temperature. The temperatures measured were 425°F for the 3/4 inch mold and 370°F for the 1-1/4 inch mold. These temperatures are somewhat higher than expected, since a rubber gasket was used to seal around the thermocouple leads. This gasket increased the foam thickness from 1 inch to about 1-1/4 inch, and the exotherm temperature increased about 50 to 60°F. However, the increase in temperature did not make a significant difference in either the density distribution or the strength.

The effect of air flow rate was tested by foaming and curing 6 by 6 by 1 blocks in an oven with the air vents fully opened, with the air vents fully closed, and with the mold sealed in a 5-gallon container to eliminate air flow from outside the oven. No difference was noted between the vent fully opened and vent fully closed. The density distributions as indicated by the E/F ratios are exactly the same.* Curing the block in the 5-gallon container with essentially no-air flow did make a difference in both the density distribution and strength. The E/F ratio is 2.1 for the no-flow compared to 1.4 for the standard air flow rate. Although the E/F ratio indicates a large variation in the block density from skin to center of the block, the range of individual specimen densities from top to bottom of the blocks is more uniform for the no-air flow block than the standard block. This phenomenon has not been explained.

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* E/F is the ratio between edge and flat strengths.

Table 8. Effects of Mold Thickness and Oven Air Flow on Compressive Strength

Test Condition	Test Temp (°F)	Orientation	Specimen Density (lb/ft^3)	Strength (psi)	E/F* Ratio	Peak Exotherm (°F)
3/4 " Mold Walls	RT	Flat	19.66	718	1.48	425
22.6 lb/ft^3 Block	RT	Edge	19.50	1060		
	200	Flat	20.37	454		
1" Mold Walls	RT	Flat	19.87	637	1.70	410
22.6 lb/ft^3 Block	RT	Edge	19.84	1082		
	200	Flat	20.64	364		
1-1/4" Mold Walls	RT	Flat	19.44	638	1.67	370
22.5 lb/ft^3 Block	RT	Edge	19.58	1064		
	200	Flat	20.00	402		
VENT OPENED	RT	Flat	19.23	713	1.39	
21.8 lb/ft^3 Block	RT	Edge	19.19	992		
	200	Flat	19.81	445		
VENT OPENED	RT	Flat	18.88	678	1.40	
21.8 lb/ft^3 Block	RT	Edge	18.91	952		
	200	Flat	19.67	435		
VENT CLOSED	RT	Flat	19.00	703	1.43	
21.0 lb/ft^3 Block	RT	Edge	19.10	1005		
	200	Flat	19.68	473		
VENT CLOSED	RT	Flat	19.06	741	1.39	
21.8 lb/ft^3 Block	RT	Edge	19.36	1030		
	200	Flat	19.68	492		
NO AIR FLOW	RT	Flat	18.90	451	2.09	
21.8 lb/ft^3 Block	RT	Edge	19.00	945		
	200	Flat	19.20	134		
NO AIR FLOW	RT	Flat	19.27	425	2.27	
21.8 lb/ft^3 Block	RT	Edge	19.78	964		
	200	Flat	19.00	132		

* E/F = ratio between edge and flat strengths.

FORMULATION VARIATION INVESTIGATION

An expanded investigation was initiated to evaluate the effect of formulation changes on compressive strength, density distribution and overall encapsulation appearance of the foam; the original intent was to determine which of the two basic fill techniques was more sensitive to formulation variations. These two fill techniques are:

- Discrete quantities of liquid epoxy in specific mold cavities; and
- Mold reservoir filled with known weight.

The design change incorporating printed circuit boards on the assembly eliminated the choice of fill technique; only the reservoir technique could conveniently be used.

Dummy units were encapsulated in the production area, using D-tested components and foam samples of several formulations. During the initial part of the test encapsulations, both fill techniques were used to pour the dummy units. After the design change only the reservoir techniques were used. In addition to the dummy encapsulations, standard size (6 by 6 by 1) test blocks were prepared. The 1-inch cube test specimens, similar to the one shown in Figure 1, were machined from each block, and compression tested per ASTM D-695.

According to the manufacturer, Ablefoam 5 is a blend of two epoxies, two amine curing agents, a silicone surfactant, and a solid blowing agent. To protect the proprietary formulation of Ablefoam 5, the vendor prepared each of the special formulations for this study. This evaluation was set up as a fractional factoral experiment with a total of 17 formulations. Table 9 is a listing of the formulations and indicates how each individual component was varied.

Since the standard formulation of Ablefoam 5 is proprietary, the individual components were varied on a basis of percentage of standard quantity.

All formulations were tested to the requirements of MS2140587. The actual tests were thaw flow, flow gage, and the compressive strength. The test values for the thaw flow and the flow gage are listed in Table 10. The compressive strength and modulus values are in Table 11. The test values for formulation 5-2 and 5-9 are from Sandia data (the BKC test cartridges were lost during shipment).

Only one of the 17 formulations met both the thaw flow and the flow gage requirements; this was Formulation 5-16, which is standard except for high curing agent-to-epoxy ratio. As mentioned above, the dummy

Table 9. Formulations for Material Variation Study

Formulation No.	Blowing Agent	Ratio of Aliphatic to		Ratio of Curing Agent To Epoxy
		Aromatic Amine	Novalac Epoxy	
5-1	0	0	0	0
5-2	-	-	-	-
5-3	+	-	-	*
5-4	-	+	-	*
5-5	+	+	-	-
5-6	-	-	+	+
5-7	+	-	+	*
5-8	-	+	+	-
5-9	+	+	+	*
5-10	+	0	0	0
5-11	-	0	0	0
5-12	0	+	0	0
5-13	0	-	0	0
5-14	0	0	+	0
5-15	0	0	-	0
5-16	0	0	0	*
5-17	0	0	0	

NOTE: + = 50% high, 0 = standard, - = 50% low, * = 25% high.

encapsulations were made and density distribution determined on Formulations 5-1 thru 5-13 (excluding 5-2 and 5-9). Only Formulation 5-4 did not make an acceptable potted unit. All the other formulations performed satisfactorily as encapsulants.

The statistical analysis of the compressive strength data was not conclusive. The variation or standard deviation between test blocks of the same formulation was greater than the effect of a formulation change. Thus the effect of varying individual components could not be separated from the expected variation within a block.

Table 10. Thaw Flow and Flow Gage Values for Material Variation Study

Formulation No.	Lot No.	Thaw Flow Test		Flow Gage Test	
		80 Min	Final (g in Min)	Height (Units)	Weight (g)
5-1	2-25-69-1	52.4	75.5	7.2	1.50
5-2	—	16.7	—	1.6	—
5-3	1-20-69-1	6.9	67.5 - 150	—	—
5-4	—	—	—	1.0	1.5
5-5	1-22-69-1	11.0	40.2 - 120	10+	1.5
5-6	2-5-69-1	82.0	Final	1/2	—
5-7	2-7-69-1	84.5	Final	11+	1.40
5-8	2-4-69-1	—	73 - 85	1.2	1.45
5-9	—	18.8	—	6.2	—
5-10	3-3-69-1	31.0	71.9	11+	1.5
5-11	3-5-69-1	71.6	—	1.0	1.5
5-12	3-12-69-1	70.0	71.6 - 100	4.0	1.5
5-13	3-21-69-1	64.6	66 - 100	4.5	1.50
5-14	5-16-69-1	85.2	Final	4.5	1.50
5-15	5-16-69-2	23.5	7.8	6.0	1.50
5-16	5-16-69-3	55.0	77 - 108	6.0	1.5
5-17	5-16-69-4	56.0	77 - 105	11+	1.5

Table 11. Compressive Strengths and Moduli for Material Variation Study

Formulation No.	Test Temp (°F)	Block Density (lb/ft³)	Specimen Density (lb/ft³)	Orient. (Flat, Edge)	Comp Modulus (psi)	Comp Strength (psi)	Edge/ Flat Ratio	Density Range (lb/ft³)	Block Range (lb/ft³)
5-3	RT		19.49	F	33,400	509	2.296	2.00	
1-20-69-1	RT	22.29	19.37	E	35,800	1169		1.78	2.65
	200		20.04	F	12,800	335		1.54	
5-5	RT		18.55	F	18,000	288	3.729	0.40	
1-22-69-1	RT		18.66	E	33,600	1074		0.75	0.75
	200		18.82	F	10,700	218		0.33	
5-6	RT		19.66	F	35,500	689	1.509	2.92	
2-5-69-1	RT	22.13	19.61	E	35,600	1039		2.72	
	200		20.65	F	18,000	365		4.56	4.56
5-7	RT		19.35	E	26,400	530	1.954	1.55	
2-7-69-1	RT	21.97	19.41	E	34,000	1016		1.51	
	200		19.79	F	9,150	344		3.15	3.15
5-8	RT		20.39	F	36,440	741	1.293	1.48	
2-14-69-1	RT	22.42	20.33	E	35,400	958		0.78	2.81
	200		20.66	F	3,640	132		1.66	
5-10	RT		18.45	F	21,600	447	1.899	4.59	
3-3-69-1	RT	21.90	18.43	E	25,900	849		4.81	5.94
	200		19.72	F	8,735	256		5.58	
5-11	RT		19.27	F	25,144	492	1.872	3.43	
3-5-69-1	RT	22.29	19.27	E	29,546	921		3.98	4.73
	200		19.53	F	7,100	237		4.42	
5-12	RT		21.04	F	30,400	727	1.340	7.63	
3-12-69-1	RT	22.16	17.88	E	29,000	974		7.01	7.71
	200		19.49	F	14,500	320		6.9-	
5-13	RT		19.61	F	24,800	538	1.942	3.26	
3-21-69-1	RT	22.61	19.55	E	32,700	1046		3.09	3.55
	200		20.36	F	11,700	568		3.32	
5-14	RT		18.84	F	27,900	515	1.794	6.89	
5-16-691-1	RT	22.40	19.03	E	28,700	924		7.09	8.37
	200		20.66	F	5,840	197		8.37	
5-15	RT		19.06	F	31,000	548	1.755	1.87	
5-16-69-2	RT	22.59	18.80	E	31,700	962		2.05	2.48
	200		19.48	F	17,500	346		1.95	
5-16	RT		19.30	F	25,700	581	1.613	1.30	
5-16-69-3	RT	22.46	19.34	E	26,900	937		1.00	1.30
	200		19.60	F	4,400	195		1.09	
5-17	RT		19.56	F	37,000	688	1.385	3.44	
5-16-69-4	RT	22.64	19.35	E	32,400	953		3.24	4.40
	200		20.52	F	19.100	417		4.16	

DEVELOPMENT OF ENCAPSULATION PROCESSES

INTRODUCTION

The electronic component assemblies of the major assembly were initially designed to be fabricated using polyurethane foam supports. These supports were molded to size, then bonded between the various components to isolate and structurally support them. In January of 1968, SLA introduced a foam-in-place design with a self-rising one-component epoxy foam encapsulant. This technique simplified design problems with tolerance interferences, reduced the cost of using individually molded supports, and reduced fabrication flow time.

The development of the encapsulation processes and tooling was closely related to the product design, the encapsulation requirements, and the properties of the rigid epoxy foam. The capability to encapsulate units free of voids and with the required density distributed uniformly throughout the unit was achieved.

The encapsulation requirement for the units was originally for a 15 lb/ft^3 density. This changed to a 20lb/ft^3 and finally a 22 lb/ft^3 density requirement. Repeatability was established through the number of tests and evaluations made on a particular process.

When Bendix developed a backup epoxy foam (Capoxyfoam I), investigations were conducted to determine if it could be used with the existing production tooling and processes. The successful encapsulation of the two component assemblies of the major assembly was accomplished in production tooling, with the only deviation from the present encapsulation process being the addition of a mold preheat of 115°F.

The following is a brief history of the processes and tooling concepts evaluated during the development program.

ENCAPSULATION PROCESSES (ABLEFOAM 5)

The first process development work was done using tooling available for development units of the AF&F and special development tooling ordered for encapsulation evaluation. This tooling consisted of molds used to encapsulate Electronic Component Assembly A and Electronic Component Assembly B. The components of these two assemblies were represented in the tests by a set of dummy aluminum components built to the nominal dimensions of the actual components.

The encapsulant specified by SLA is a frozen one-component epoxy foam (Ablefoam 5) that is stored at -65°F. It is packaged in a Semco cartridge and must be thawed at room temperature for 50 minutes before it can be used. When the foam thaws it is extruded into the mold with a cartridge air gun. The viscosity of Ablefoam 5 during the pouring is approximately 200,000 to 400,000 centipoises. As the foam is heated in the oven, it becomes more fluid before it begins to react. This allows the material to level off before it begins its foam rise. In the original development molds which had approximately 3/4-inch-thick aluminum walls, the foam took about an hour to complete its rise. This included 30 to 40 minutes warmup time after the room temperature mold had been placed in a 165°F oven. The foam began to react when it reached a temperature of 120°F and completed its rise in these molds in 20 to 30 minutes. After 75 minutes the foam was rigid.

To achieve a complete fill, the first encapsulation technique consisted of painting each component with Ablefoam 5 and adding the remainder of the foam required into the cavities between the components. This technique evolved into squirting the sides of the components instead of painting them, and eventually changed to squirting foam into the cavities only. This method was acceptable because the foam will flow into very small crevices while rising. During the development tests, the actual amount of foam in each component assembly was determined by weighing the component assembly before it was poured, then weighing the final foamed assembly. The test units were cured for 4 hours in a 165°F oven. The foamed assemblies were then dissected to remove the foam from the components; care was taken to remove large sections of foam. The foam density of each section was then determined in accordance with ASTM D972. From this data the following factors were determined.

- The quantity of foam to put into a component assembly to maintain the required overall density; and
- The quantity of foam to put in each cavity to keep density variation to a minimum throughout the assembly.

Several encapsulations of both Assembly A and Assembly B were produced to determine the processing parameters necessary to meet encapsulation requirements.

During these encapsulation tests two other techniques were evaluated. Approximately 80 percent of the foam required was added to the center area of Assembly B rather than applying it proportionally to each cavity. The resultant density gradient was less than 4 lb/ft^3 throughout the unit; in fact, regardless of where the material was placed, the density gradient was less than 4 lb/ft^3. This compared well with the density gradient of 2 to 3 lb/ft^3 in Assembly B using the individual cavity fill technique. The Assembly A density gradient was 3 to 4 lb/ft^3 for the individual cavity fill method. This data led to the development of a totally new technique for encapsulating the component assemblies. The method is based on the use of a reservoir cavity attached to one end of the mold with rise holes going into each cavity between the components. (Evaluation of this new process began in June 1968.) With this method it is possible to inject a given amount of foam into one large cavity instead of injecting a given quantity of foam into each individual cavity. (Assembly B contains six individual cavities and Assembly A contains seven individual cavities.) This method not only saves time for the operator but also reduces the chance for error six times. During development, the aft end of Assembly B mold and the forward end of Assembly A mold were reworked to accommodate a reservoir.

The placement of the reservoir was determined by accessibility to the component cavities as dictated by product design. The rise holes connecting the reservoir to the mold cavity were 1/4-inch diameter and approximately 1/4-inch long. The reservoir itself was approximately 5/16-inch deep and the same diameter as the mold cavity. Originally it was intended to keep all of the foam below the assembly and let it rise into the assembly. Another similar concept tested was a very thin reservoir with most of the foam staying up in the assembly and the rise holes serving only as a leveling medium for the foam. The results from foaming A and B assemblies using the reservoir technique were very good. The density variations within the assembly were 2 to 3 lb/ft^3, and coverage was good with no incomplete fills and few air pockets.

The product design at this stage of development called for flexible wire circuits, or flex circuits, to be used as electrical interconnections. In Assemblies A and B the flex circuits were connected to the components and went directly to the outside of the encapsulated assembly. The circuits (or simulations of them) were not used in the initial encapsulation tests since their size did not appreciably affect the fill or density of the overall assembly. The flex circuits were very thin (0.013 to 0.026) and had an irregular surface on one side. Foam leakage around these circuits was one of the major tooling problems associated with using Ablefoam 5. To solve this problem room temperature vulcanizing (RTV) seals were molded and used in the tooling to seal the flex circuits. This did not stop all of the flash and this problem was not completely solved at the time the assembly's design was changed.

Development studies were continuing with the reservoir techniques when the assembly was completely redesigned. This change eliminated flexible circuits as interconnecting devices between the components and replaced them with printed circuit boards and hard wiring. This redesign created several new problems affecting the encapsulation process. With the previous design, the cross-section through the diameter of the assemblies consisted of components with cavities between them. These cavities ran the length of the assembly.

The flex circuits went directly to the outside of the assembly from the components. With the new design, printed-circuit boards covered the entire assembly cross-section at each end of both assemblies. Many of the cavity areas were filled with wiring and small components. This not only added more restrictions to the foam rise but made filling each cavity with foam a very involved process. During the development of the new product design, Assemblies A and B were combined into one unit. This concept nearly doubled the area to be encapsulated and, for all practical purposes, eliminated the processing technique of filling individual cavity areas. New development molds were ordered along with dummy circuit boards to use in mock-up component assemblies representing the new design.

The initial attempts to encapsulate the new combined A-B Assembly uncovered several problems, emphasizing that previous encapsulation techniques were inadequate. Low density areas and voids created by entrapped air were present in nearly every encapsulated unit. The primary factors which affected the encapsulation process were the method of filling the mold, the direction of the foam rise, and the venting of the mold. It was found that encapsulating the assembly across its diameter worked better than encapsulating along the length. This meant that the foam had a shorter distance to rise and that during its rise, it developed an equal pressure on each side of the printed circuit boards. This also reduced the flow restrictions imposed by the presence of the circuit boards. To eliminate voids, venting became mandatory. Experiments were done with venting to the atmosphere, flush venting into a reservoir, and venting through a filter. The direction of foam rise with respect to component orientation also affected the fill and density. An orientation was selected which gave the most uniform density throughout the unit. These studies revealed that a large cavity inside the assembly will have a lower foam density than a small cavity. Because of the design and size of the new assembly the density gradient was 8 to 10 lb/ft^3 throughout the unit. The three basic methods of pouring the material were:

- To introduce the foam directly into the mold using no reservoir;
- To pour through a reservoir at the top; and
- To pour through a reservoir at the bottom.

It was determined that the method of fill did not appreciably affect the final foamed unit, due to the long work life of Ablefoam 5 and its viscosity during the warmup period.

A reliable encapsulation process for the new product design was developed as the void and density uniformity problems were solved. The fill technique was refined to include utilizing a narrow 1 by 1/4-inch reservoir along the length of the mold with five 3/16 diameter fill holes feeding the mold. (See Figure 20.) Numerous encapsulation tests revealed that using a small

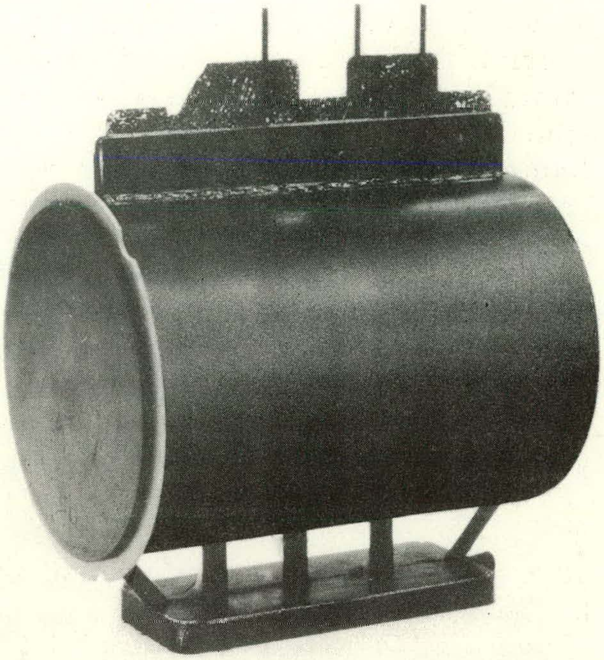


Figure 20. Dummy A-B Assembly
Encapsulated With Ablefoam 5
Showing Foam Reservoir,
Rise Holes, and Venting

reservoir and allowing most of the material to be injected up into the mold produced as uniform a density as other techniques used. The reservoir technique of filling is the most efficient because it allows all of the material to be poured into the mold through a single fill hole. This resulted in the final mold configuration which includes a 1/2 by 1/4-inch reservoir running the length of the mold with five 3/16 diameter fill holes only 1/4-inch long.

The mold was designed with the reservoir at the bottom of the mold, to allow the foam rise to push air out through the vents at the top of the mold. The addition of venting in the mold eliminated the void problem. During development encapsulation tests it was noted that by removing a RTV seal between the forward end plate and the mold body most of the voids were eliminated. This seal had originally been added to the mold to prevent foam leakage. Removal of the seal did not allow any foam to leak out and did eliminate several air pockets at the end of the assembly. Several tests were run with different venting methods. It was found that a thin flash vent across the entire length of the unit at the top of the mold eliminated all voids and did not create any problems with cleanup of the unit. It was determined that, for the encapsulation of the A-B Assembly, the optimum vent was a 0.006

flash area along the top surface of the mold and at the top third of the end plate. During these tests a 0.003 to 0.006 vent provided enough flash to eliminate voids without losing much material. A 0.010 vent was tried, but resulted in excessive leakage of the foam material. One void continued to appear in a small pocket counterbored in the mold end plate. This was eliminated by drilling a vent hole from the counterbored area to the outside of the mold. Here it was found that a 0.015 to 0.031 diameter hole would flash material and seal itself off. A 0.045-inch diameter hole that was tried resulted in excessive leakage.

Concurrently with the development work done on the A-B Assembly, processes were also developed for the encapsulation of Electronic Component Assembly C with Ablefoam 5. Since all of the cavity areas of this assembly are open to the top, a simple method of pouring was developed. All of the foam required is introduced into three main cavity areas. Theoretical and empirical data were used to determine the amount of foam needed to obtain the density required for this assembly. The sealing of the wires emerging from Assembly C was a major problem. Any hole larger than 0.020 diameter would cause enough leakage to make the unit unacceptable because of too low a density. To solve this problem, the wires are sealed from the inside of the unit with RTV, preventing excessive leakage; this is accomplished prior to encapsulation of the unit with Ablefoam 5.

FACTORS AFFECTING ENCAPSULATION PROCESSES (Ablefoam 5)

Many tests were run during the development program studying variable factors associated with the processing of Ablefoam 5. These tests included a study of exotherm temperatures and pressures which occur during the encapsulation process, a mold release study, a study of the effects of atmospheric pressure and humidity on the encapsulation process, and a study of cure times, temperatures and types of ovens. Test data taken from cylindrical specimens have less variation than data from block specimens; the cylindrical specimens are tested in only one direction. Block specimens are preferred for measurement of foam mass distribution between the center and skin areas of the foam, using the ratio of edgewise to flatwise test values.

Ablefoam 5 reacts exothermally during its oven cure cycle. The temperatures generated by this reaction increase proportionately with foam mass. A temperature recorder with four thermocouples was used to monitor and to record the exotherm temperature developed during cure of an A Assembly and a B Assembly. One of the thermocouples was used to record the oven temperature.

The others were positioned within the units being tested at:

- The greatest foam mass;
- The component surface near center of the module; and
- The component surface near the wall.

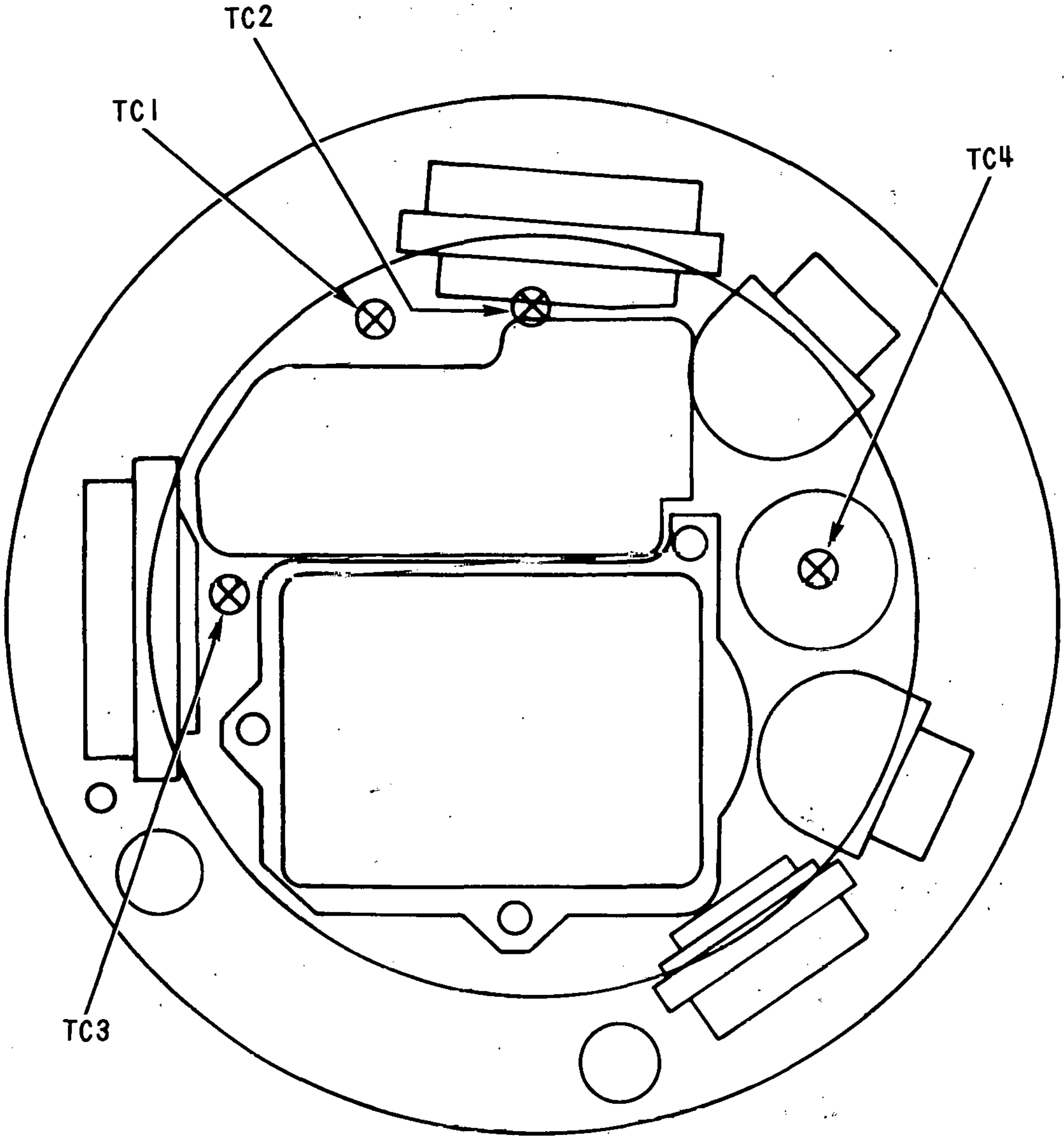
In the A module, no temperature increase because of exotherm was recorded for cure temperatures of 180, 160, and 155°F. Slight increases in temperature above the cure temperature were recorded in the B module. Temperatures of up to 10°F higher were obtained in the center cavity. Only very low temperature increases of 2 to 3°F were obtained at or near the surface of the components. Theoretically, under adiabatic conditions, the maximum temperature rise should be about 9°C (16°F). This value is based upon a heat capacity of 0.3 cal/g°C for epoxy and 0.23 cal/g°C for aluminum. The heat of reaction for the epoxide groups was taken as 24,000 cal/g-mole. The charge weight of epoxy was assumed to be about 50 grams and the mold weight about 3,000 grams.

An exotherm test was made using a mold without the components. At 20 lb/ft^3 overall density and a cure temperature of 165°F, a maximum exotherm temperature of 555°F was recorded. Two other tests of densities of 20 lb/ft^3 and 15 lb/ft^3 recorded peak temperatures of about 400°F and 470°F. The exotherm is mass-dependent and a thermocouple shift of even several millimeters could greatly change the recorded peak temperatures. To determine what temperatures are present during the oven cure of Assembly C, four termocouples were placed in this unit.

The oven cure temperature for this unit is 160 to 170°F. The following list shows temperatures reached during the 4-hour cure of Assembly C, at an oven temperature of 162°F. A preproduction Assembly C mold was used for this test.

Thermocouple	Time to Reach 160°F (Minutes)	Time Between 160°F to 170°F (Minutes)	Time Above 170°F (Minutes)	Peak Temp (°F)
1	0 to 37	37 to 44	44 to 61	176
2	0 to 41	41 to 50	50 to 69	173
3	0 to 42	42 to 4 hr	0	166
4	0 to 39	39 to 45	45 to 68	174

Note: All temperatures were 164°F to 166°F after 90 minutes. All temperatures leveled at oven temperature (162°F) after 2 hours 6 minutes.



VIEW LOOKING THROUGH AFT END OF CASE SECTION

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Encapsulation Pressure Tests

Special tests were run at BKC to determine the pressures occurring during the foaming. The tests were run on instrumented assemblies with D-tested components and flexible circuits in preproduction molds. The assemblies simulated, Assemblies A and B, were fabricated from drawings supplied by SLA. Each assembly contained a pressure transducer and several thermocouples which were located according to the drawings. SLA provided two calibrated recorders, the D-tested components, the pressure transducers and the thermocouples. Two complete tests were run on each assembly, with each test plotting both internal pressure and temperature versus time. Test readings were taken from the time the room temperature mold went into the oven, through the entire oven cure, until the mold cooled to room temperature after removal from the oven.

The internal pressures were measured in each assembly during the foam blowing and curing process of the 4-hour oven cure. There was one bridge type pressure transducer (Statham PA208TC, 350 ohm) in each assembly. Pressure began to develop in both assemblies after 30 minutes and reached a maximum within 90 minutes. The internal pressure did not exceed 42 psig in Assembly B and did not exceed 27 psig in Assembly A.

During the cure cycle microminiature threaded probe thermocouples (BLH Inc.) measured the exotherm temperature of the foam, while copper constantan wire thermocouples measured the temperature of the oven, of the outside of the mold, and of the components being encapsulated. The ovens were calibrated to 165 ± 5°F. None of the exotherm temperatures exceeded 175°F.

Mold Release Investigation

Replaceable type mold releases, such as carnauba wax, fluorocarbon sprays, polyvinyl alcohol, and urethane release agents have been evaluated in both 6 by 6 by 1 test blocks and in early design module molds. Permanent release agents including DC23, DC800 (both Dow Corning silicone-based) and Teflon spray coatings were applied to aluminum panels. These panels were lightly sandblasted, vapor degreased, and then coated following the manufacturer's recommended procedure. All the materials tested were effective as release agents. When the testing first started, the type of release seemed to affect the surface appearance of the foam blocks. After a formulation change in July 1968 the surface imperfections disappeared regardless of the release agent used. The fluorocarbon spray MS4702664 was the best for ease of application but this release must be applied for each molding.

A test was set up to determine the relative degree of transfer of mold release from the mold to the part. It is assumed that mold release on the cured epoxy foam would be detrimental to any adhesive bond. Therefore, tensile test specimens were prepared using epoxy foam blocks molded against the following six release agents:

- DuPont Teflon S (green); MS5084052
- DuPont Teflon S (black); MS5084062

Figure 22. **Deleted.**

Figure 23. Deleted.

- Miller Stevens MS143; MS4702665
- Ceara Carnauba wax (no Material Standard)
- Plastilease 560; MS4702064
- Dow Corning 23; MS4702077

Care was taken during demolding and tensile specimen preparation to prevent contamination of the bonding surface. Five specimens per mold release were prepared from the epoxy foam blocks as molded and five specimens per mold release were prepared from blocks with the molded surface cleaned. The cleaning consisted of light abrasion with sandpaper followed by high pressure air to remove dust, and finally a solvent wipe. Table 12 is a summary of test results.

Table 12. Mold Release Effect on Bond Strength

Material	Uncleaned Specimens*		Cleaned Specimens*	
	Strength (psi)	Failure	Strength (psi)	Failure
Teflon S Black	273	0	272	0
Teflon S Green	273	0	251	0
MS 143	219	3	260	0
Carnauba Wax	162	5	281	0
Plastilease 560	244	3	296	0
DC 23	290	0	297	0

* Number of specimens that failed at the bond-line from total of five specimens.

The following conclusions can be obtained from the data:

- The MS143, carnauba wax, and Plastilease 560 tend to transfer to the foam more than the permanent-type release agents. In fact, the transfer was severe enough to cause failure at the bond-line for the majority of specimens of the three agents.
- The permanent types, two Teflon S mold releases and the DC23, had the least amount of transfer indicated by the mode of failure. All of the specimens tested for the permanent types failed in tensile within the foam.

- Light cleaning of the foam after demolding can effectively remove any mold release that transfers. After cleaning, all of the specimens tested failed within the foam.

Bonding Strength Tests

To determine the adhesive strength of Ablefoam to printed circuit boards, tensile specimens were prepared. Dummy boards were made from FR45 material, using the circuit pattern from another MC. After plating, the boards were dipped into peanut oil at 450°F to reflow the tin-lead and then bonded with epoxy resin-versamide adhesive to aluminum tensile blocks. The test boards (and blocks) were 2 inches by 2 inches to give a bonding area of 4 square inches. After cleaning by vapor degreasing, the boards previously bonded to the tensile blocks were assembled in a foaming fixture. A total of 16 foamed specimens was submitted. The effect of foam thickness on bonding strength was checked by using specimens prepared with 0.160 inch and 1.0 inch foam between the boards. The effect of peanut oil on adhesion was checked by using boards dipped in room temperature peanut oil after cleaning by vapor degreasing. The excess peanut oil was removed with a paper wipe, but no attempt was made to actually reclean the boards. All specimens were made at 22 lb/ft^3 and cured 2 hours at 165°F. The test results on LTR 212719 indicate the following:

- The bonding strength of the foam is greater for the 0.160 inch thick foam than the 1.0 inch foam. In all of the 16 specimens the failure was not at the foam-printed circuit board interface. Five of the specimens did fail at the aluminum board interface instead of in the foam, indicating improper specimen preparation. The 0.160 thick specimens tested at about 675 to 700 psi, while the 1.0 thick specimens were about 250 to 300 psi.

- The specimens exposed to peanut oil have approximately half the tensile strength of the clean, vapor degreased specimens. However, the failure was still in the foam and not at the circuit board interface. A possible explanation is that the peanut oil contaminated the liquid epoxy during foaming and weakened the resulting cured foam.

Foam Porosity Tests

Several methods of removing the air and evolved gases from the mold during foaming have been investigated. Tests have been run using glass filter disks; three different porosities and two sizes were evaluated in eight tests. Overall, the glass filter disks are effective as a method of venting. The largest porosity filter did not block the foam, so porosity of the filter is a critical parameter. The two finer porosity filters were quite effective in allowing the gases to escape and restricting the foam. Although the filters are methods of reducing overall pressure, the disks would need to be strategically placed to prevent entrapped air during foaming.

Flexible urethane foam can also be used as a filter material since it is 100 percent open cell. The three dimensional, random structure of the cells offer little resistance to the air or gases, but the flow of foam is restricted. As the viscosity of the curing foam increases, the resistance of flow increases. The foaming fixture used in the evaluation of the open cell urethane was not of optimum design. In all tests, part of the epoxy foam was able to flow between the urethane and the mold. Although the tests were not totally successful, they did show that the 100 and 80 cells/inch urethane could be utilized as filters. The 40 cells/inch open cell foam was not acceptable. Based upon these tests, the epoxy foam could be expected to force itself through about 1 inch of the 100 cell/inch urethane before curing.

Samples of Ablefoam 5 have also been used as gas filter material. Air picnometer tests have shown Ablefoam to be about 60 to 70 percent open cell at 22 lb/ft^3, and directly proportional to the density. Two types of specimens have been tested. First, 0.200 thick rings were machined from 1-inch thick molded blocks. The density should have been fairly uniform throughout the ring. The second type of specimens was molded to 0.230 and then the ring was machined; these rings have a definite density gradient across the 0.230 thickness.

The filter rings cut from the 6 by 6 by 1 blocks gave inconsistent results. In some cases the foaming epoxy extruded through the ring, but in other tests the foam was blocked. Material variations resulting in different open cell contents could change the effective porosity of the rings for a constant overall density. Only one test has been made with the molded ring. No foam extruded through the ring and the foaming pressure remained at zero. Since the ring was not sealed, the gases could escape from between the mold and the ring and not pass through the ring.

Most foam molds allow for venting by flash grooves cut in the mold or by the metal-to-metal contact of the mold. This method has proved to be very satisfactory in molding test blocks and in general encapsulation. If the flow properties of material remain constant, controlled flash grooves would be a simple and adequate method of venting.

Mold Preheat Effects

The effect of mold preheat on compressive strength was studied at both room temperature and 200°F; Figure 24 shows the results of these tests. Graphs A through D are for data taken from 6 by 6 by 1 molded test blocks while Graphs E and F are for cylindrical test specimens; all specimens were normalized to 22 lb/ft^3. In each case preheating the molds up to 90 to 100°F increases the compressive strength of the test specimens. At preheats greater than 100°F, the strength decreases.

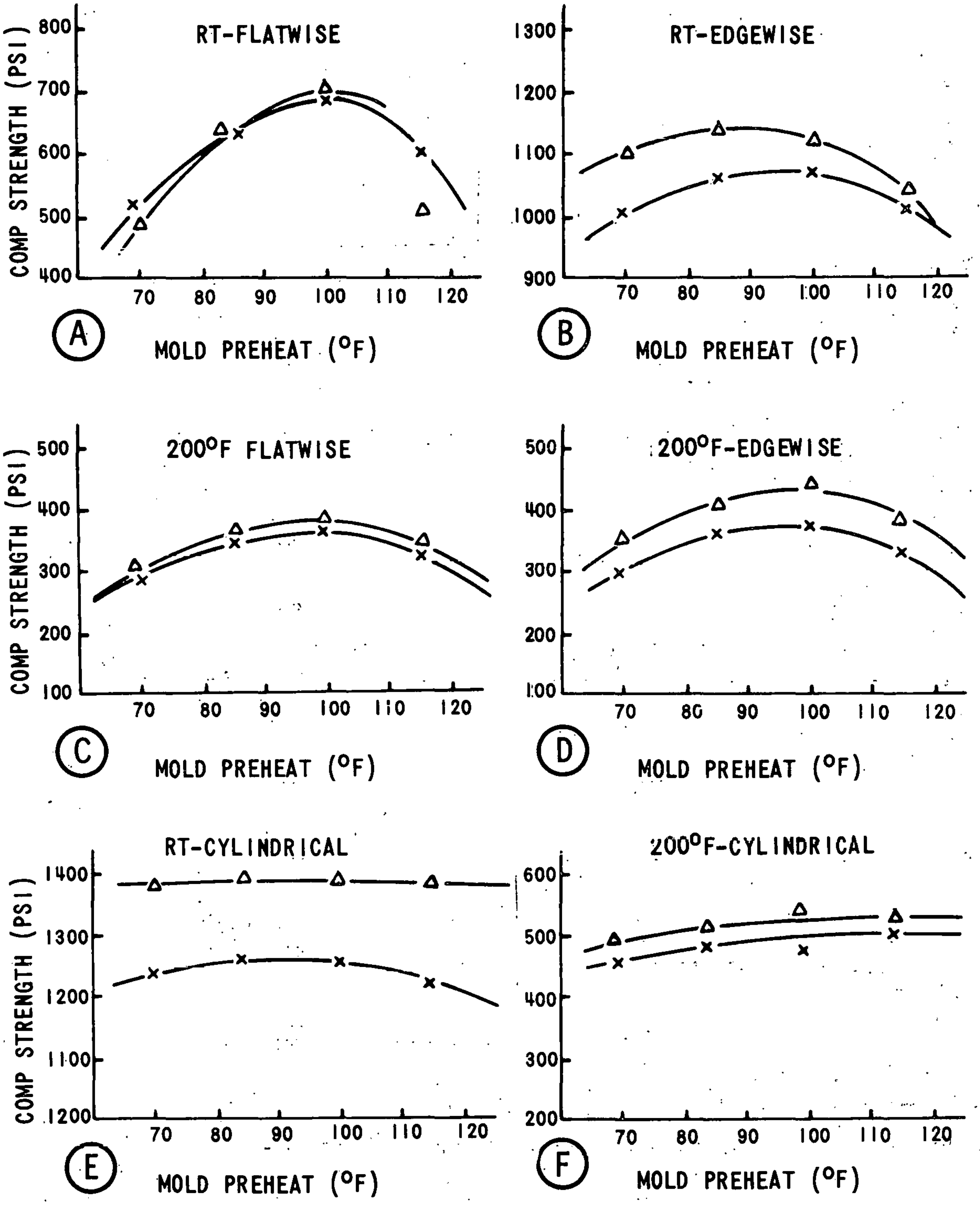

Figure 24. Effects of Mold Preheat on Compressive Strength (Cured 4-Hours at 165°F. Conditioning Atmosphere Legend: x-x = 50 Percent RH; Δ-Δ = 10 Percent RH)

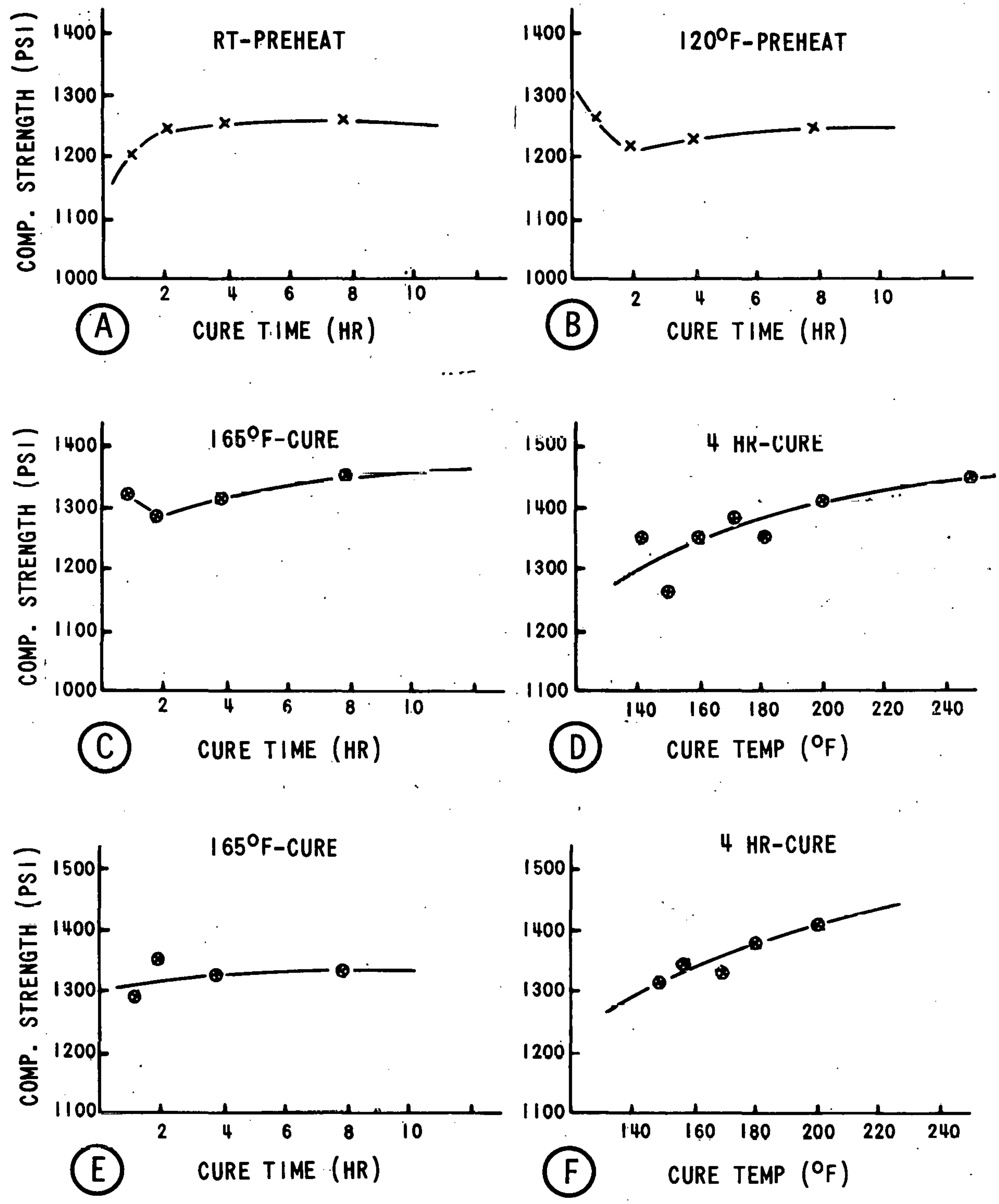

Figure 25. Effects of Cure Time and Cure Temperature on Compressive Strength (Cylindrical Specimens at 22 lb/ft^3 Normalized. Test Load Directions: A Through D are Parallel-to-Foam Rise, E and F are Perpendicular-to-Foam Rise)

Humidity Factor

SLA test data show significant differences in strength depending upon the relative humidity of the specimen conditioning atmosphere prior to physical testing. These test data show that the foam strength increases with decreasing moisture content. Bendix test data verifies this. Evidently, the water absorbed acts as a plasticizer to the foam. In every case, except the flatwise testing at room temperature, the specimens conditioned at 10 percent RH were stronger than the specimens conditioned at 50 percent RH. The unit-to-unit variations were eliminated by testing part of the individual blocks at both 10 and 50 percent RH.

Cure Time and Cure Temperature Effects

The effects of cure time and cure temperature are shown in Figure 25. Increasing the cure temperature from 140°F to 250°F increases the strength by about 11 percent. Increasing the cure time from 4 to 8 hours increases the strength somewhat. Cure times of 1 to 2 hours give conflicting and inconsistent results. The effect of cure time and cure temperature on compressive strength was also measured on test samples similar to the Ablefoam ring spacer. The information from this test indicates that the compressive strength of Ablefoam is directly proportional to both the cure time and cure temperature.

This study of cure conditions led to an interest in the actual degree of cure of the epoxy foams. Samples of the Ablefoam rings cured at various cure times and cure temperatures, as well as at different preheats at constant cure time and temperature, were submitted for glass transition temperature (Tg) measurements. (The glass transition temperature of a material is a measure of the relative cross-link density or degree of cure of the material.) The results of these measurements are listed in Table 13.

These tests definitely show that the cure of 4 hours at 165°F is not a full cure. No attempt has been made to determine Tg of Ablefoam cured for up to 16 to 20 hours at 165°F. Judging from the data for 250 and 325°F, increasing cure time will raise the Tg.

Direction of Test Load (Orientation) Effects

The orientation or direction of foam rise in relation to test load direction does not seem to significantly alter the strength of the foam. This would mean that the cells are relatively uniform and the direction of loading does not affect the strength of the foam.

Density Effects

The effect of density on compression has been measured on both block and cylindrical test specimens, with the data plotted in Figure 26. The slope of the curve is about 1.9 with an intercept of 3.6. The block specimens tested primarily had slopes of 1.7 to 1.9 and intercepts of 3 to 5, but the repeatability between lots was not as good as with the cylinders. This would indicate that a larger part of the variation noted in earlier test data was due to unit variation as well as lot variations.

OUTLINE OF ENCAPSULATION PROCESSES (Capoxyfoam I)

To prevent subjecting fabrication schedules to single source control, Bendix formulated and developed a one-component epoxy foam, Capoxyfoam I. When a workable formulation was developed, it was necessary to determine if Capoxyfoam I would process the same as Ablefoam 5. Development work was initiated to determine if Capoxyfoam I would encapsulate the assemblies with the existing production tooling and processes.

Dummy assemblies were encapsulated with Capoxyfoam I using production molds. Both the A-B Assembly and Assembly C were represented by the same dummy components used in the development of Ablefoam 5. Capoxyfoam I was found to have a higher viscosity at room temperature than Ablefoam 5. The high viscosity of the new foam did not allow pouring of the A-B Assembly through the mold fill hole. Before altering the tool or enlarging the fill hole, a mold preheat was tried. Preheating the mold to 115°F solved the flow problem and enabled the Capoxyfoam I to be poured through the fill hole in approximately the same time as Ablefoam 5. All of the test units filled well with no major void problems. The density variation of the foam throughout the entire unit was 8 to 9 lb/ft^3 for the Capoxyfoam I units. This compares favorably to the 8 to 10 lb/ft^3 variation for units encapsulated with Ablefoam 5. Encapsulation of Assembly C was done successfully using the same process as used with Ablefoam 5; no mold preheat was required.

A discussion of Capoxyfoam I development is presented in the next section.

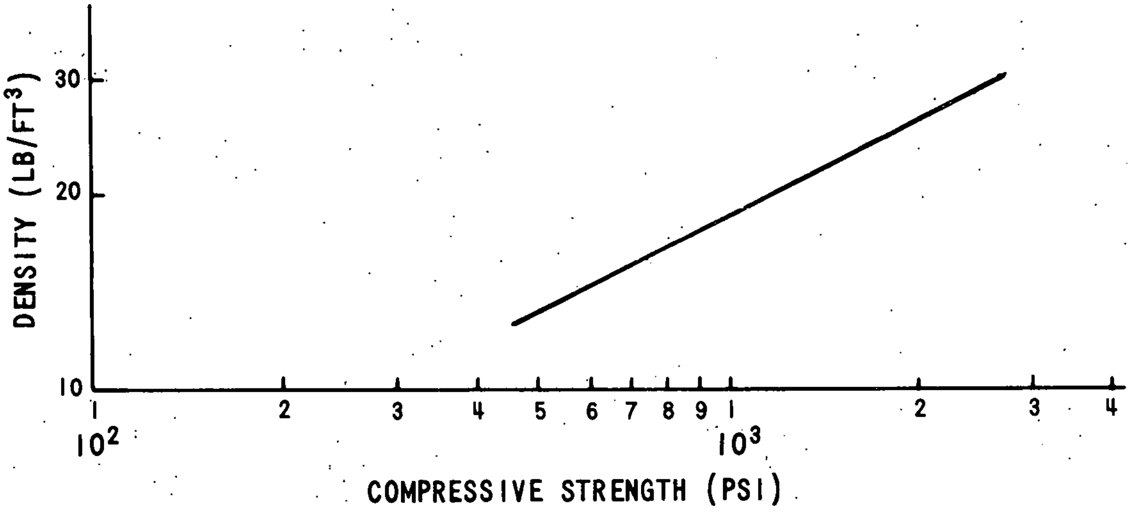

Figure 26. Effect of Density on Compressive Strength (Perpendicular to Foam Rise)

Table 13. Glass Transition Temperature Measurements

Cure Conditions		Glass Transition Temperature	
Temperature (°F)	Time (hr)	(°C)	(°F)
165	4 (mold preheat - RT)	101	214
165	4 (mold preheat - 85°F)	113	235
165	4 (mold preheat - 100°F)	110	230
165	4 (mold preheat - 115°F)	103	217
250	2	124	255
250	4	138	280
250	4	137	278
250	8	140	284
325	2	133	271
325	4	140	284
325	8	150	320

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DEVELOPMENT OF CAPOXYFOAM I

INTRODUCTION

This section describes the development, by the Polymer Laboratory of BKC, of a polymeric epoxy resin-based foam system capable of at least duplicating the properties of Ablefoam 5. A literature survey was made of polymeric epoxy technology. The search encompassed the chemistry of epoxy resins, blowing agents, curing agents, cell-stabilizers, and possible formulation compositions of epoxy foam systems. The information derived from this literature survey was used to establish a program of investigation which began with chemical and physical analysis of Ablefoam 5.

CHEMICAL AND PHYSICAL ANALYSES

Investigation of the solvency properties of uncured Ablefoam 5 indicated the presence of an insoluble solid identified as ammonium carbonate, the blowing agent. In addition to the ammonium carbonate precipitate, small black particles were discovered. These particles were insoluble in organic and inorganic solvents and acids and had a melting point greater than 300°C (572°F). Further analysis revealed the solid to be carbon black, an inert compound, possibly intended to color (blacken) the Ablefoam 5.

Gel Permeation Chromatography

To further aid the analyses, a coordinated test effort was initiated with the Bendix Test Laboratory. Preliminary examinations subjected uncured Ablefoam 5 to gel permeation chromatography (GPC) for component identification through molecular weight separation. After determining the standard molecular weight curves for the two commercial epoxy resins, Dow Epoxy Novalacs DEN 431 and DEN 438 (Dow Chemical Co), and for Ablefoam 5, it was disclosed that the Ablefoam 5 system did contain novalac resins similar to DEN 431 and DEN 438.

It was observed, also through the use of GPC, that the two aromatic amines, meta-phenylenediamine and methylenedianiline, were found to be present in the Ablefoam 5 system as organic curing agents (Figure 28). These two amines are present in a eutectic blend of Epon Cure Agent Z, which is commercially prepared by Shell for use in curing epoxy resins. To support these findings, comparative thin layer chromatography (TLC) was performed using the two amines and uncured Ablefoam 5. The spot depositions of the two amines gave conclusive evidence that they are present in the Ablefoam 5 system.

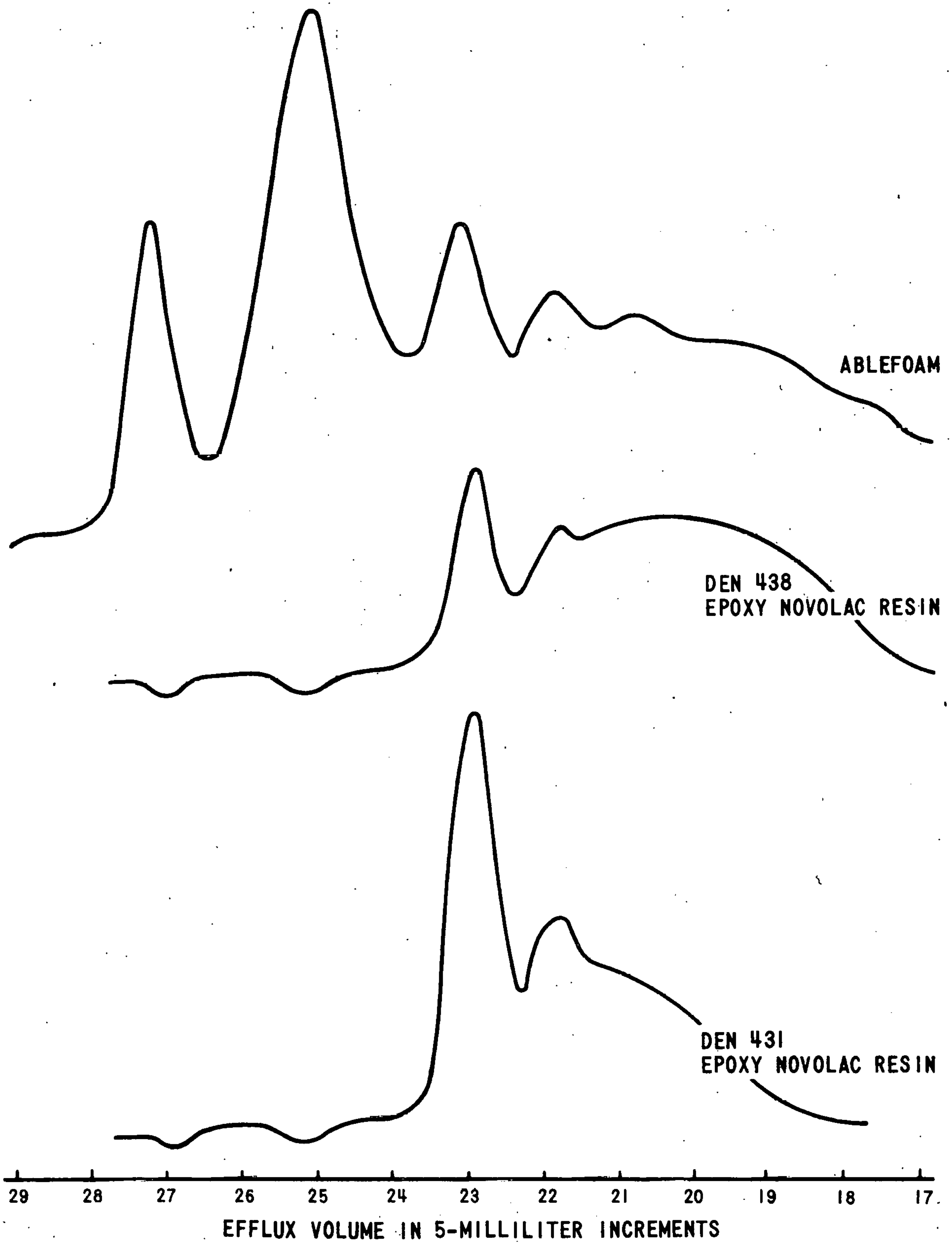


Figure 27. Gel Permeation Chromatography Analysis, Ablefoam 5 and Related Epoxy Novolac Resins

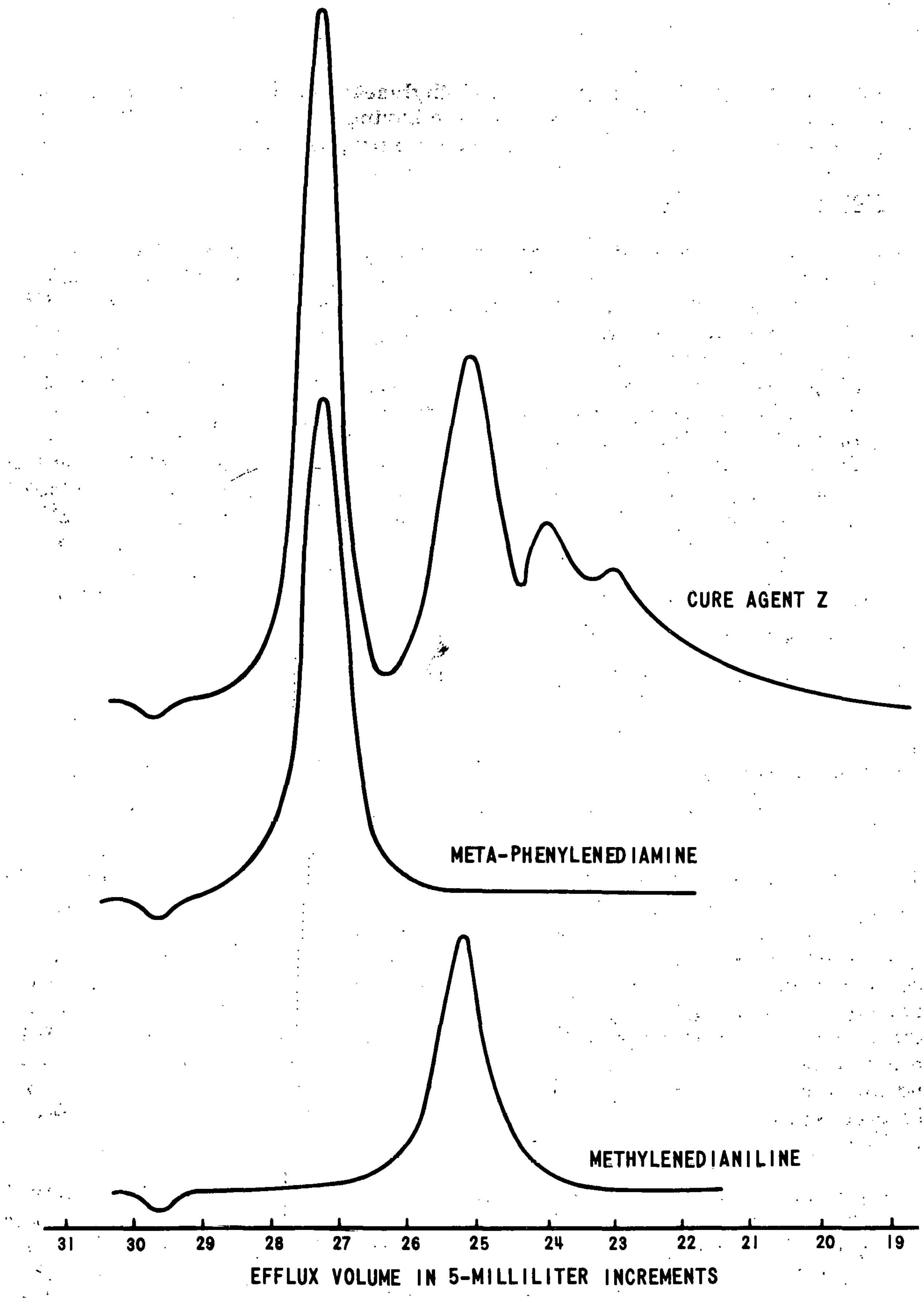
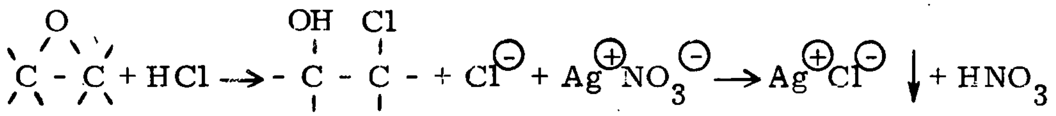


Figure 28. Gel Permeation Chromatography Analysis of Cure Agent Z, Meta-Phenylenediamine and Methylenedianiline

An aliphatic amine, thought to be diethylenetriamine (DETA), was also found to be present. This is an amine having high reactivity with epoxy groups and is presumably present for the purpose of initiating the cure cycle.

Potentiometric Titration

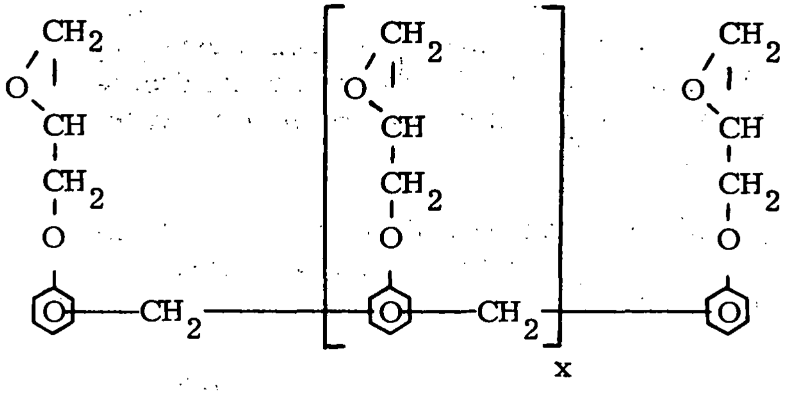
Ablefoam 5 was also analyzed by potentiometric titration, a technique adopted by the BKC Polymer Laboratory to establish the epoxide equivalent (content) of epoxy resins and to analyze the percent cure of the epoxy foam. This procedure determines the number of oxirane (epoxy) rings in the epoxy resin. It is then feasible to ascertain stoichiometric amounts of specific curing agents that are added to the resins. After mixing the resin with a curing catalyst, the reaction between the two can be monitored. Such monitoring consists of accounting for the number of existing epoxy sites reacted upon by the chemical compound and the number of epoxy sites left unreacted. The quantitative procedure for the determination of the epoxide equivalent for cured and uncured epoxy resins by potentiometric titration is summarized in the Appendix. Potentiometric titration, in this instance, measures the consumption of the remaining chloride ions from a 1.0 N HCl solution, by the titratible silver ion from a 1.0 N $AgNO_3$ solution, through the following reaction.



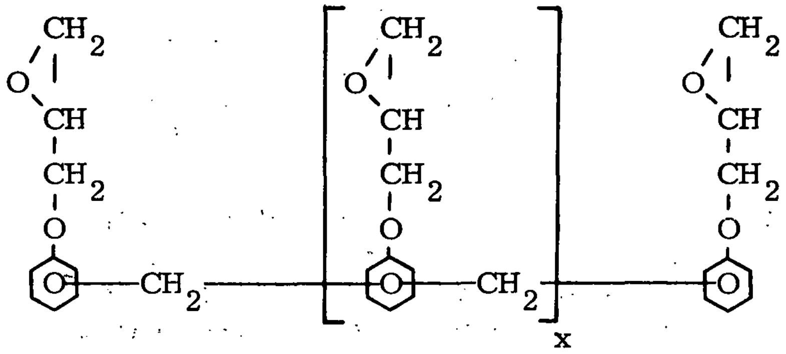
"The difference between the amount of acid (chloride ion) added and the amount unconsumed is a measure of the epoxy content."[2]

Consideration was given to this analytical procedure in determining the selection of the various epoxy resins to be employed in the foam formulation process. Based upon the information from the GPC curves, the preliminary laboratory formulations were made up of various combinations of DEN 431, an epoxy novolac resin; its higher molecular weight complement, DEN 438; and a lower viscosity bisphenol-A type epoxy resin, Shell's Epon 828, which has a comparable molecular weight. The chemical structures for these epoxy resins are shown below.

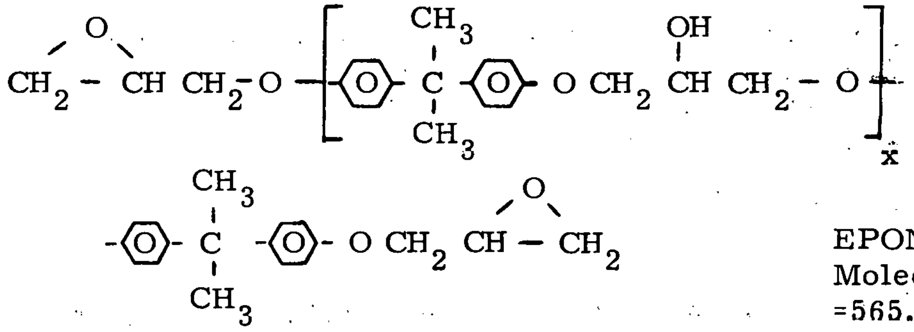
A comparison of the various resins and possible combinations revealed that a blend of DEN 431 and Epon 828 yielded stronger and more uniform foams. Amounts of the two epoxy resins in variable ratios indicated that no substantial difference was evident in the compressive strength values of the cured foams. However, as the amount of Epon 828 was increased proportionately, the flowability during foaming became too great and resin



DEN 431
Molecular Weight
= 534.9, where x = 1.35.



DEN 438
Molecular Weight
= 571.2, where x = 1.6.



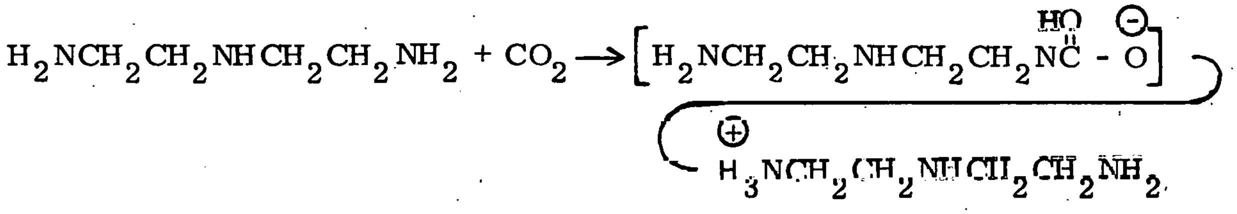
EPON 828
Molecular Weight
=565.8, where x = 0.8.

sedimentation was prevalent. A study of the flow characteristics of the uncured foam and compressive strength values of the cured foams indicated the optimum blend ratio of the two resins to be 50:50. The organic reactive diluent, 1,2-epoxy-3-phenoxypropane, was added to the resin blend to reduce the resin viscosity to a workable consistency.

Blowing Agents

In the course of formulating the epoxy foam system, various blowing agents were examined. Acetone and the lower-boiling Freons were unsuitable because of their high volatility, since temperatures exceeding room temperature were required to cure the foam.[3, 4]

A laboratory synthesized compound known as diethylenetriamine (DETA) carbamate was prepared by the reaction of DETA and carbon dioxide to form the following complex salt.[5]



$$H_2NCH_2CH_2NHCH_2CH_2NH_2 + CO_2 \longrightarrow \left[H_2NCH_2CH_2NHCH_2CH_2\overset{H}{N}\overset{O}{\overset{\|}{C}} - \overset{\ominus}{O}\right] \overset{\oplus}{H_3}NCH_2CH_2NHCH_2CH_2NH_2$$

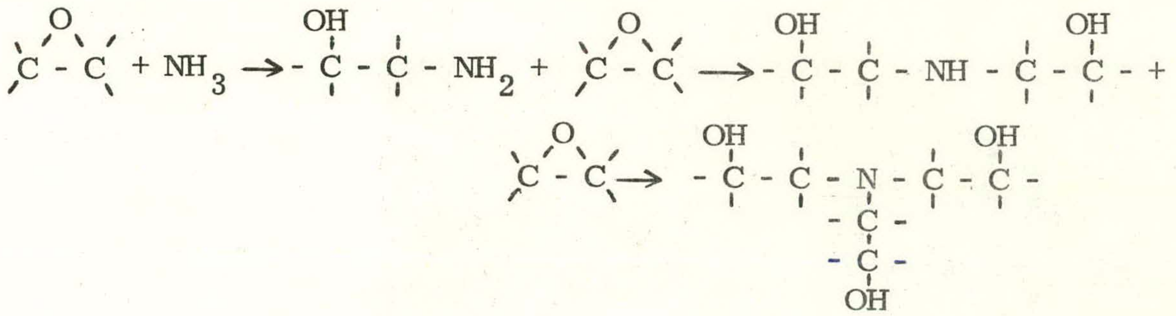
When heated, the amine carbamate decomposes into carbon dioxide (the active blowing agent) and DETA (the amine curing agent for the epoxy resins). The dual character of this compound was not useful, however, since extremely large concentrations were required for minimal blowing and curing of the foam.

Ammonium carbonate, present as the blowing agent in Ablefoam 5, was found to be quite suitable. Ammonium carbonate decomposes at 58°C (136.4°F) through the following reaction.

$$(NH_4)_2CO_3 \xrightarrow{\Delta} 2\ NH_3 + CO_2 + H_2O$$

Because all three decomposition products--ammonia, carbon dioxide, and water vapor--contribute to the foam system, this compound was practical as a blowing agent. With this compound, the blowing action is a controllable factor since the ambient temperature of the foam and mold must approach 58°C (136.4°F) before the foam will blow.

Results from potentiometric titration of the epoxy resins indicated a decrease in their epoxy content when they were mixed with the ammonium carbonate. This fact suggests that, in addition to the blowing action, ammonium carbonate acts as a curing agent; therefore, that part of the manufacturing process where the ammonium carbonate is added to the epoxy resin must be closely controlled to minimize lot-to-lot variation in the foam reactivity. The reaction shown below is the process by which the evolved ammonia gas reacts with the epoxy ring to effect an actual curing response.



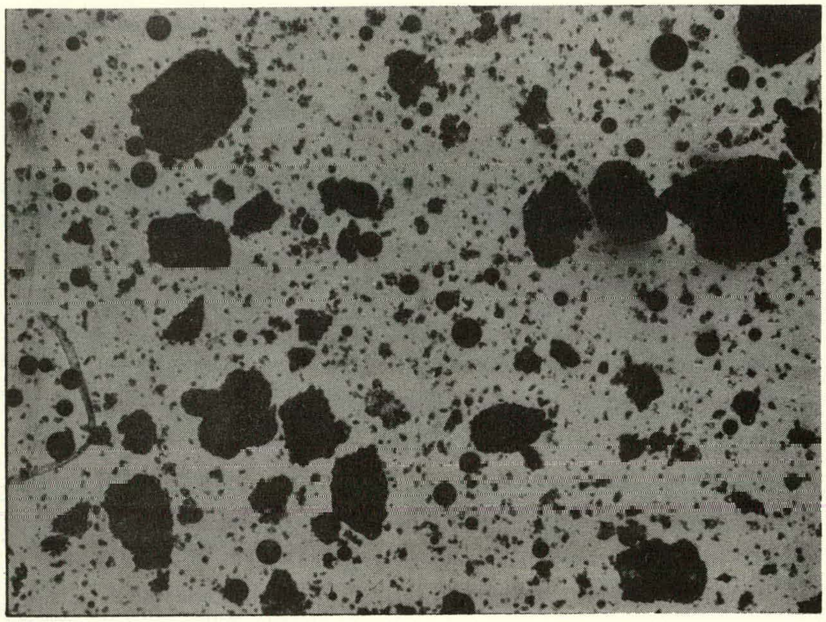
Mixing

In the preliminary formulation stages, numerous inconsistent test results were obtained for those foams mixed with a high speed air stirrer. Resin sedimentation and cell voids were directly caused by insufficient mixing. To eliminate these problems it became necessary to employ a laboratory type, three-roll mill to evenly blend the foam components; primarily to disperse the solid ammonium carbonate with the epoxy resin and other foam constituents. Before the ammonium carbonate was blended with the epoxy foam premix, it was passed through a Number 40 U. S. sieve.

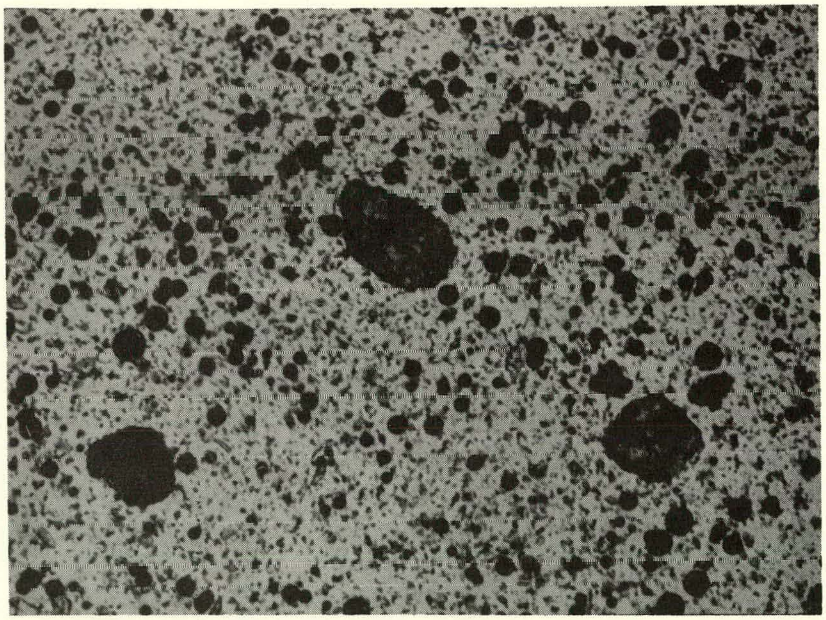
Photomicrographs of the blended mixture indicated that as the mill-roll distances decreased, the solid-to-resin dispersement increased. With an increase in the number of times the mixture passed through the mill, the solid-to-resin dispersement increased, in conjunction with a breaking up of the larger ammonium carbonate crystals into a much smaller size (Figure 29 A and B).

The difference in solid dispersement between the second and third mill passes appeared to be so slight that the milling process was terminated after the second pass (Figure 29-B). This was desirable since the additional time required for a third mill pass would cause a decrease in the epoxide content of the resin system, thereby reducing the reactivity of the resin complex. Figure 30 illustrates that the greatest decrease in epoxy content following the addition of ammonium carbonate occurs in the first twelve hours of storage.

Since, as previously mentioned, a reaction upon the epoxy resins occurs when ammonium carbonate is added, it was necessary to expedite the processing technique. A method was developed to collect the blended foam mixture in plastic polyethylene cartridges as it flows off the mill. The cartridges are then sealed and immediately immersed in liquid nitrogen to quick-freeze the foam mixture. Each cartridge is hand-held with forceps as it is lowered into the container of liquid nitrogen. This method halts any subsequent reaction between the chemical components of the foam system. When needed, the one-component frozen foam[1] is allowed to thaw to an extrudable temperature. The foam is then poured into the desired mold. (See Figure 31.)

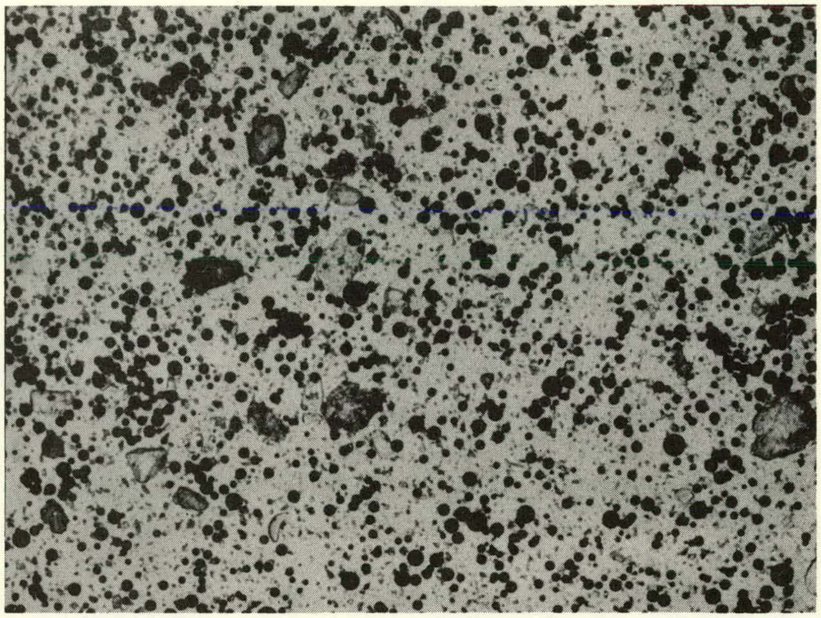


Ammonium Carbonate Dispersement With the Epoxy Foam Premix Mixed With a High-Speed Air Stirrer

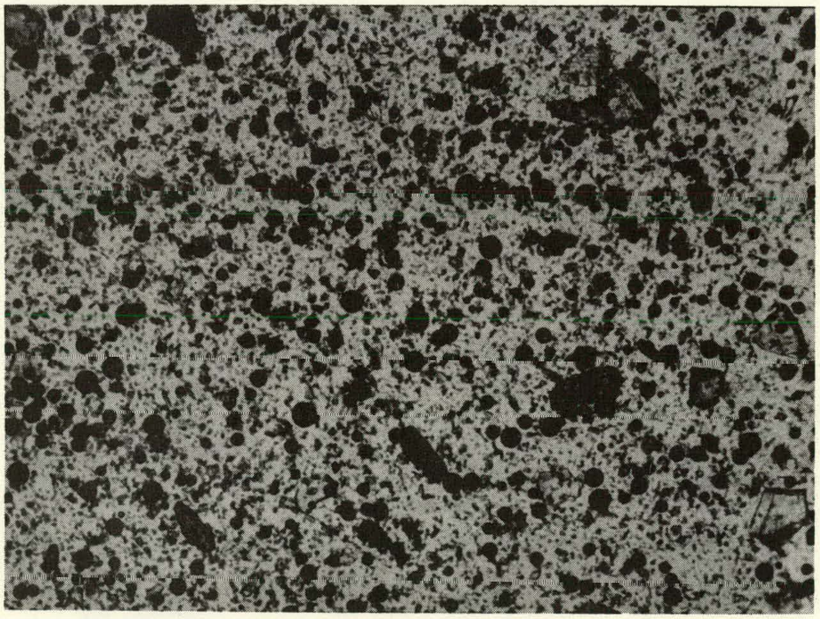


Ammonium Carbonate Dispersement With the Epoxy Foam Premix, Following One Mill Pass

Figure 29A. Photomicrographs of Ammonium Carbonate Dispersement With the Epoxy Foam Premix



Ammonium Carbonate Dispersement With the Epoxy Foam Premix, Following Second Mill Pass



Ammonium Carbonate Dispersement With the Epoxy Foam Premix, Following Third Mill Pass

Figure 29B. Photomicrographs of Ammonium Carbonate Dispersement With the Epoxy Foam Premix

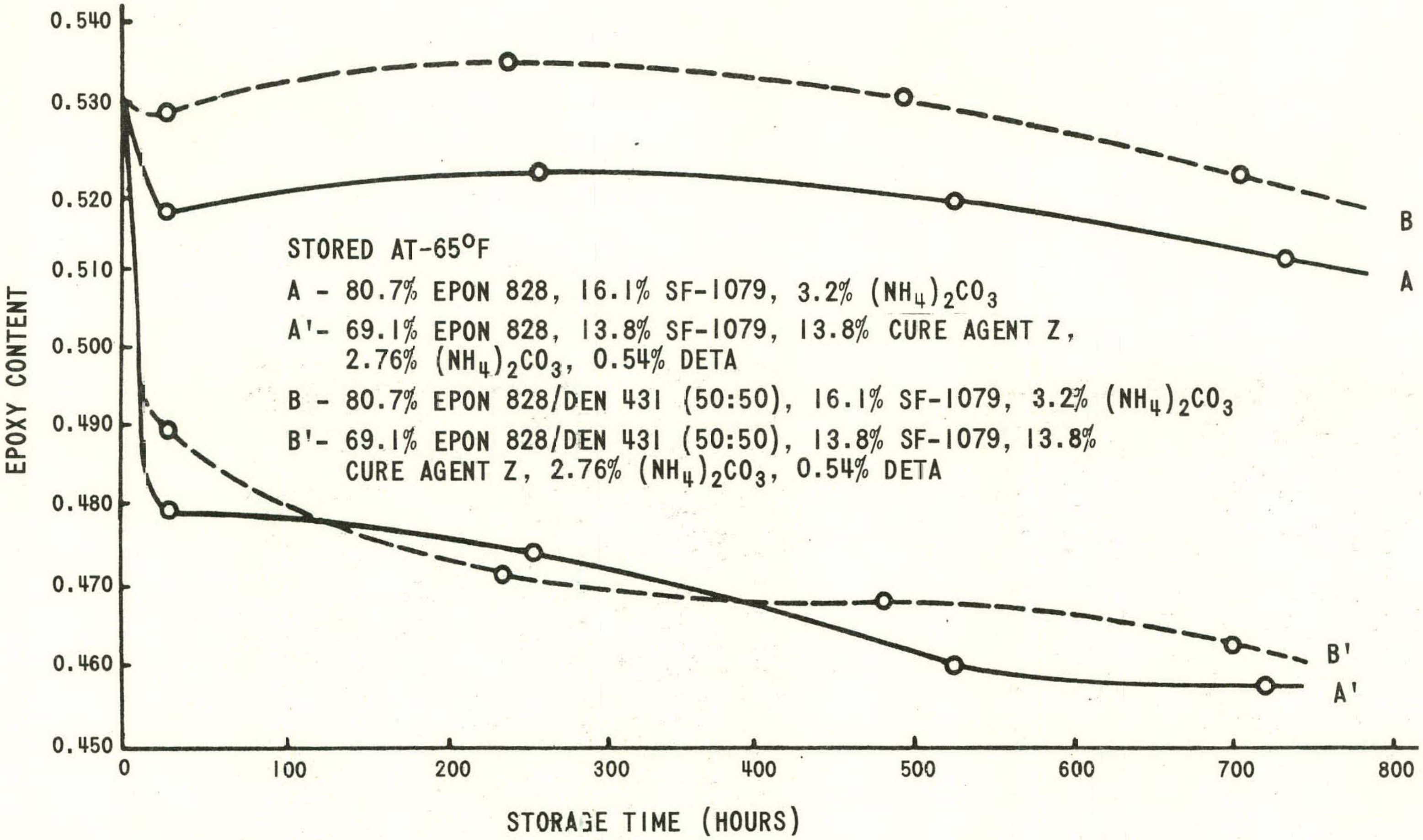


Figure 30. Effect of Adding Ammonium Carbonate to Epoxy Foam Premix, Showing Epoxy Content as a Function of Storage Time (Foam Stored at -65°F)

Since the shelf life of the frozen foam is limited (six months for Ablefoam 5 per SS282997), it was decided to study the effects that storage time had on the epoxy content. Assuming the epoxy contents to be identical for the various lots of Ablefoam 5 upon initial storage, it is evident from Figure 32 that the epoxide content of Ablefoam 5 decreases as a function of storage time (storage is at -65°F).

Compression Testing (Contract)

A contract was established with Midwest Research Institute for the screening of potential foam formulations by compression testing.[6] The testing was performed on 1-inch by 1.129-inch diameter foam specimens cut from an 8-inch by 1.129-inch diameter foam cylinder (Figure 33). The specimens were tested edgewise (parallel to foam rise). The same 8-inch by 1.129-inch diameter cylinder mold was subsequently used to optimize the formulation of a suitable back-up epoxy foam.

The various foam formulations which were developed were evaluated for their potential applicability. Samples were screened from further consideration if they did not meet the requirements of SS282997 for density and compressive strength:

- Density, 20.0 lb/ft^3 minimum averaging 22 lb/ft^3;
- Compressive strength, 1050 psi minimum at room temperature testing; and 250 psi minimum at 200°F testing.

All foam systems were cured at 74 ± 4°C (165 ± 5°F) for 4 hours.

Because of insufficient blowing action employing an unpreheated mold, it was necessary to study the effects of mold preheat conditions on compressive strength. It was found that a mold preheat of 44°C (110°F) yielded foams with optimum compressive strengths. (See Figure 34.)

Cure Agents

Several formulation studies were used to aid the development of the epoxy foam system. In one study the effects of the two aromatic amines, metaphenylenediamine and methylenedianiline, were compared. A stoichiometric amount of each amine was dissolved in 10 percent by weight of boiling 1,2-epoxy-3-phenoxypropane to make individual mixtures. Each amine mixture was then added to an epoxy foam premix. Table 14 indicates that in certain instances, the individual amines yielded high compressive strengths, some even as high as those foams cured with Cure Agent Z.

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Figure 31. Extruding the Thawed Foam Premix From a Semco Tube

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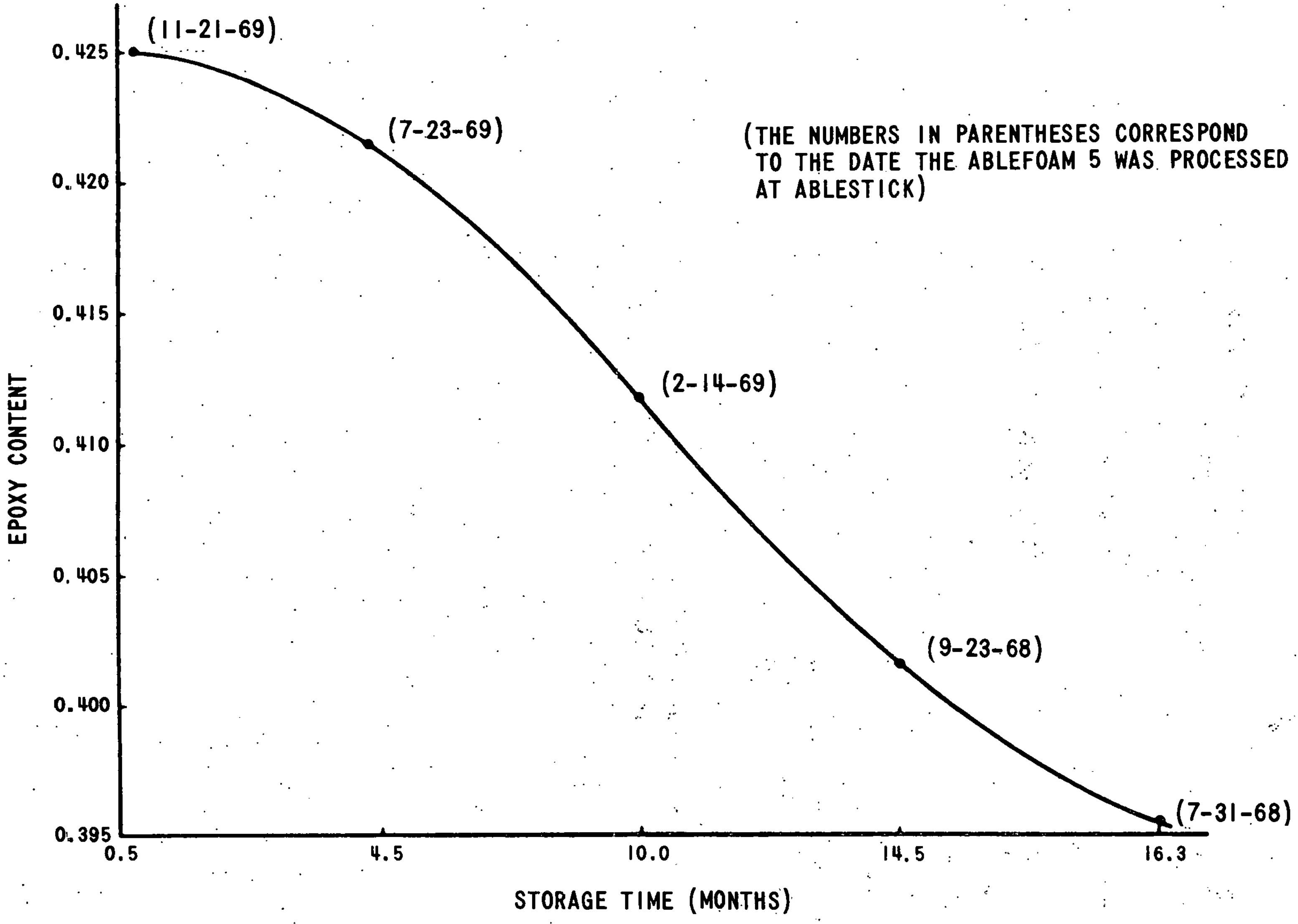
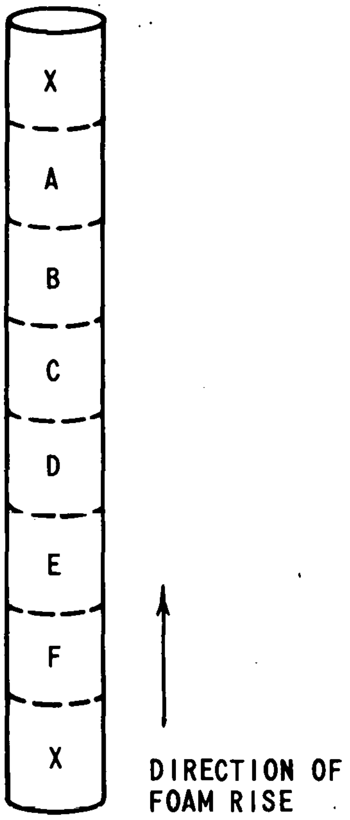


Figure 32. Potentiometric Titration Analysis of Epoxy Content of Ablefoam 5 Versus Storage Time (Storage is at -65°F.)



DIMENSION OF EPOXY FOAM CYLINDER:

HEIGHT - 8.000
DIAMETER - 1.129

DIMENSIONS OF INDIVIDUAL TEST SAMPLE:

HEIGHT - 1.000
DIAMETER - 1.129

(THE VOLUME OF EACH TEST SAMPLE IS EQUAL TO 1 CUBIC INCH)

Figure 33. Example of Test Samples From Foam Cylinder Specimen

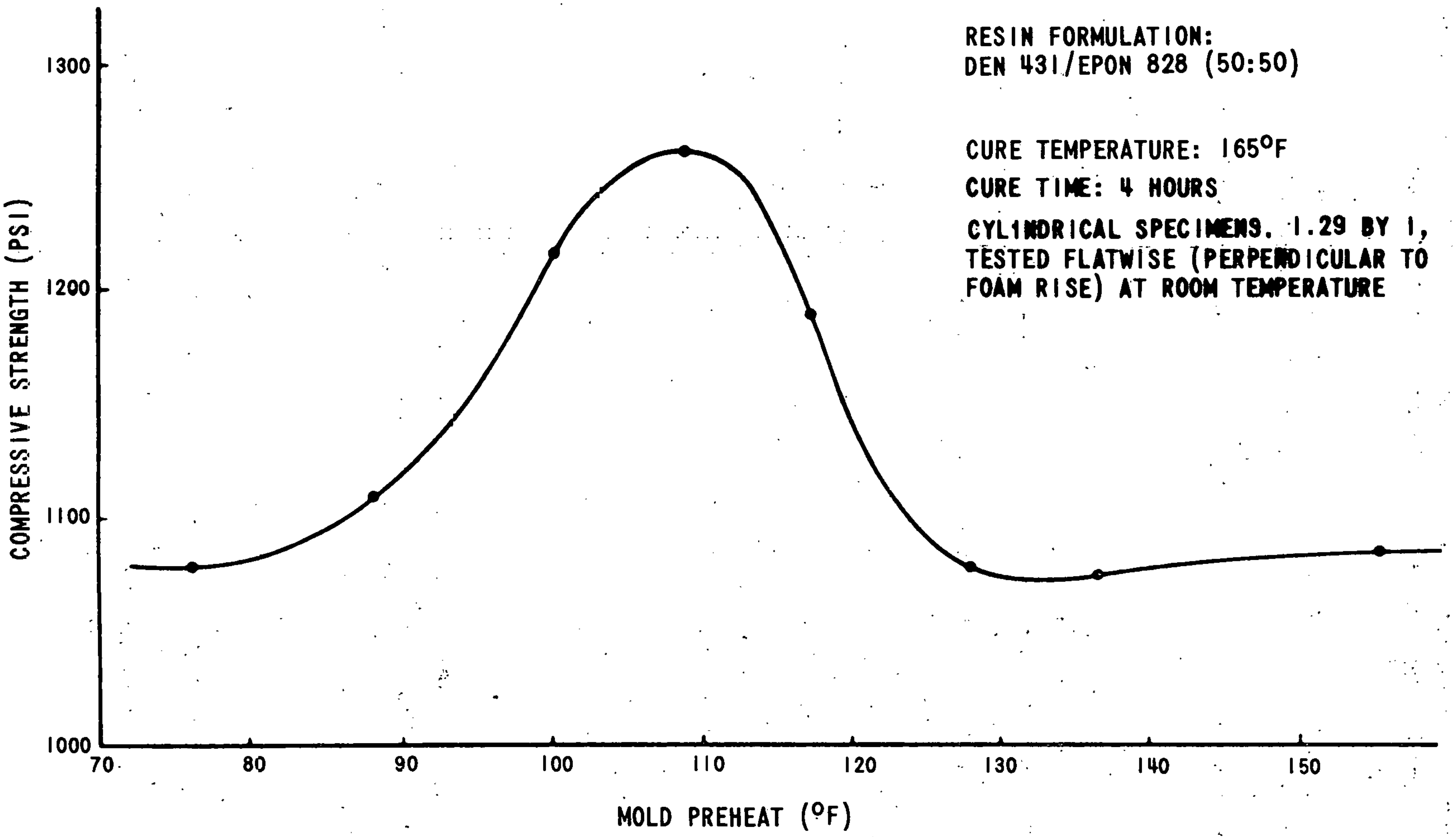


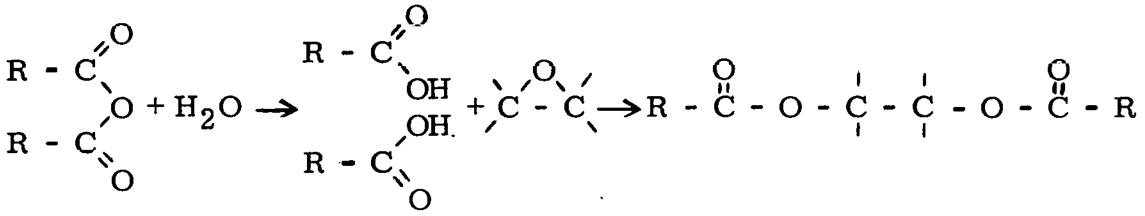
Figure 34. Graph of Mold Preheat Versus Compressive Strength for Epoxy Foam

However, the difficulty in processing the two amines with the epoxy resins rendered them unsuitable.[7] Since these two amines are inherent to the composition of Cure Agent Z, the eutectic blend was selected as the aromatic amine curing agent.[8,9]

Table 15 shows the results of a study done to determine the optimum concentration of Cure Agent Z to obtain the highest foam compressive strengths. The experimental amount of Cure Agent Z is identical with that of the theoretical stoichiometric amount of 20 parts per hundred parts by weight of resin (phr).

In addition to the Cure Agent Z study, a cell-surfactant examination using Union Carbide's Silicone L-5320 indicated that its use at low concentrations produced high compressive strengths and uniform density gradients (Table 16).[10] Much higher concentrations of other cell stabilizers were required for the same results. Consequently, the use of other cell stabilizers was undesirable since with them it was possible that the silicone fluid would settle out of the cured foam at some time following storage.

The addition of a 4 phr concentration of methyl Nadic anhydride (MNA) to the foam system improved density uniformity and increased the compressive strengths as indicated in Table 17. The anhydride appeared to function simultaneously as a gel-agent and cure agent.[11] The curing mechanism for the anhydride requires the formation of the diacid from the anhydride. The eventual reaction upon the epoxide ring is shown below.



The aliphatic amine, DETA, was employed in the MNA study. The compressive strengths when using DETA were of consistent quality. In nearly every instance, however, the foams failed to pass the flow gage requirements per SS282997, therefore, the DETA curing agent was omitted from the foam formulations.

A cure temperature study was conducted comparing compressive strengths at the specified 165°F cure and a 200°F cure. Epoxy foams were tested with and without the addition of MNA. Table 18 shows that a slight increase in compressive strengths at 200°F was attained. It was also observed that localized shrinking was inherent to those foams cured at 200°F, therefore, rendering the 200°F cure temperature undesirable.

Text continued on Page 108.

Table 14. Effects of Various Aromatic Amines on Compressive Strengths of Epoxy Foams (Meta-Phenylenediamine and Methylenedianiline)

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi) 10% of Total	Ultimate	Density (lbs/ft^3)	Comments
MPDA*	19.44	75	910		A-22.30**	EPON 828/ DEN 431 (50:50) 10% PGE* Cure temp at 165°F 4 hr
	19.44	75	955		C-23.10	
	19.44	75	825		E-21.75	
MDA with 0.8 phr DETA	19.44	75	1160		A-23.26	
	19.44	75	1125		C-22.89	
	19.44	75	1085		E-22.26	
MPDA	19.44	200	325		B-22.71	
	19.44	200	310		D-22.12	
	19.44	200	320		F-25.26	
MDA with 0.8 phr DETA	19.44	200	445		B-23.21	
	19.44	200	420		D-22.96	
	19.44	200	400		F-23.42	
MDA*	35.6	75	1350		A-25.62	
	35.6	75	1325		C-25.62	
	35.6	75	1275		E-25.98	
MDA with 0.8 phr DETA	35.6	75	1340		A-24.50	
	35.6	75	1270		C-23.77	
	35.6	75	1190		E-23.09	
MDA	35.6	200	415		B-25.68	
	35.6	200	380		D-25.63	
	35.6	200	370		F-25.91	
MDA with 0.8 phr DETA	35.6	200	425		B-24.35	
	35.6	200	430		D-23.41	
	35.6	200	385		F-22.61	
MPDA	19.44	75	1055		A-21.72	EPON 828/ DEN 438 (50:50) 10% PGE Cure temp at 165°F 4 hr
	19.44	75	1110		C-22.90	
	19.44	75	1040		E-22.26	
MPDA with 0.8 phr DETA	19.44	75	1140		A-23.12	
	19.44	75	1205		C-24.23	
	19.44	75	1050		E-22.59	
MPDA	19.44	200	590		B-22.59	
	19.44	200	615		D-22.74	
	19.44	200	600		F-23.14	
MPDA with 0.8 phr DETA	19.44	200	605		B-23.39	
	19.44	200	595		D-23.22	
	19.44	200	560		F-22.61	
MDA	35.6	75	1290		A-24.78	
	35.6	75	1185		C-23.91	
	35.6	75	1100		E-21.77	

Table 14 Continued. Effects of Various Aromatic Amines on Compressive Strengths of Epoxy Foams (Meta-Phenylenediamine and Methylenedianiline)

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi) 10% of Total	Compressive Strength (psi) Ultimate	Density (lbs/ft^3)	Comments
MPDA with	35.6	75	1240		A-24.27**	
0.8 phr	35.6	75	1250		C-24.40	
DETA*	35.6	75	1200		E-23.71	
MDA*	35.6	200	610		B-24.77	
	35.6	200	560		D-23.38	
	35.6	200	510		F-22.61	
MDA with	35.6	200	590		B-24.69	
0.8 phr	35.6	200	560		D-23.74	
DETA	35.6	200	520		F-23.05	
MPDA*	19.44	75	890		A-23.04	DEN 431
	19.44	75	1025		C-23.49	10% PGE*
	19.44	75	890		E-22.15	Cure temp
						at 165°F
MPDA with	19.44	75	995		A-22.06	4 hr
0.8 phr	19.44	75	1020		C-22.21	
DETA	19.44	75	1035		E-22.86	
MPDA	19.44	200	545		B-23.28	
	19.44	200	550		D-22.98	
	19.44	200	530		F-24.48	
MPDA with	19.44	200	505		B-22.11	
0.8 phr	19.44	200	510		D-22.51	
DETA	19.44	200	615		F-26.67	
MDA	35.6	75	1260		A-24.38	
	35.6	75	1210		C-24.25	
	35.6	75	1085		E-23.01	
MDA with	35.6	75	1300		A-24.46	
0.8 phr	35.6	75	1100		C-23.65	
DETA	35.6	75	1100		E-23.59	
MDA	35.6	200	555		B-24.72	
	35.6	200	530		D-23.59	
	35.6	200	460		F-22.74	
MDA with	35.6	200	505		B-24.04	
0.8 phr	35.6	200	510		D-23.64	
DETA	35.6	200	530		F-24.50	
MPDA	19.44	75	1120		A-23.14	EPON 828
	19.44	75	1105		C-23.79	10% PGE
	19.44	75	1130		E-24.47	Cure temp
						at 165°F
MPDA with	19.44	75	1270		A-24.16	4 hr
0.8 phr	19.44	75	1230		C-23.92	
DETA	19.44	75	960		E-22.18	

Table 14 Continued. Effects of Various Aromatic Amines on Compressive Strengths of Epoxy Foams (Meta-Phenylenediamine and Methylenedianiline)

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density lbs/ft^3	Comments
			10% of Total	Ultimate		
MPDA*	19.44	200	230		B-23.21**	
	19.44	200	220		D-23.91	
	19.44	200	195		F-25.76	
MPDA with 0.8 phr DETA*	19.44	200	250		B-24.13	
	19.44	200	195		D-22.73	
	19.44	200	95		F-22.36	
MDA*	35.6	75	1440		A-26.48	
	35.6	75	1230		C-24.90	
	35.6	75	1000		E-22.41	
MDA with 0.8 phr DETA	35.6	75	1340		A-24.90	
	35.6	75	1230		C-24.06	
	35.6	75	1090		E-22.87	
MDA	35.6	200	200		B-25.94	
	35.6	200	130		D-23.89	
	35.6	200	80		F-22.12	
MDA with 0.8 phr DETA	35.6	200	155		B-24.74	
	35.6	200	130		D-23.44	
	35.6	200	55		F-22.89	

* phr: parts per hundred parts by weight of resin
MPDA: meta-phenylenediamine
PGE: phenylglycidyl ether
DETA: diethylenetriamine
MDA: methylenedianiline

**Capital letters indicate locations of specimens as cut from test cylinder (Figure 33).

Table 15. Effects of Differing Concentrations of Cure Agent Z on Compressive Strengths of Epoxy Foams

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
Cure Z*	8.0	75		840	A-23.43**	DEN 431/ EPON 828 MNA* 4 phr Cured at 165°F for 4 hr
	8.0	75		840	C-22.66	
	8.0	75		820	E-22.28	
	8.0	200	4		B-23.04	
	8.0	200	2		D-22.28	
	8.0	200	10		F-22.28	
	10.0	75	1030		A-22.85	
	10.0	75	1000		C-22.28	
	10.0	75	980		E-22.03	
	10.0	200	10		B-22.86	
	10.0	200	12		D-21.90	
	10.0	200	15		F-22.09	
	12.0	75		1090	A-22.70	
	12.0	75		1090	C-22.09	
	12.0	75		1050	E-21.71	
	12.0	200	50		B-22.51	
	12.0	200	80		D-21.75	
	12.0	200	85		F-21.79	
	14.0	75	1160		A-23.00	
	14.0	75	1140		C-22.36	
	14.0	75	1110		E-21.98	
	14.0	200	190		B-22.55	
	14.0	200	220		D-22.06	
	14.0	200	220		F-22.09	
	16.0	75			A-22.74	
	16.0	75	1180		C-22.32	
	16.0	75	1150		E-22.09	
	16.0	200		435	B-22.66	
	16.0	200		460	D-22.09	
	16.0	200		455	F-22.21	
	18.0	75	1200		A-23.24	
	18.0	75	1210		C-22.89	
	18.0	75	1200		E-22.55	
	18.0	200		520	B-23.16	
	18.0	200		500	D-22.59	
	18.0	200		520	F-22.66	
	20.0	75	1250		A-22.85	
	20.0	75	1230		C-22.66	
	20.0	75	1200		E-22.55	
	20.0	200		550	B-22.85	
	20.0	200		530	D-22.59	
	20.0	200		530	F-22.70	

Table 15 Continued. Effects of Differing Concentrations of Cure Agent Z on Compressive Strengths of Epoxy Foams

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
Cure Z*	22.0	75	1230		A-22.85 **	
	22.0	75	1230		C-22.62	
	22.0	75	1220		E-22.44	
	22.0	200		505	B-22.78	
	22.0	200		525	D-22.44	
	22.0	200		510	F-22.44	
	24.0	75	1235		A-22.74	
	24.0	75	1200		C-22.66	
	24.0	75	1180		E-22.24	
	24.0	200		450	B-22.51	
	24.0	200		440	D-22.28	
	24.0	200		425	F-22.24	
	26.0	75	1320		A-22.51	
	26.0	75	1320		C-22.32	
	26.0	75	1270		E-22.21	
	26.0	200		375	B-22.47	
	26.0	200		385	D-22.17	
	26.0	200		320	F-22.28	
	28.0	75	1340		A-22.59	
	28.0	75	1320		C-22.51	
	28.0	75	1245		E-22.28	
	28.0	200		378	B-22.70	
	28.0	200		366	D-22.21	
	28.0	200		320	F-22.28	
	30.0	75	1320		A-22.44	
	30.0	75	1300		C-22.28	
	30.0	75	1250		E-22.06	
	30.0	200		310	B-22.40	
	30.0	200		303	D-22.06	
	30.0	200		279	F-22.06	

* phr: parts per hundred parts by weight of resin
Cure Z: Shell's eutectic blend of meta-phenylenediamine and methylenedianiline
MNA: methyl nadic anhydride

**Capital letters indicate locations of specimens as cut from test cylinder (Figure 33).

Table 16. Effects of Differing Concentrations of L-5320 Cell Surfactant on Compressive Strengths of Epoxy Foams

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
L-5320*	2.0	75	1480		A-22.59**	DEN 431/ EPON 828 (50:50)
	2.0	75	1520		C-22.40	
	2.0	75	1480		E-22.40	
	2.0	200	620		B-22.40	No DETA;* cured at 165°F 4 hr
	2.0	200		557	D-22.28	
	2.0	200		450	F-22.51	
	4.0	75	1530		A-22.34	
	4.0	75	1520		C-22.09	
	4.0	75	1500		E-22.09	
	4.0	200		505	B-22.09	
	4.0	200		388	D-22.02	
	4.0	200	401		F-22.21	
	8.0	75	1540		A-22.28	
	8.0	75	1540		C-21.98	
	8.0	75	1500		E-21.79	
	8.0	200	128		B-22.24	
	8.0	200	148		D-21.90	
	8.0	200	500		F-22.28	
	12.0	75	1480		A-22.44	
	12.0	75	1500		C-22.17	
	12.0	75	1420		E-21.94	
	12.0	200	164		B-22.36	
	12.0	200	110		D-22.06	
	12.0	200	110		F-22.55	
	16.0	75	1300		A-21.71	
	16.0	75	1250		C-21.37	
	16.0	75	1250		E-21.45	
	16.0	200	90		B-21.71	
	16.0	200	80		D-21.14	
	16.0	200	67		F-21.79	

* phr: parts per hundred parts by weight of resin
L-5320: Union Carbide's silicone cell surfactant
DETA: diethylenetriamine

**Capital letters indicate locations of specimens as cut from test cylinder (Figure 33).

Table 17. Effects of Differing Concentrations of Methyl Nadic Anhydride on Compressive Strengths of Epoxy Foams

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
MNA*	0	75	1125		A-22.73**	EPON 828/ DEN 431 (50:50)
	0	75	1075		C-22.36	
	0	75	1050		E-21.78	
MNA with 0.7 phr DETA*	0	75	1039		A-. . . .	
	0	75	1062		C-. . . .	
	0	75	1112		E-. . . .	
MNA	0	200	550		B-22.71	
	0	200	510		D-22.21	
	0	200	460		F-21.31	
MNA with 0.7 phr DETA	0	200	465		B-. . . .	
	0	200	505		D-. . . .	
	0	200	530		F-. . . .	
MNA	4.0	75	1275		A-23.80	
	4.0	75	1270		C-23.54	
	4.0	75	1250		E-23.53	
MNA with 0.7 phr DETA	4.0	75	1320		A-23.92	
	4.0	75	1270		C-23.39	
	4.0	75	1260		E-23.41	
MNA	4.0	200	505		B-23.75	
	4.0	200	505		D-23.46	
	4.0	200	490		F-23.64	
MNA with 0.7 phr DETA	4.0	200	600		B-23.42	
	4.0	200	610		D-23.42	
	4.0	200	590		F-23.46	
MNA	6.0	75	1300		A-24.06	
	6.0	75	1280		C-23.53	
	6.0	75	1265		E-23.56	
MNA with 0.7 phr DETA	6.0	75	1375		A-24.45	
	6.0	75	1280		C-23.50	
	6.0	75	1290		E-23.70	
MNA	6.0	200	510		B-23.85	
	6.0	200	500		D-23.50	
	6.0	200	490		F-23.81	
MNA with 0.7 phr DETA	6.0	200	----		B-. . . .	DEN 431/ EPON 828 (50:50)
	6.0	200	----		D-. . . .	
	6.0	200	----		F-. . . .	
MNA	8.0	75	1320		A-24.29	
	8.0	75	1290		C-23.89	
	8.0	75	1295		E-23.94	
MNA with 0.7 phr DETA	8.0	75	1330		A-23.99	
	8.0	75	1275		C-23.41	
	8.0	75	1270		E-23.69	

Table 17 Continued. Effects of Differing Concentrations of Methyl Nadic Anhydride on Compressive Strengths of Epoxy Foams

Variable in the Formulation	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
MNA*	8.0	200	370		B-24.03**	
	8.0	200	390		D-23.92	
	8.0	200	365		F-23.99	
MNA with	8.0	200	470		B-23.69	
0.7 phr	8.0	200	495		D-23.69	
DETA*	8.0	200	455		F-23.78	
MNA	10.0	75	1230		A-23.94	
	10.0	75	1260		C-23.92	
	10.0	75	1285		E-23.77	
MNA with	10.0	75	1300		A-23.69	
0.7 phr	10.0	75	1260		C-23.42	
DETA	10.0	75	1250		E-23.46	
MNA	10.0	200	305		B-23.89	
	10.0	200	325		D-23.88	
	10.0	200	310		F-24.19	
MNA with	10.0	200	380		B-23.44	
0.7 phr	10.0	200	400		D-23.44	
DETA	10.0	200	345		F-23.76	
MNA	12.0	75	1210		A-23.35	
	12.0	75	1186		C-23.19	
	12.0	75	1185		E-23.35	
MNA with	12.0	75	1280		A-23.49	
0.7 phr	12.0	75	1285		C-23.42	
DETA	12.0	75	1270		E-23.53	
MNA	12.0	200	240		B-23.21	
	12.0	200	250		D-23.27	
	12.0	200	----		F-. . . .	
MNA with	12.0	200	----		B-. . . .	
0.7 phr	12.0	200	----		D-. . . .	
DETA	12.0	200	----		F-. . . .	

* phr: parts per hundred parts by weight of resin
MNA: methyl nadic anhydride
DETA: diethylenetriamine

**Capital letters indicate locations of specimens as cut from test cylinder (Figure 33).

Table 18. Effects of Cure Temperature on Compressive Strengths of Epoxy Foams, With and Without Methyl Nadic Anhydride

Variables in the Formulation (4-Hr Cure)	Conc (phr)*	Test Temp (°F)	Compressive Strength (psi)		Density (lbs/ft^3)	Comments
			10% of Total	Ultimate		
165°F		75	1039		A-21.32**	DEN 431/ EPON 828 (50:50)
		75	1062		C-21.64	
		75	1112		E-21.90	
200°F		75	1060		A-21.14	
		75	1128		C-21.86	
		75	1070		E-21.41	
165°F		200	465		B-21.33	
		200	505		D-21.71	
		200	530		F-22.32	
200°F		200	598		B-21.48	
		200	600		D-21.90	
		200	606		F-22.09	
165°F MNA* at 4 phr		75	1212		A-22.02	
		75	1205		C-21.94	
		75	1190		E-21.94	
200°F MNA at 4 phr		75	1202		A-22.06	
		75	1218		C-21.83	
		75	1205		E-21.90	
165°F MNA at 4 phr		200	508		B-22.17	
		200	548		D-21.86	
		200	548		F-22.09	
200°F MNA at 4 phr		200	685		B-21.98	
		200	700		D-21.86	
		200	685		F-21.98	

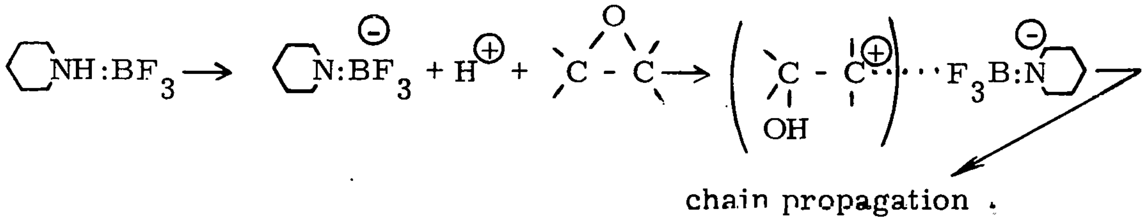
* phr: parts per hundred parts by weight of resin
MNA: methyl nadic anhydride

**Capital letters indicate locations of specimens as cut from test cylinder (Figure 33).

To insure an effective anhydride cure, maleic anhydride (MA) was added. It has a low melting point (53°C, 127.4°F) and a high degree of reactivity as a curing agent. The foams containing this anhydride possessed a more uniform cell structure and a better surface finish.

After the various formulation factors had been considered, a back-up epoxy foam was finally adopted and named Capoxyfoam I. A typical example of the back-up formulation is presented in Table 19. The processing includes addition of the components in the order listed, use of the three-roll mill, and the principle of quick-freezing the foam mixture.

Coincident with the development of Capoxyfoam I was the preparatory evaluation of a borontrifluoride-piperidine complex as an auxiliary curing agent. The crosslinking mechanism of this chemical complex substantially increased the compressive strengths of the foams to 1490 psi at room temperature testing and 890 psi at 200°F testing at a density of 22 lbs/ft^3. These values are compared to compressive strength valves of other foam systems in Figure 35. The secondary amine complex reacts with the epoxy ring in the following manner.



Because of the unique character of this foam mixture, it was adopted as a second formulation and named Capoxyfoam II. A typical example of this formulation is found in Table 19.

Physical Properties Comparison

Following the development of these polymeric epoxy resin-based foam systems, the property values of Capoxyfoam I and Capoxyfoam II were compared with those of Ablefoam 5. Figure 35 illustrates the compressive strength values as a function of density for Ablefoam 5 and Capoxyfoam I. Their strengths are nearly identical for the tests at room temperature, with a greater difference appearing at the 200°F test temperature.

The possibility that the silicone cell stabilizer would settle out of the cured foam and eventually leak onto the electrical components was considered. A Soxhlet extraction experiment was performed to determine the amount of silicone, if any, that could be removed from the cured foam systems. The organic solvent, methylethylketone, was used as the extracting medium.

Table 19. Typical Formulation of Capoxyfoam I and Capoxyfoam II (Chemical Components Listed in Order of Addition)

Capoxyfoam I	Quantity (g)	Proportion (phr)*
Shell's Epon 828 Bisphenol-A Epoxy Resin	100.0	
Dow's DEN 431 Epoxy Novolac Resin	100.0	
1, 2-Epoxy-3-phenoxypropane	2.0	1
Union Carbide's L-5320 Cell-Stabilizer	4.0	2
Shell's Epon Cure Agent Z	40.0	20
Ammonium Carbonate	12.0	6
Maleic Anhydride	2.0	1
Methyl Nadic Anhydride	8.0	4
Capoxyfoam II		
Shell's Epon 828 Bisphenol-A Epoxy Resin	100.0	
Dow's DEN 431 Epoxy Novolac Resin	100.0	
1, 2-Epoxy-3-phenoxypropane	2.0	1
Union Carbide's L-5320 Cell-Stabilizer	4.0	2
Shell's Epon Cure Agent Z	40.0	20
Ammonium Carbonate	12.0	6
Maleic Anhydride	2.0	1
Methyl Nadic Anhydride	8.0	4
Borontrifluoride-Piperidine Complex	2.0	1

*phr - parts per hundred parts by weight of resin

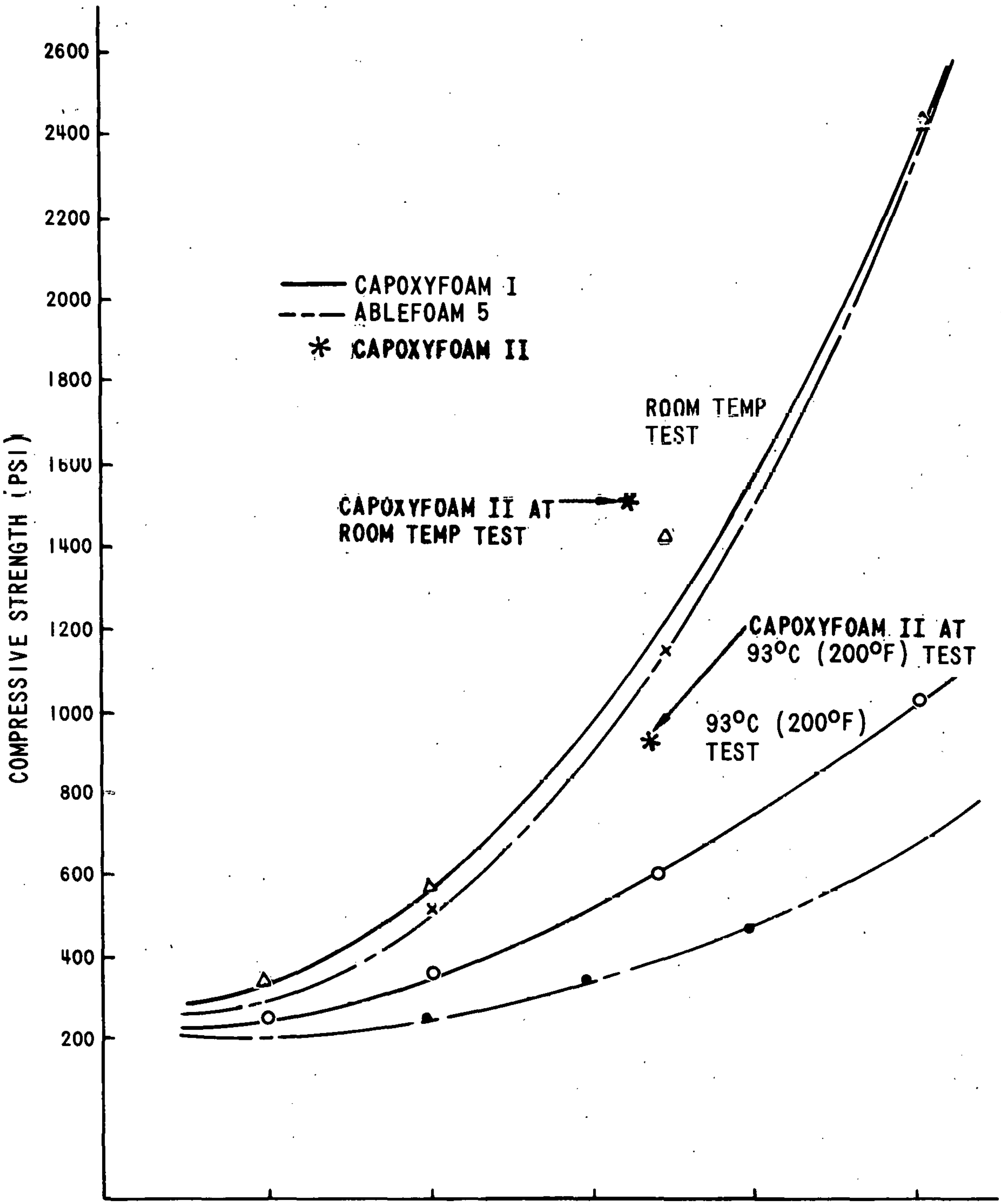


Figure 35. Density Versus Compressive Strength Comparison for Ablefoam 5, Capoxyfoam I, and Capoxyfoam II, Cured at 74°C (165°F) for 4 Hours

Although infrared results showed no silicone deposition with either Capoxyfoam I or Ablefoam 5, a partial constituent extraction had occurred since Capoxyfoam I exhibited an average weight loss of 0.97 percent and Ablefoam 5 exhibited a 1.01 percent weight loss.

To verify this weight loss, thermogravimetric analysis (TGA) was performed on each foam. The weight loss per sample as a function of temperature, as shown in Figure 36, occurred at the thermal degradation point of 375°C (707°F) for Capoxyfoam I, 309°C (588°F) for Ablefoam 5, and 357°C (675°F) for Capoxyfoam II. (The Capoxyfoam II curve was omitted because of consistent overlap with the Capoxyfoam I curve.) The 66°C difference between Capoxyfoam I and Ablefoam 5 clearly indicates a greater thermal stability for Capoxyfoam I; a somewhat higher amount of residue is noted for Ablefoam 5 than for Capoxyfoam I, which probably results from a high filler content.

Commensurate with the TGA analysis is the differential thermal analysis (DTA) of the two foams, as shown in Figure 37; the overlapping Capoxyfoam II curve is omitted. These thermograms illustrate that the thermal decomposition of the foams is in the form of an exothermic reaction. It can be observed that the thermal degradation for Capoxyfoam I is approximately 57°C higher than for Ablefoam 5, again indicating the greater thermal stability of Capoxyfoam I.

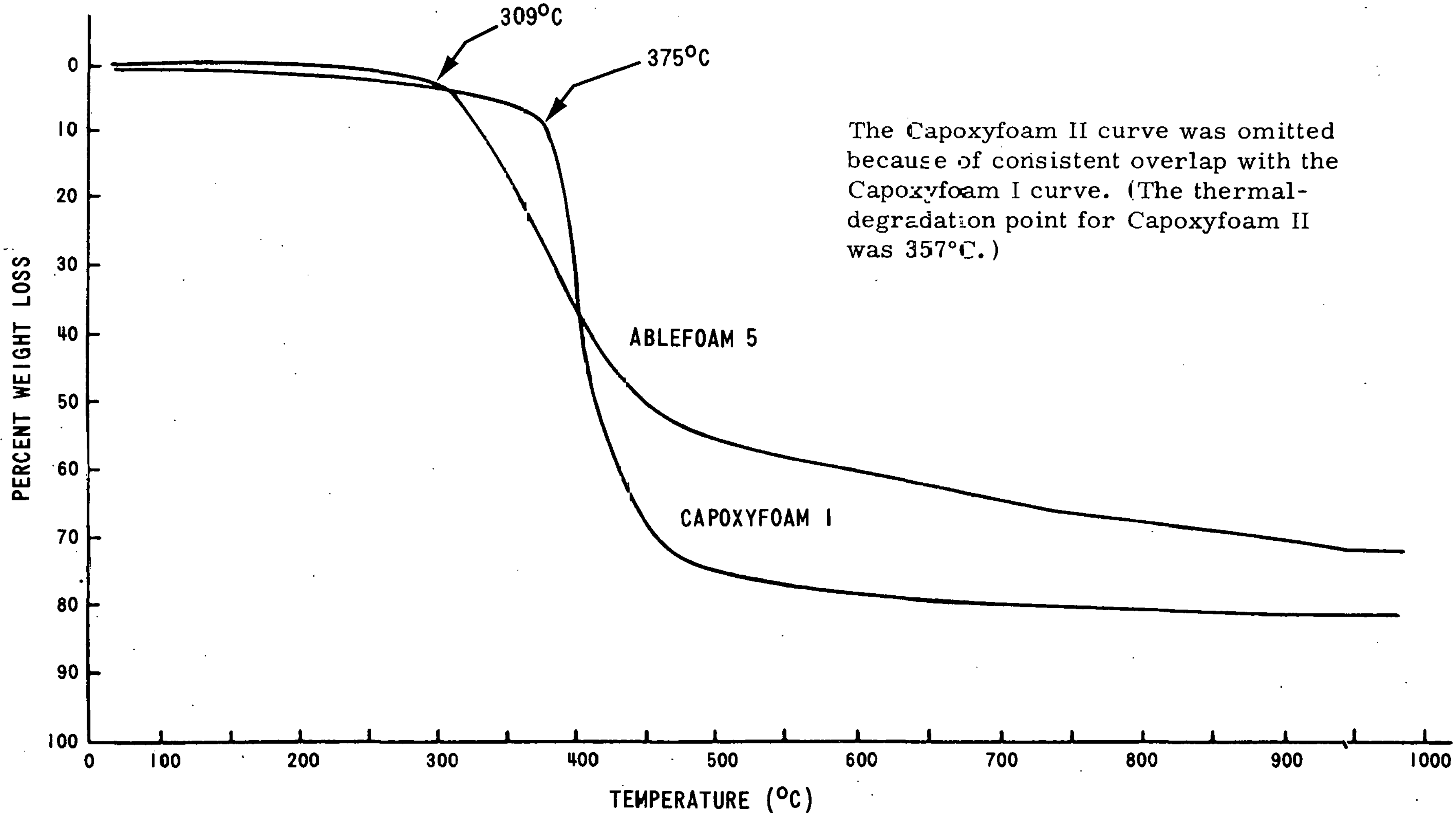
Thermomechanical analysis (TMA) was employed to determine the initial softening point of the three foams. The penetration curves as shown in Figure 38 indicate a close relationship for all three foams.

To further examine the thermal stability of the foams, SLA conducted a heat-aging study that included subjecting Capoxyfoam I and Ablefoam 5 to a 205°C (400°F) temperature environment as a function of time. While the compressive strength for Ablefoam 5 had decreased significantly with only a 35 percent retention strength, Capoxyfoam I averaged nearly 93 percent in retention strength.

One primary difference in the two foam systems is the open-to-closed cell content of the foams, compared below.

	Capoxyfoam I	Ablefoam 5
Open-Cell Void Content, %	5.03	62.00
Closed-Cell Void Content, %	67.03	11.40
Total Void Content, %	72.06	73.40

Figure 40 illustrates the difference in cell structures of Capoxyfoam I and Ablefoam 5.



The Capoxyfoam II curve was omitted because of consistent overlap with the Capoxyfoam I curve. (The thermal-degradation point for Capoxyfoam II was 357°C.)

Figure 36. Comparative Thermogravimetric Analysis for Capoxyfoam I and Ablefoam 5 (Heating Rate: 20°C/Minute, Corrected for Chromel Alumel Thermocouples)

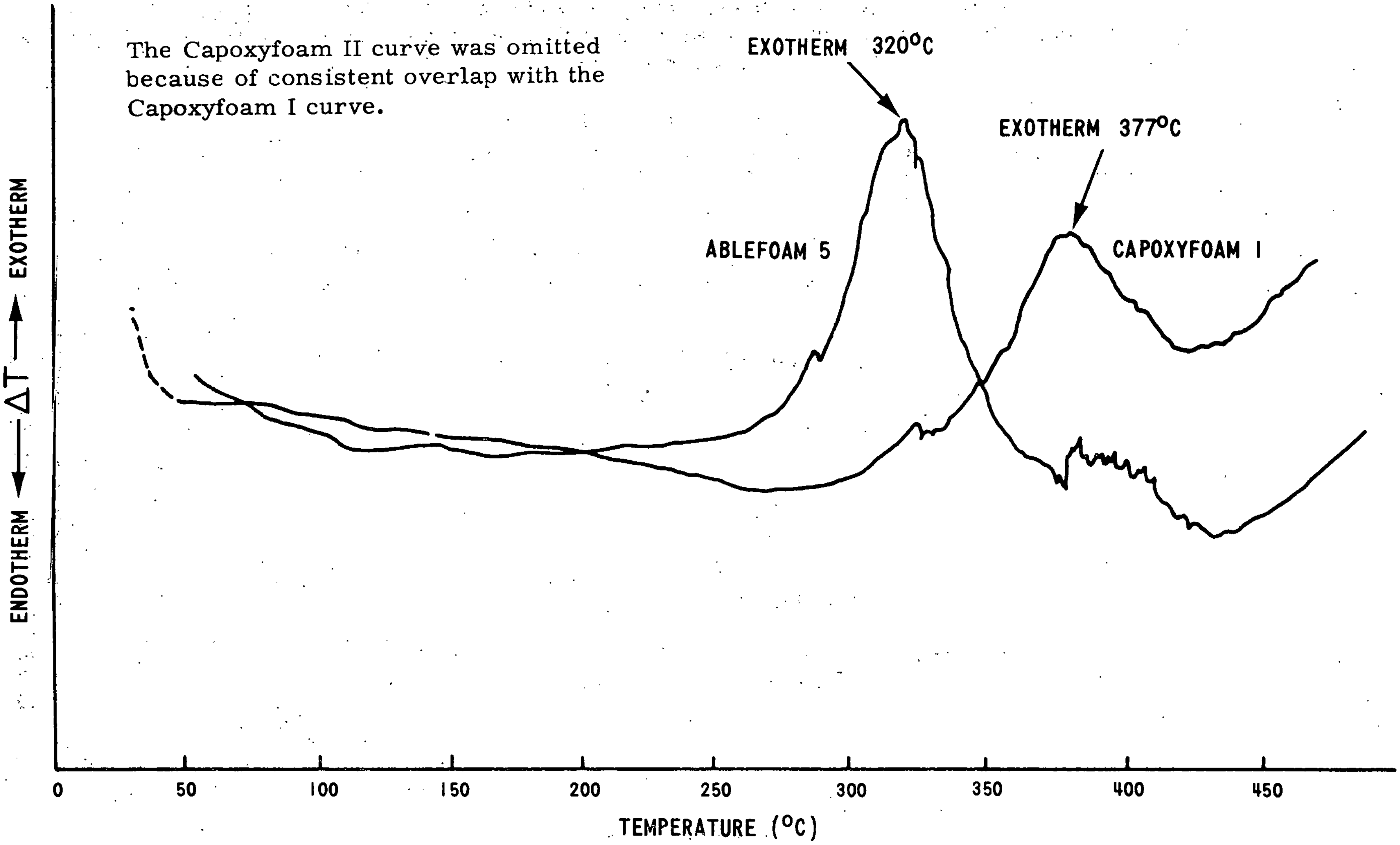


Figure 37. Comparative Differential Thermal Analysis for Capoxyfoam I and Ablefoam 5 (Heating Rate: 20°C/Minute, Corrected for Chromel Alumel Thermocouples)

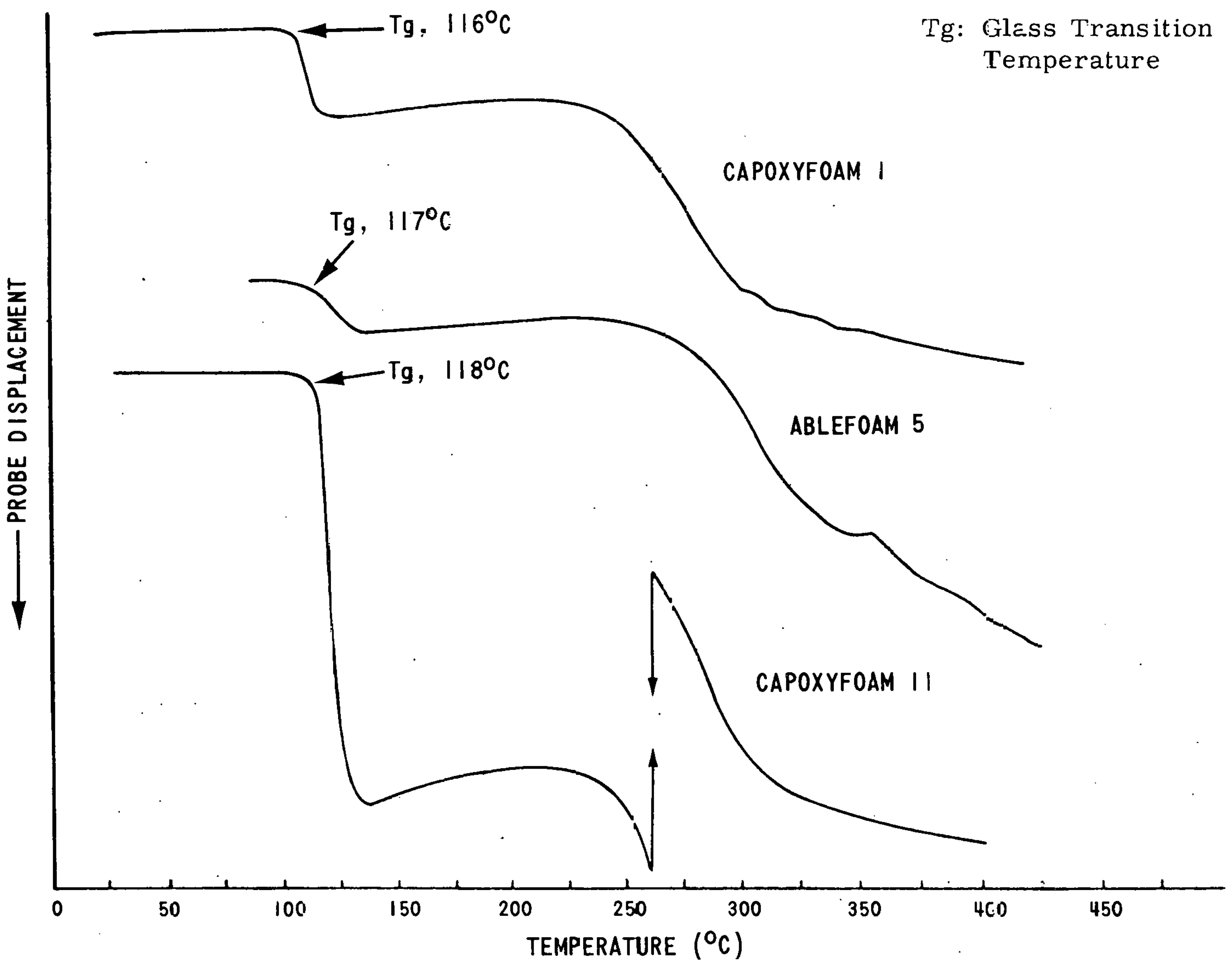


Figure 38. Comparative Thermomechanical Analysis (Penetration) for Capoxyfoam I, Ablefoam 5, and Capoxyfoam II, Showing Glass Transition Temperature

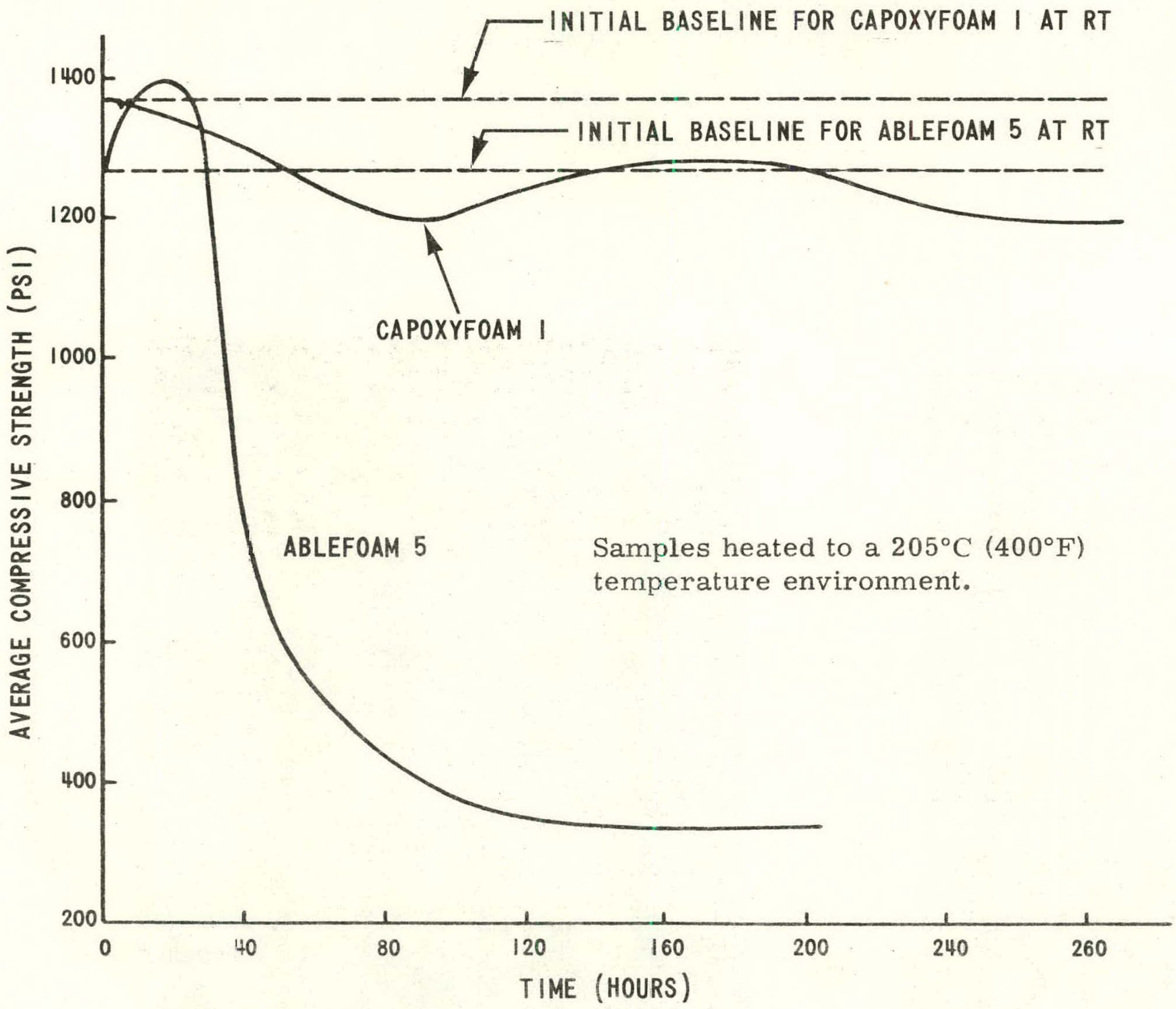
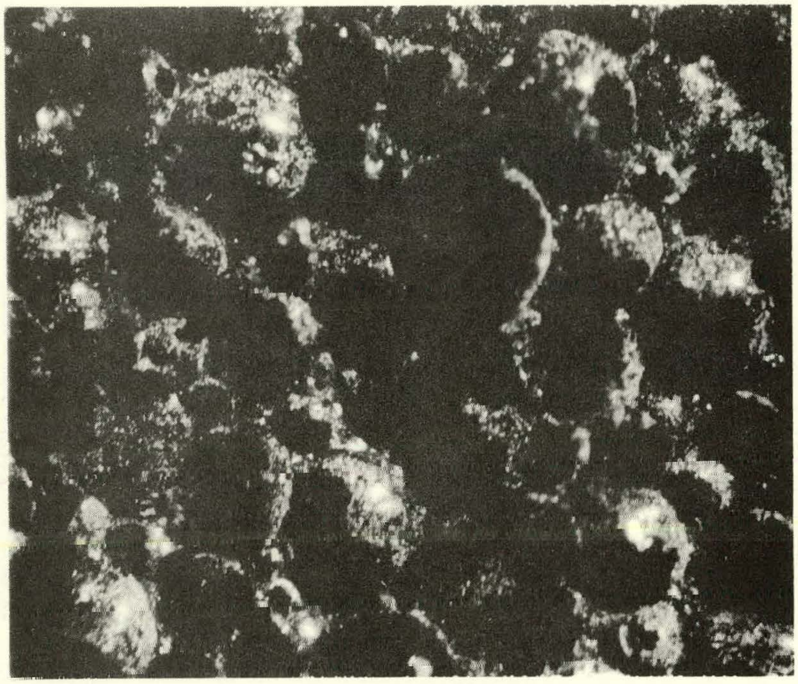


Figure 39. Comparative Heat Aging Analysis, Showing Compressive Retention Strength as a Function of Time for Capoxyfoam I and Ablefoam 5


Ablefoam 5

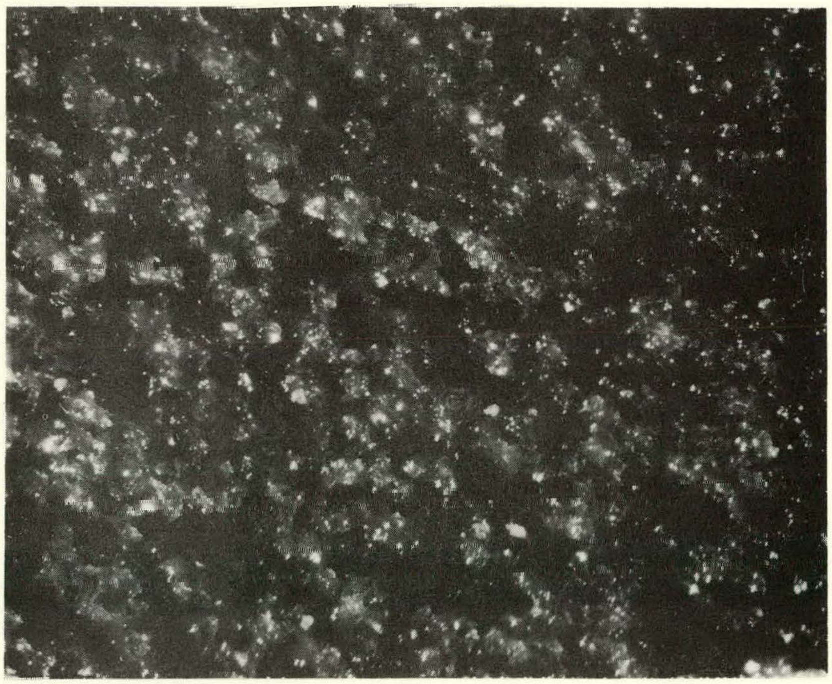

Capoxyfoam I

Figure 40. Photomicrographs of Cell Structures of Ablefoam 5 and Capoxyfoam I, at 30X

Additional observations of the closed-cell nature of Capoxyfoam I and Capoxyfoam II, and the open-cell matrix of Ablefoam 5 are shown in the Scanning Electron Microscope (SEM) Figures 41, 42, and 43. During the formulation of Capoxyfoam I, no restrictions were placed on the type of cell condition acceptable for the back-up epoxy foam system, therefore, no special efforts were made to develop an open-cell material.

Percent Cure Comparison

Because of the prominent closed-cell nature of Capoxyfoam I and the open-cell nature of Ablefoam 5, it was resolved to determine what effect the open-to- closed cell structure had on the percent cure of the foam systems. On the differential scanning calorimetry (DSC) graphs in Figure 44, the area between the curve and the drawn baseline is representative of the relative percent of cure. No mathematical terms have been calculated to demonstrate this; however, the observable results show that there is very little difference in the percent cure of the three foams.

To further justify this claim, the percent cure of Capoxy foam I and Ablefoam 5 was determined using potentiometric titration (Figure 45). Both foams approach asymptotically an 85 percent maximum cure after 8 hours, and both approximate the same degree of cure after 4 hours.

A study of Capoxyfoam I and Ablefoam 5 as free-rise foams was performed to evaluate their respective internal exotherms. Thermocouples were positioned within the center of the free-rise foams to obtain an average exotherm temperature. As Figure 46 typifies, the apparent internal free-rise exotherm for Ablefoam 5 is approximately 55°F higher than for Capoxyfoam I. This indicates that although both foams possess approximately the same degree of cure, the Ablefoam 5 could subject the electronic assembly components to higher temperatures during foaming than does Capoxyfoam I.

Electrical Properties Comparison

The electrical properties of the two foams were compared for the dielectric constant, dissipation factor, and volume resistivity. The foams were molded to 6 by 6 by 1/8 inches at a density of 22 lb/ft^3. The dielectric constants of the two foams were 1.60 at 10^6 Hz for Ablefoam 5 and 1.703 at 10^6 Hz for Capoxyfoam I. The dissipation factor, which is a tangent of the loss angle, was 0.0018 for Capoxyfoam I and 0.0250 for Ablefoam 5, both values falling within the literature-cited values for epoxy foams. The volume resistivity for the two foams was 13.2 by 10^{13} ohms-cm for Ablefoam 5 and 6.27×10^{13} ohms-cm for Capoxyfoam I.

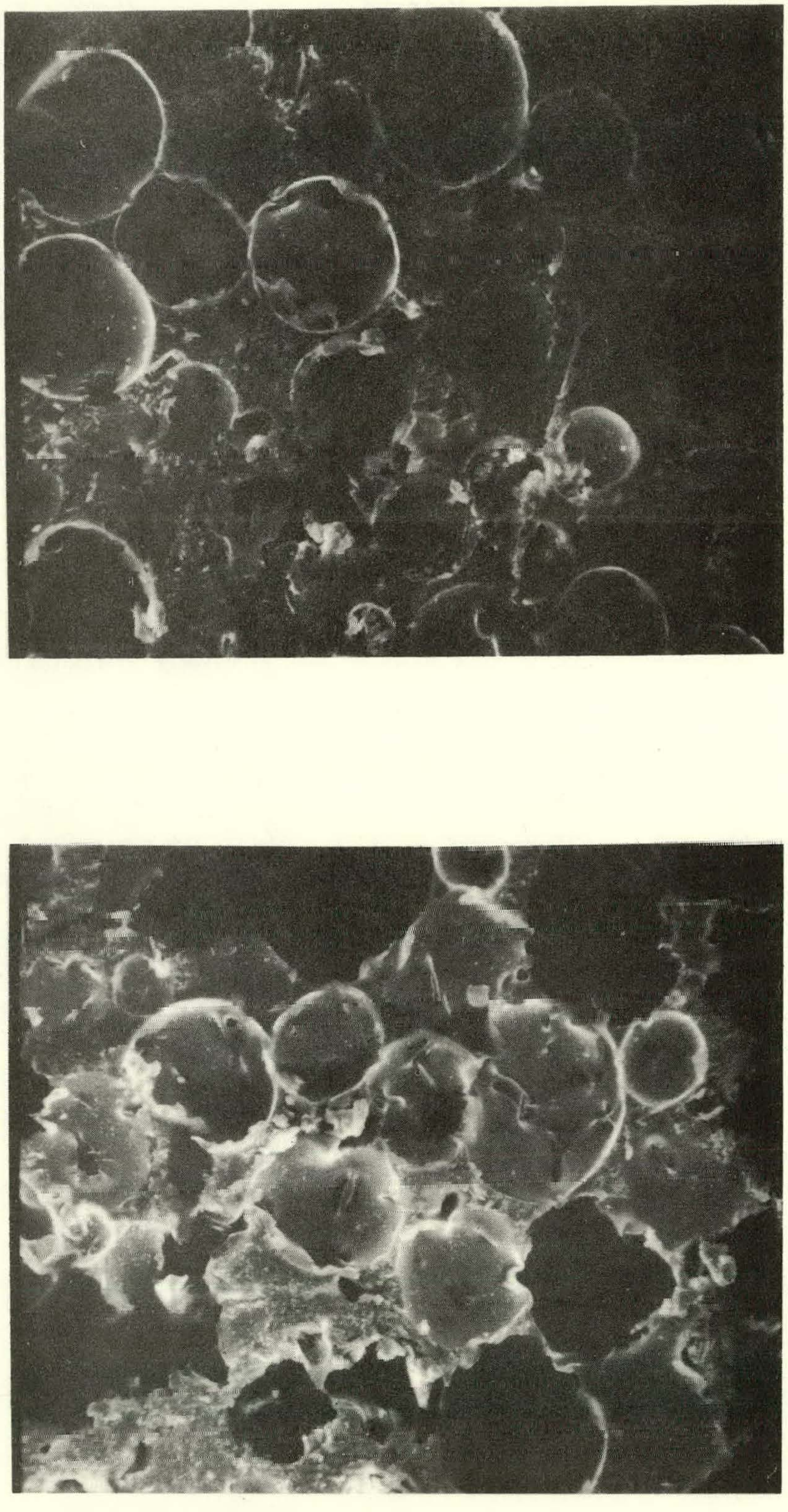


Figure 41. Scanning Electron Microscope (SEM) Analysis of the Closed-Cell Structure of Capoxyfoam I (Upper Photograph is Perpendicular-to-Foam Rise, Lower Photograph is Parallel-to-Foam Rise), at 100X

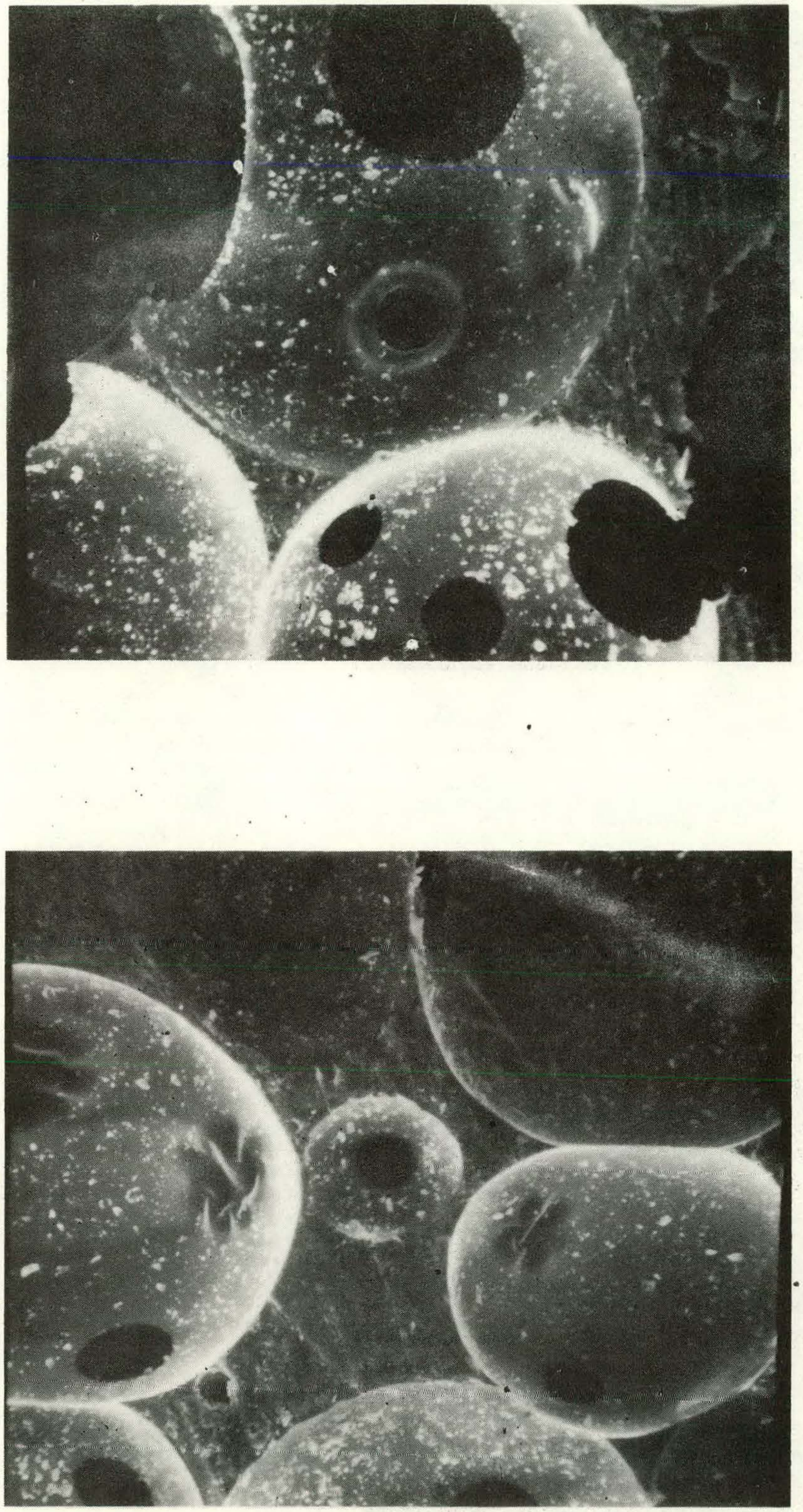
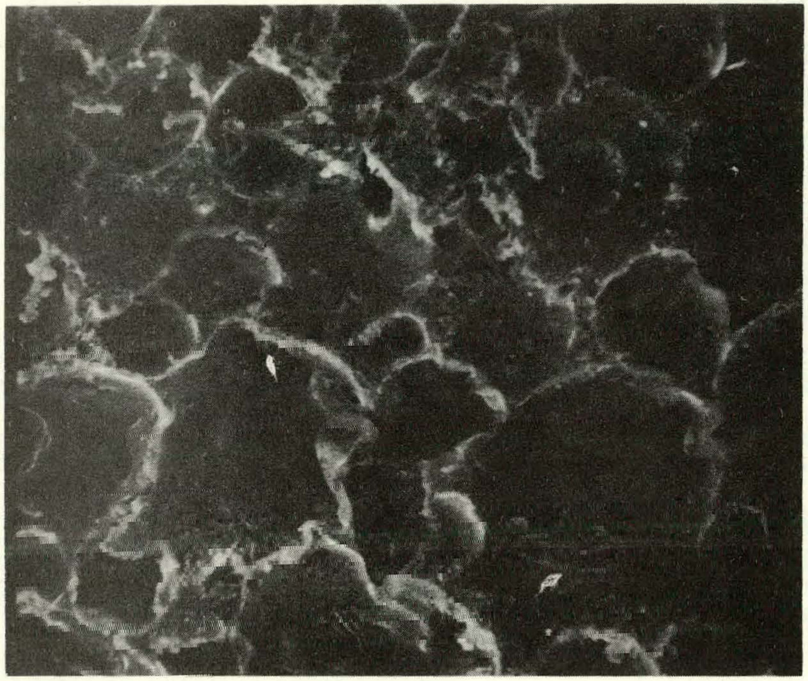


Figure 42. Scanning Electron Microscope (SEM) Analysis of the Open-Cell Structure of Ablefoam 5 (Upper Photograph is Perpendicular-to-Foam Rise, Lower Photograph is Parallel-to-Foam Rise), at 100X



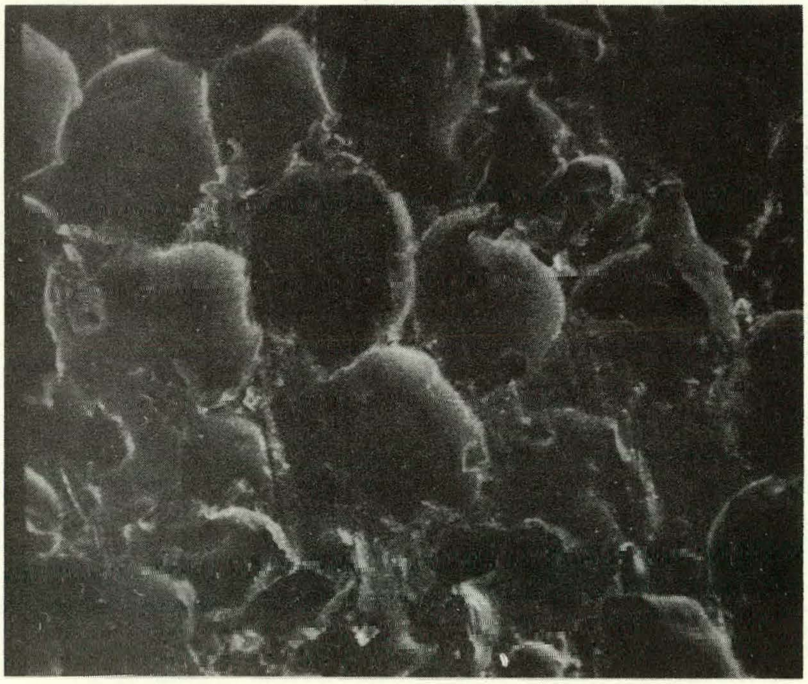


Figure 43. Scanning Electron Microscope (SEM) Analysis of the Closed-Cell Structure of Capoxyfoam II (Upper Photograph is Perpendicular-to-Foam Rise, and Lower Photograph is Parallel-to-Foam Rise), at 100X

Epoxy Content Comparison

A notable feature of the Capoxyfoam I system is its ability to be reproduced with consistency. A lot-to-lot examination of the epoxide values for Ablefoam 5 indicated a range of differing epoxide values with an average deviation of 2.43. By contrast, lot-to-lot examination of the epoxide values for Capoxyfoam I revealed a definite uniformity with an average deviation of 0.7.

Encapsulation Properties

The preliminary trials of encapsulating dummy assemblies with Capoxyfoam I were barely satisfactory. Since Capoxyfoam I is more viscous than Ablefoam 5, extruding the thawed Capoxyfoam I into the reservoir section of the mold was difficult. Preheating the mold to approximately 46°C (115°F) solved the problem. The thawed premix flows into the mold reservoir with no difficulty and well within the workable pot-life of the foam.

Numerous dummy A-B assemblies were encapsulated with the Capoxyfoam I system. Mold fill characteristics and part surface finish were of excellent quality and the density distribution of the various foam sections varied less than ±0.5 lb/ft^3. The units shown in Figure 47 were visually acceptable. Figure 47 displays dummy A-B units molded from Ablefoam 5 and Capoxyfoam I.

Capoxyfoam I was developed to provide a back-up epoxy foam system for Ablefoam 5. The Capoxyfoam I formulation is produced using approximately the same processing methods as Ablefoam 5. The Capoxyfoam I system appears to be more easily reproduced, more physically uniform, and consistently more thermally and mechanically stable than Ablefoam 5. The processing properties of Capoxyfoam I are similar to those of Ablefoam 5. The handling and storage details are identical for the two foam premixes. Capoxyfoam I is ready for use when the cartridge of frozen foam premix is thawed to an extrudable temperature. The only modification of the existing encapsulation process necessary is the addition of a mold preheat. Capoxyfoam I does possess a higher closed cell content than Ablefoam 5 and the full significance of this difference would have to be determined before production use of Capoxyfoam I.

A second formulation was developed and named Capoxyfoam II. This system possesses higher compressive strengths than Capoxyfoam I and was developed for future applications requiring a high-strength epoxy foam.

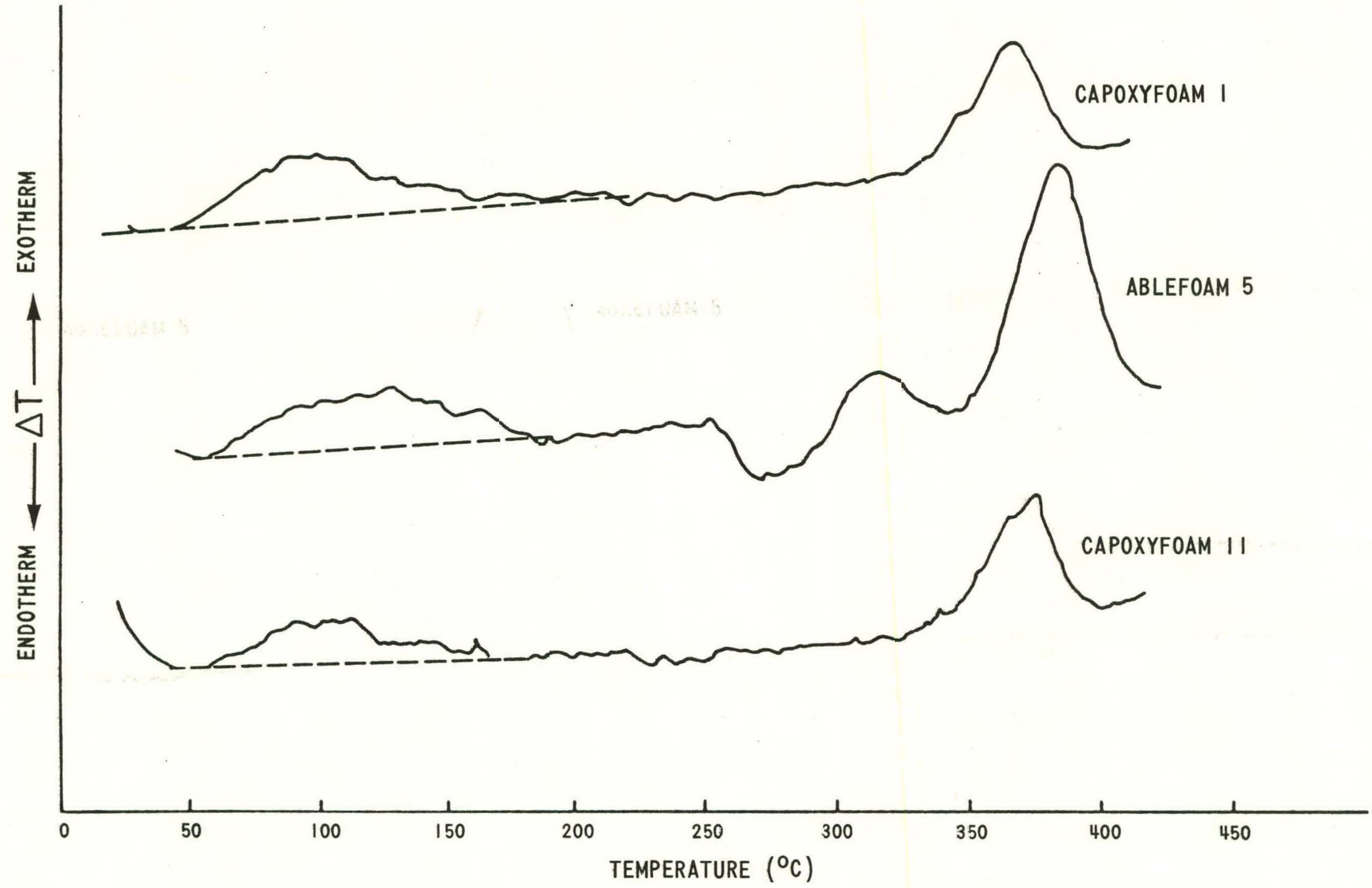


Figure 44. Comparative Differential Scanning Calorimetry of Capoxyfoam I, Ablefoam 5, and Capoxyfoam II, Showing the Relative Degree of Cure. (Heating Rate: 10°C/Minute, Corrected for Chromel Alumel Thermocouples)

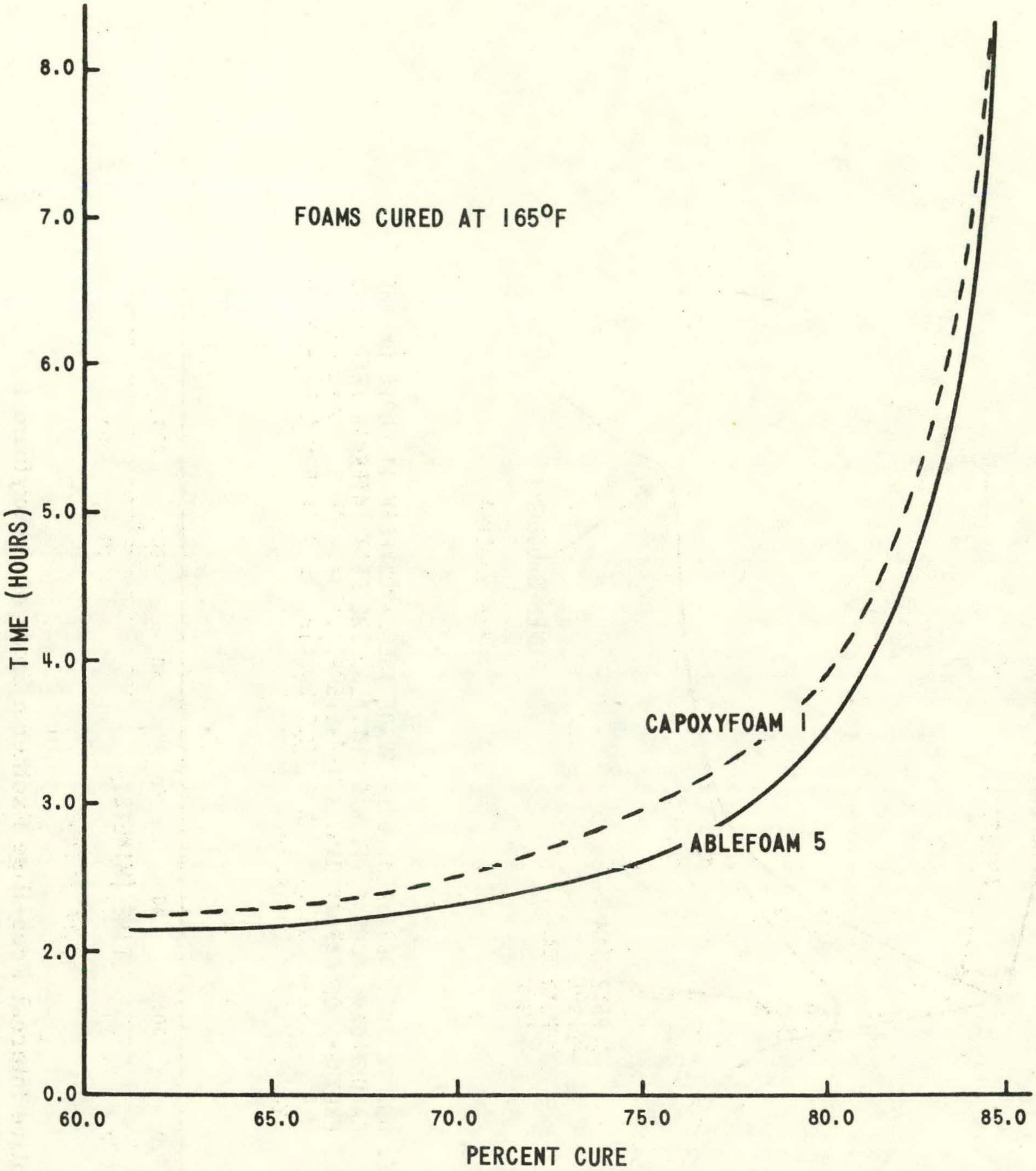
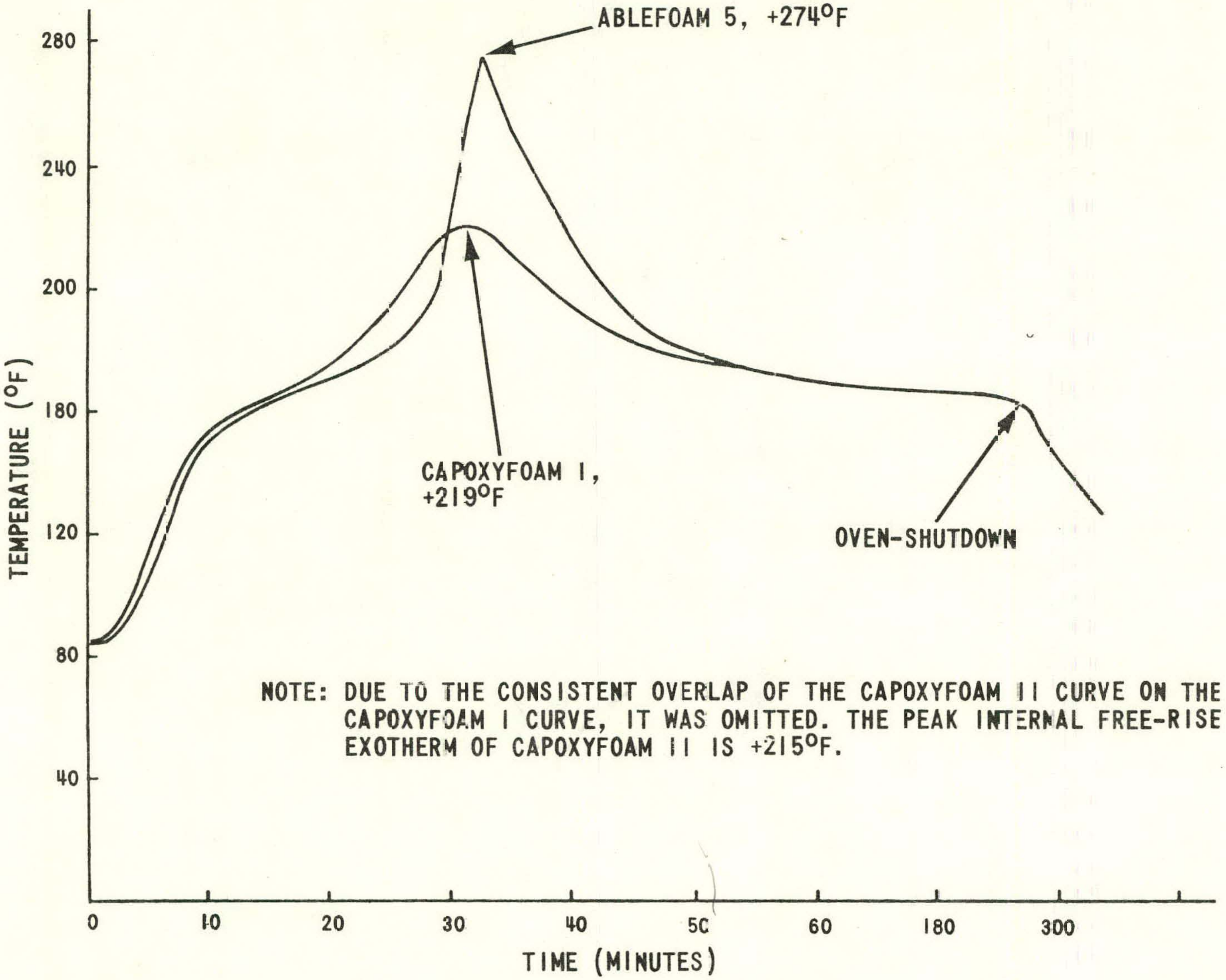


Figure 45. Cure Time Versus Percent Cure for Ablefoam 5 and Capoxyfoam I



NOTE: DUE TO THE CONSISTENT OVERLAP OF THE CAPOXYFOAM II CURVE ON THE CAPOXYFOAM I CURVE, IT WAS OMITTED. THE PEAK INTERNAL FREE-RISE EXOTHERM OF CAPOXYFOAM II IS +215°F.

Figure 46. Comparative Internal Free-Rise Exotherm Study of Capoxyfoam I and Ablefoam 5 (Oven Temperature 165°F)

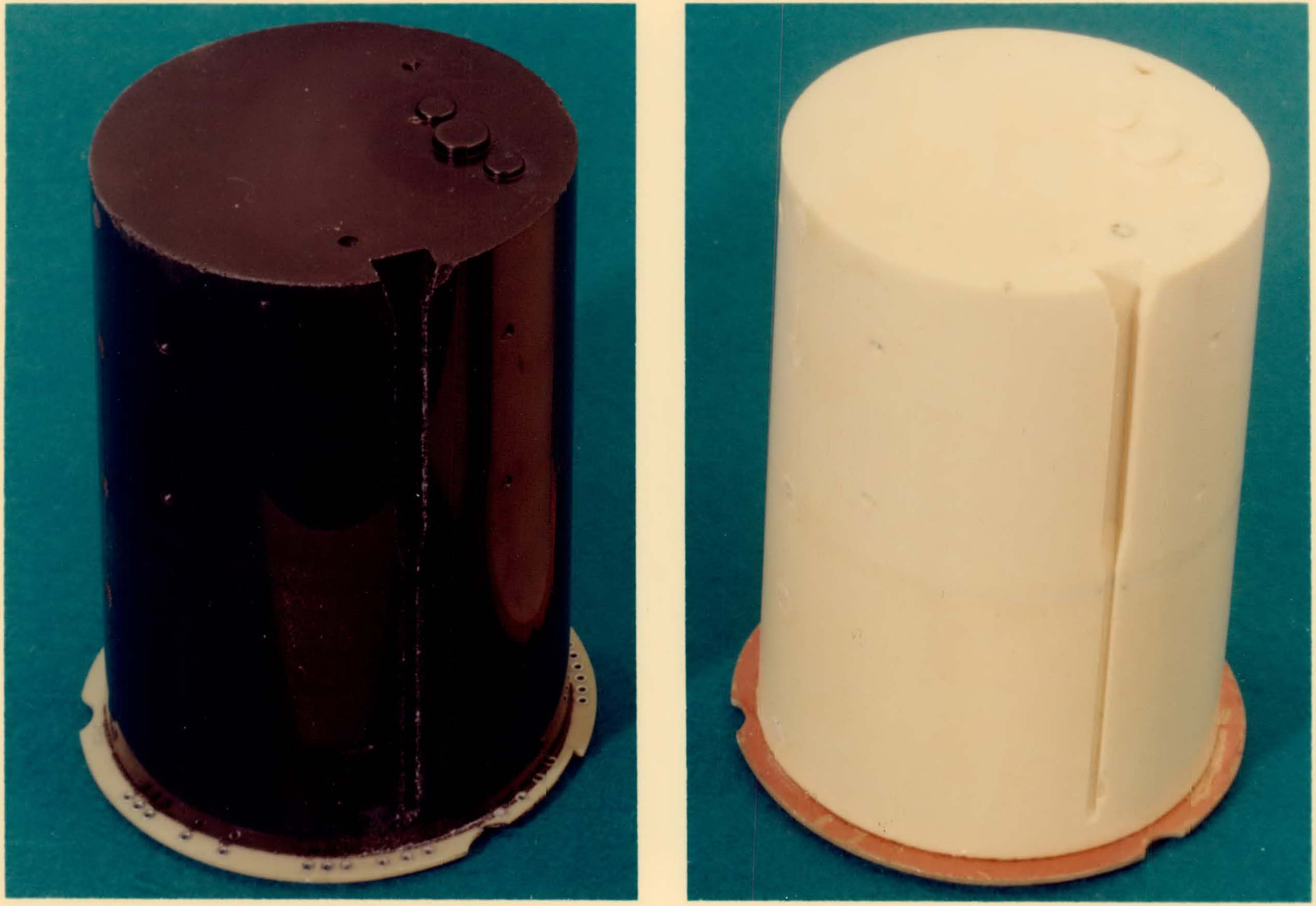


Figure 47. Comparison of A-B Dummy Unit [redacted]
Employing Ablefoam 5 and Capoxyfoam I

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REFERENCES

1. Deleted.

2. Lee, H. and Neville, K., Handbook of Epoxy Resins, New York: McGraw-Hill, 1967, 1. 4-14.

3. U. S. Patent 3,223,654 (December 14, 1965).

4. Canadian Patent 761,048 (June 13, 1967).

5. U. S. Patent 3,320,187 (May 15, 1967).

6. January 14, 1970 - PDO

7. October 8, 1969 - PDO

8. Soldatos, A. C., Burhans, A. S., Cole, L. F., Mulvaney, W. P., "Advances in Chemistry Series 92," Epoxy Resins. Washington, D. C.: American Chemical Society Publications, 1970.

9. U. S. Patent 2,837,497 (June 3, 1958).

10. U. S. Patent 3,282,863 (November 1, 1966).

11. U. S. Patent 3,440,216 (April 22, 1969).

Appendix

QUANTITATIVE ANALYSIS FOR THE DETERMINATION OF EPOXIDE EQUIVALENT FOR CURED AND UNCURED EPOXY RESINS BY POTENTIOMETRIC TITRATION

SCOPE

This method describes a procedure for the quantitative determination of α-epoxide groups in cured and uncured epoxy resins. Essentially, the method is a reaction of the oxirane oxygen in the epoxy group with an excess of HC1 employing dioxane as the solvent and then back-titrating with $AgNO_3$ to a potentiometric end point. Calculation procedures are used to determine the epoxide equivalent of cured and uncured epoxy resins, and also to describe the extent of cure or percent of conversion of the epoxy groups in a curing reaction.

APPARATUS AND REAGENTS

- Analytical Balance (readout to the nearest 0.1 mg);
- Beakers, 250 ml;
- Burr Mill or other suitable grinder to reduce particle size of cured samples to pass a U. S. Sieve No. 60;
- Cylinders, graduated 25 ml and 50 ml;
- Glass Container, opaque, stoppered, for $AgNO_3$ solution;
- pH Meter with metallic silver and silver-silver chloride electrode system. (A Beckman 39187 silver billet combination electrode is recommended.)
- Magnetic Stirrer;
- Microburette, 10 ml capacity (a Kimax No. 17115 10 ml-capacity precision bore, micro, three-way glass stopcock is recommended; precision bore to have a 0.02 ml tolerance.);
- Pipets, measuring 2 ml and 10 ml capacity (Mohr type);
- Acetone, reagent grade;
- Dioxane, reagent grade;

- Hydrochloric Acid, approx 1N, 85 ml, conc HCl diluted to 1000 ml with distilled H_2O;
- Nitric Acid, approx 4N, 250 ml, conc HNO_3 diluted to 1000 ml with distilled H_2O;
- Silver Nitrate, 1N, 84.5 g $AgNO_3$ (reagent grade) dissolved in distilled H_2O up to a volume of 500 ml (must be kept in light proof container). Standardize against HCl or NaCl.

PROCEDURE

Uncured Materials

- Into a 250 ml beaker weigh to the nearest 0.1 mg, a quantity of the sample to be tested containing 0.002 to 0.004 equivalents of an α-epoxide (approx 0.4 to 0.8 grams).

  Note: When the sample to be tested is of a frozen nature, the specified thaw time is one hour.

- Immediately add to this sample 25.0 ml of reagent grade dioxane.
- Stir via a magnetic stirrer to dissolve the resinous material.

  Note: When stirring with a magnetic stirrer, it is advisable to suspend the beaker 1/2 to 1 inch above the stirrer so as to minimize the heat transfer imparted by the stirrer to the sample solution. Also, use a constant-size magnetic stirring bar.

- Upon reaching a homogeneous solution, carefully pipet 10.0 ml of 1N HCl. Be certain not to pipet or splash any HCl on the beaker walls.
- Stir the solution slowly for 20 minutes.
- Now, add 50 ml of reagent grade acetone.
- Add 35 ml of distilled H_2O.
- Pipet 2.0 ml of 4N HNO_3.
- Increase stir speed to a suitable rate, and keep constant on all titrations.
- Insert clean electrode system into the stirring solution.
- Titrate with 1N $AgNO_3$ to a 300 millivolt end point.

Cured Materials

- Into a 250 ml beaker weigh to the nearest 0.1 mg a quantity of the cured sample having a particle size suited to pass a U.S. Sieve No. 60 (approx 0.5 to 1.0 grams).
- Add 25.0 ml of reagent grade dioxane.
- Stir slowly for 2 hours, enabling the cured material to swell.
- Carefully pipet 10.0 ml of 1N HCl, cover with watch glass, and slowly stir for 24 hours.
- Follow up with Step 6 as described for Uncured Materials.

Note: It is doubtful that the small cured particles will be dissolved by the dioxane or HCl; therefore approach the end point very slowly to allow for the reaction by diffusion.

Blank Sample

By omitting the test sample, blank determinations are run with the same procedure (beginning with Step 2) as followed for Uncured Samples. Run 3 blanks with each series of samples that are run at one time. Use the average of the three determinations for the blank value.

If possible, run test samples in duplicate and report the average value.

Caution: Strong $AgNO_3$ solutions are corrosive and stain very badly. Use utmost care when handling such solutions.

Since $AgNO_3$ is subject to chemical decomposition by light, it is suggested that the container for the $AgNO_3$ solution be of such nature as not to allow passage of light into the solution. It is convenient to adjust the normality of the HCl to just slightly below one normal in order to obtain blank readings of between 9.0 to 10.0 ml on the microburette.

CALCULATIONS:

Weight per epoxy equivalent (WPE) = $\frac{1000\ WR}{(B-S)\ N}$

$$\frac{\text{Epoxy Content}}{100\ g} \qquad \frac{(B-S)\ N}{10\ WR}$$

Where: B = Blank titer (ml)
S = Sample titer (ml)
N = Normality of $AgNO_3$
W = Sample weight (grams)
R = Percent resin (as decimal) in sample

Degree or extent of cure, % cure = $\frac{C-A}{C}$ x 100%

Where: A = Epoxy content of the <u>cured</u> resin sample
C = Epoxy content of the <u>uncured</u> resin sample