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A THERMOMECHANICAL (TMA) TEST METHOD FOR EVALUATION OF CURED PO--ETC(U)
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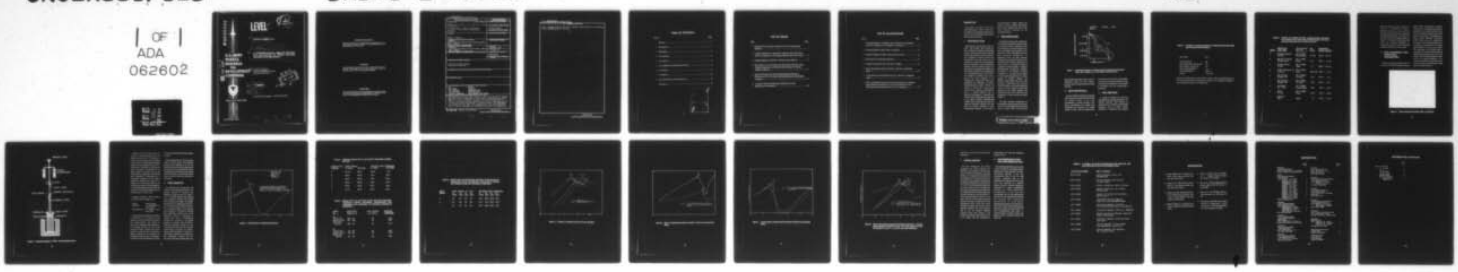

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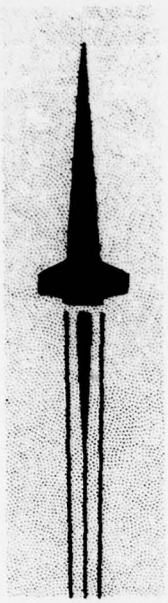

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(6) A THERMOMECHANICAL (TMA) TEST METHOD FOR EVALUATION OF CURED POLYMER ENCAPSULATING MATERIALS

U.S. ARMY MISSILE RESEARCH AND DEVELOPMENT COMMAND

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Test and Evaluation Directorate
Engineering Laboratory

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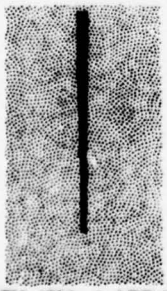

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TEST MATERIALS	TEMPERATURE RATE
TEST EQUIPMENT	SOFTENING POINT
OPERATING PARAMETERS	SHORE HARDNESS TEST METHOD

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thermomechanical Analysis (TMA) penetration test method was used to measure the softening point temperature of cured polymer encapsulating and coating materials. This test method was compared with the Shore Hardness Test Method by measuring softening temperature and hardness change that occurred in encapsulating materials exposed to humidities greater than 90 percent and temperatures above 82°C. The thermomechanical test method definitely offers a distinct advantage when evaluating the quality of a manufactured

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20. ABSTRACT (Continued)

item. The TMA method is very rapid, requires a small amount of test specimen and is nondestructive to the part.

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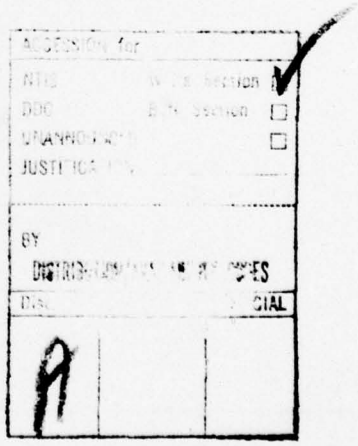

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OBJECTIVE

The purpose of this MTT was to utilize Thermomechanical Analysis (TMA) as a test method for evaluating the cured thermal history of polymer materials used in plastic encapsulated missile items.

1. INTRODUCTION

Specification requirements (MIL-I-16923, MIL-P-46838, MIL-P-47298 and MIL-I-46058) for coating and encapsulating polymer materials call out many chemical and physical properties of the uncured resin; this is adequate for quality control and manufacture of the resin. There are also standard test methods for determining the physical properties of cured encapsulating materials. All these methods require test specimens to be a certain size, thickness and free of defects and flaws. The configuration of most manufactured parts will not allow the standard test methods to be used to measure the cured properties of an encapsulated or potted part. This report investigates the practicality of using a thermomechanical analysis (TMA) test method to measure the cured polymer material that is applied to manufactured parts. In general additives such as plasticizers, antioxidants, UV stabilizers and colorants will modify the thermal properties of an organic polymer. Manufacturing variables such as shelf life, mix ratio and moisture (hydrolytic stability) will also affect the thermal properties of cured encapsulating materials. In this study a thermomechanical analysis (TMA) test method was used to measure and identify these thermal changes that occur in the cured polymer material on the manufactured item.

2. BACKGROUND

Most plastics soften at some temperature. The softening temperature is closely related to the glass transition temperature (Tg). Cured polymers are usually amorphous or have an amorphous like component. Such materials are hard, rigid glasses below the glass transition temperature. At temperature above the glass transition temperature the amorphous polymer is soft and flexible and is either an elastomer or a viscous liquid. As a polymer is heated it undergoes a transition similar to a classical thermodynamic second-order transition. According to the literature, softening temperature is a complex property related to such mechanical properties of a plastic material as modulus, elasticity, and plasticity. Many studies show that a cured polymer's mechanical and electrical properties display pronounced change in the region of the glass transition and softening temperature. The elastic modulus may decrease by a factor of over 100 times as the temperature is raised through this region (*Figure 1*).

The glass transition temperatures of cured polymer resin material will vary from -123°C for polydimethyl siloxane (silicone resin) to above 100°C for epoxy and

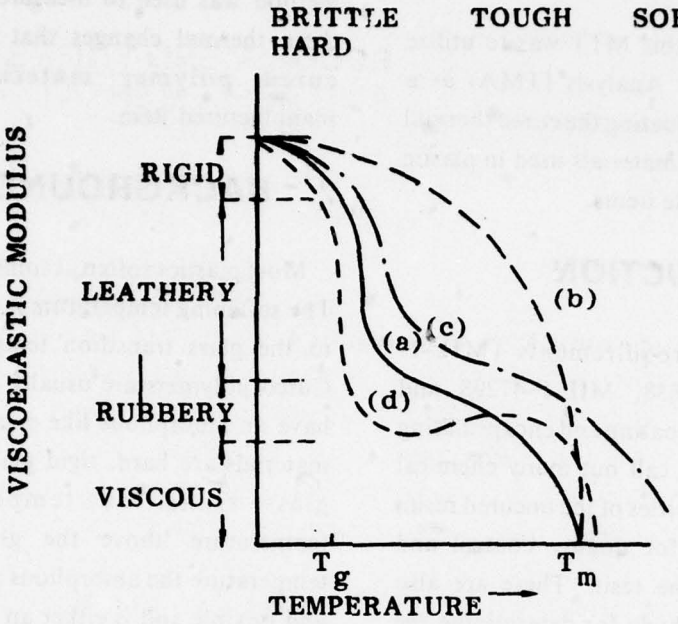

Figure 1. Viscoelastic behavior of different types of polymer (a) Amorphous linear. (b) Crystalline. (c) Cross-linked. (d) Elastomeric.

polyurethane type material. *Table 1* gives Tg temperature values for many common polymers used as encapsulating and potting materials.

3. TEST MATERIALS

Since the TMA test method for softening point temperature is intended for measuring the thermal history of the cured encapsulated or potted end-item, only epoxy, polyurethane and silicone type compounds were utilized as test sample specimen. *Table 2* lists the manufacturers trade name, mix ratio and curing schedule for each of the compounds selected. All the compounds were prepared, cured and aged in accordance with the manufacturer's instruction.

4. TEST METHOD

A number of methods are known for determining the softening temperature of a polymer material. Most depend on measurement of a change in some physical parameter, such as specific volume, coefficient of expansion, heat capacity,

TABLE 1. LISTING OF GLASS TRANSITION TEMPERATURE FOR SOME ENCAPSULATING MATERIALS

POLYMER	Tg°C
POLYSTYRENE	100
POLYDIMETHYL SILOXANE	-123
POLYVINYL CHLORIDE	87
POLYCHLOROPRENE	-50
POLYURETHANE	-50 to 10
EPOXY	*-10 to 100*

All the above temperatures represent the pure polymer: Most encapsulating polymers are cured with the addition of plasticizers, extenders and hardeners as a means of controlling the properties of the finished item.

TABLE 2. LISTING OF MANUFACTURER, SPECIFICATION, MATERIAL TYPE, MIXED RATIO AND CURE TEMPERATURE OF THE ENCAPSULATING MATERIALS USED IN STUDY

SAMPLE	MANUFACTURE TRADE NAME	SPECIFICATION AND TYPE	MIX RATIO	RECOMMENDED CURING SCHEDULE
A	Product Research PR-1592	MIL-M-24041 Polyurethane	53:100	180°F - 16 hrs
B	Emerson & Cuming Stycast 2651	MIL-I-16923 Epoxy	10:1	250°F - 4 hrs
C	Furane Plastic EP 203	MIL-I-16923 Epoxy	1:1	300°F - 36 hrs
D	Freed Transforer Co. DI Resin	MIL-I-16923 Epoxy	100:8.34	150°F - 2 hrs
E	Dow Corning Sylgard 182	MIL-P-46838 Silicone	10:1	212°F - 1 hr
F	Dow Corning Sylgard 184	MIL-P-46838 Silicone	10:1	212°F - 1 hr
G	Conathane CE - 1155	MIL-I-46058 Polyurethane	10:7	60°F - 3 hrs
H	Hysol PC-16M	MIL-I-46058 Epoxy	10:8	65°C - 4 hrs
I	Humiseal 2A53	Epoxy	1:1	93°C - 2 hrs

dielectric constant or dynamic modulus as a function of temperature. Thermomechanical analysis is a rather new but extremely useful technique for measuring the softening temperature of polymers. By measuring dimensional changes (expansion mode) or viscoelastic changes (penetration mode) the softening temperature of encapsulating materials can be determined precisely and rapidly on small samples.

5. TEST EQUIPMENT AND OPERATING PARAMETERS

Thermal analytical equipment used for this study was a Thermomechanical Analyzer Model TMS-1 manufactured by Perkin-Elmer (*Figure 2*). The instrument consists of an analyzer unit, analyzer control unit and the UU-1 temperature program control. The analyzer unit (*Figure 3*) is equipped with a linear variable differential transformer (LVDT) which serves as a displacement transducer to sense sample changes by way of a probe and connects them to electrical signals directed to the y-axis of a recorder. The temperature of the sample space is continually monitored by a chromel-alumel thermocouple connected to the x-axis of the recorder. The furnace heating element range, -150 to 325 degrees centigrade, is surrounded by an aluminum heat sink; the test sample is cooled by pouring liquid nitrogen into the insulated reservoir.

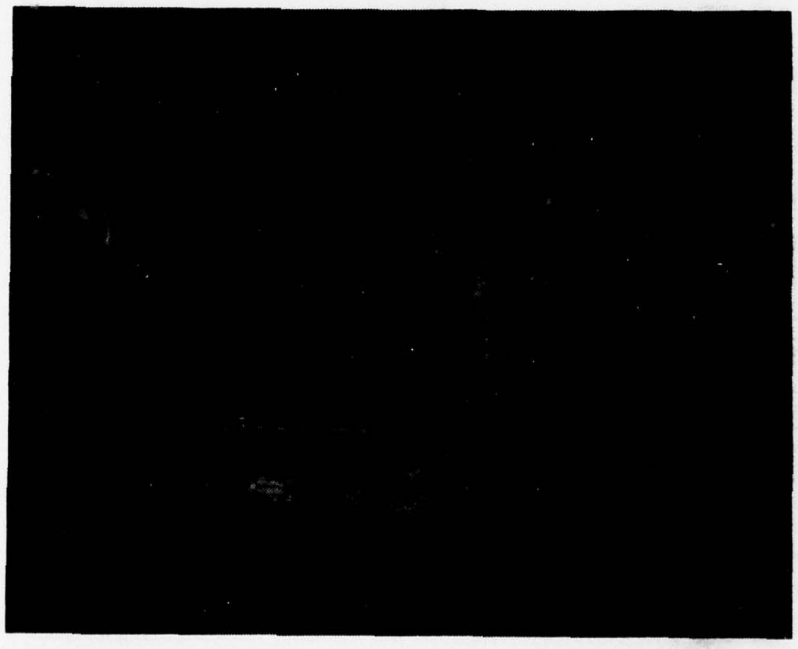

Figure 2. Thermomechanical analyzer TMA-1 equipment.

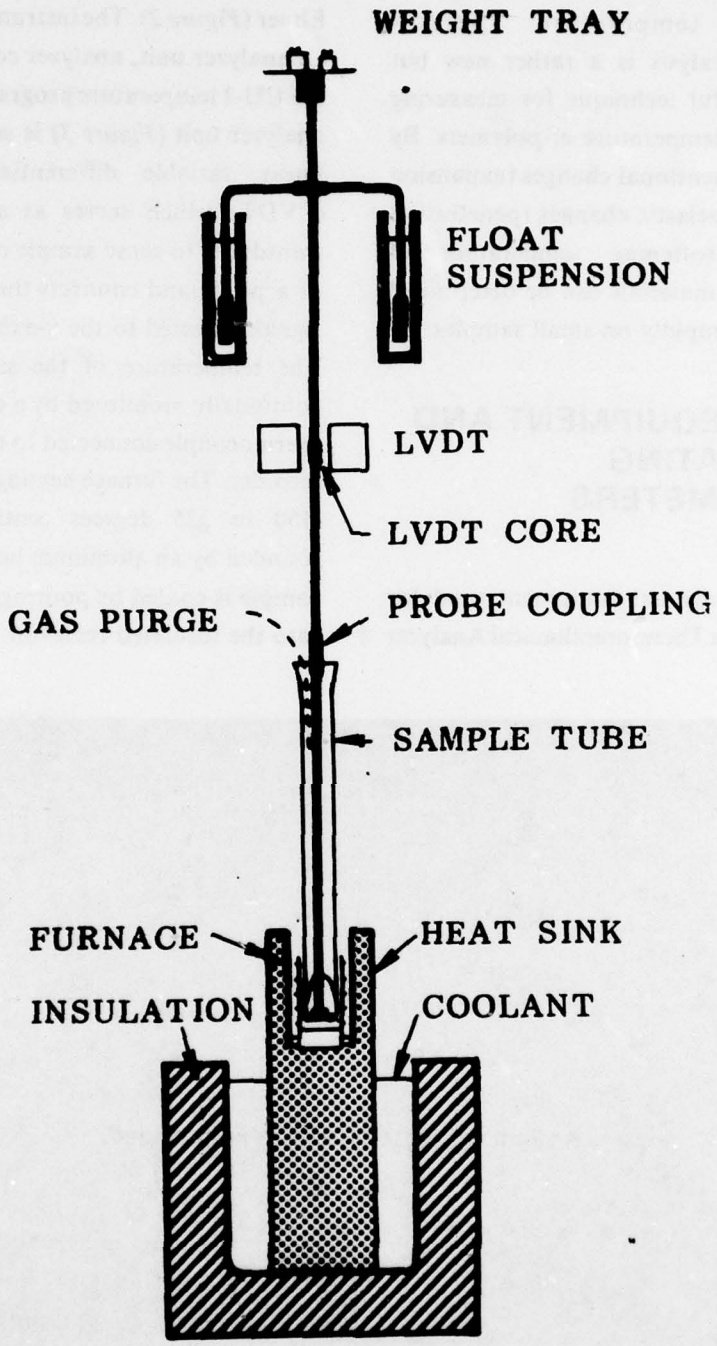

Figure 3. Schematic diagram of TMS-1 with penetration probe.

Sample specimens are placed directly on the floor of the quartz sample tube. The penetration probe tip is maintained in contact with the sample. Pressure is applied to the sample as it is being heated by adding weight to a tray coupled above the LVDT. Penetration of the sample can be observed when the viscosity of the sample can no longer support the probe; this is the softening point temperature. The softening point temperature is determined by a construction procedure on the original temperature deflection curve (*Figure 4*), a straight line is constructed tangent to the curve below the transition and a straight line is constructed tangent to the curve above the transition. The softening temperature is at the intersection of the two lines.

Operating parameters which remained the same for all test samples were:

Coolant:	liquid nitrogen
Purge Gas:	dry nitrogen at rate of 50 cc/min
Temperature rate:	10 degrees centigrade/min

The loading of the sample probe (*Figure 3*) varied from 5 to 30 grams. For the penetration probe a 20 gram load is a good first approximation. The degree of penetration is dependent on sample loading. If the sample becomes very soft in the transitional region, a lighter load will be necessary to keep the curve on the chart, Heavier loading will be necessary for detecting the transition point if a sample is very hard. Usually at some point, the probe will rise after a penetration, unless loading is too great.

Sample preparation for the penetration probe is relatively simple. The test sample specimens were punched to fit into the quartz platform properly by using a number one corp borer. One condition that should be observed is that the bottom of the sample be flat. All samples were first heated with the probe in place to relieve any stress due to processing.

6. TEST RESULTS

The softening point temperature and hardness value measurements data for the samples exposed to humidity and temperature aging are shown in *Tables 3* and *5*. Increasing change in the softening point temperature indicates these samples were becoming more highly cross-linked, hard materials. Encapsulating compound F was the exception and displayed reversion, by a decreasing change in the softening point temperature. The change in softening point temperature appears to be a more quantitative means of measuring the changes that occur in encapsulating materials after exposure to the ageing processes of humidity and temperature. Softening temperature change was also measurable when the mix ratio of two part encapsulating materials was slightly changed (*Table 4*and *Figure 5*). *Figures 6*, *7* and *8* display graphically a typical epoxy and polyurethane material with the increased softening point temperature as the

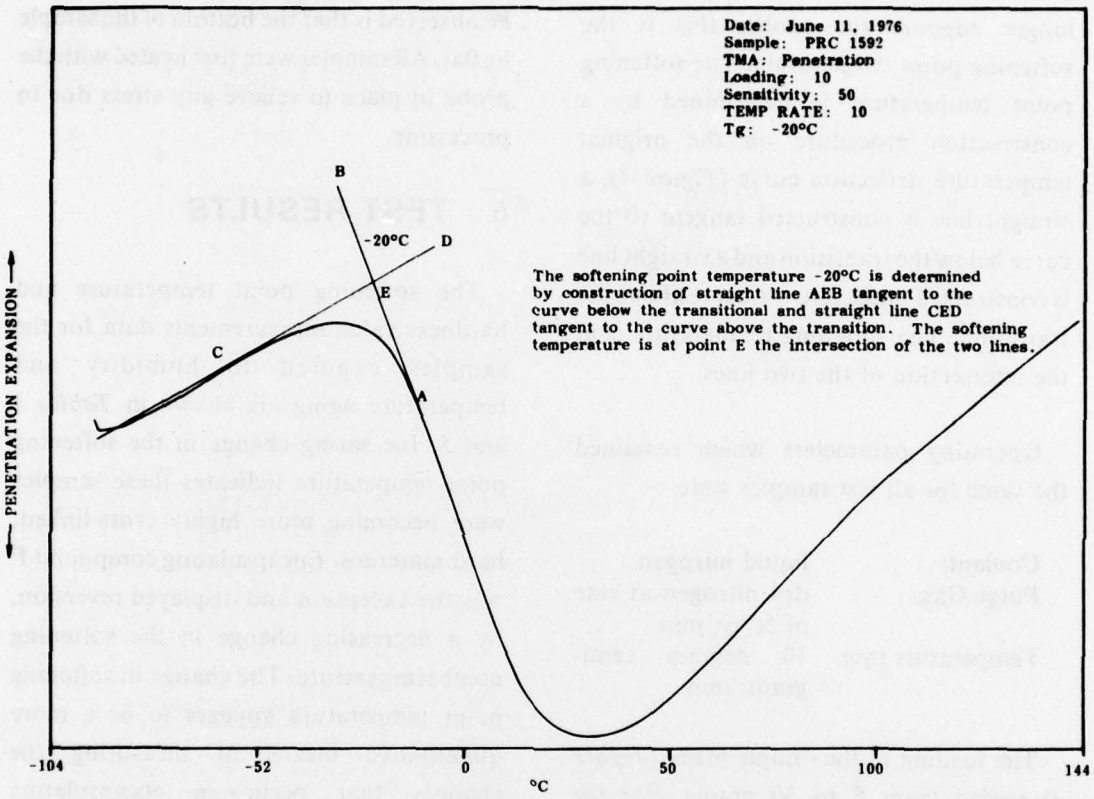

Figure 4. Determination of softening temperature.

TABLE 3. SAMPLES SUBJECTED TO 240 HOURS "PRESSURE COOKER METHOD"

ENCAPSULATING COMPOUND	SHORE HARDNESS AS CURED	240 HOURS	SOFTENING POINT TEMPERATURE AS CURED	240 HOURS
A	85 "A"	84"A"	-20°C	-7°C
B	88"D"	90"D"	76°C	99°C
C	86"C"	90"D"	76°C	101°C
D	90"D"	90"D"	63°C	97°C
E	40"A"	45"A"	-92°C	-29°C
F	57"A"	50"A"	-38°C	-92°C

TABLE 4. MIXED RATIO OF TWO PART EPOXY AND POLYURETHANE MATERIALS VARIED; SOFTENING TEMPERATURE AND HARDNESS DATA COMPARED TO MEASURE CHANGES IN MATERIALS

SAMPLE NR	MIXED RATIO RATIO A + B	SHORE HARDNESS "D" UNITS	SOFTENING TEMPERATURE
#G			
Correct Mix	100 - 70	70	43°C
Excess Part B	100 - 100	60	24°C
Deficiency Part B	100 - 40	80	71°C
#H			
Correct Mix	50 - 40	80	34°C
Excess Part B	50 - 50	70	53°C
Deficiency Part B	50 - 30	80	32°C

TABLE 5. EPOXY AND POLYURETHANE ENCAPSULATING MATERIALS SUBJECTED TO 95% RN AND 85°C FOR 84 DAYS; SOFTENING TEMPERATURE AND HARDNESS COMPARED

SAMPLE NUMBER	SHORE HARDNESS "D" UNITS				SOFTENING POINT TEMPERATURE			
	AS CURED	28 DAYS	56 DAYS	84 DAYS	AS CURED	28 DAYS	56 DAYS	84 DAYS
G	70	85	85	85	43°C	68°C	69°C	84°C
H	65	80	80	80	31°C	27°C	46°C	49°C
I	40	80	80	80	25°C	55°C	56°C	74°C

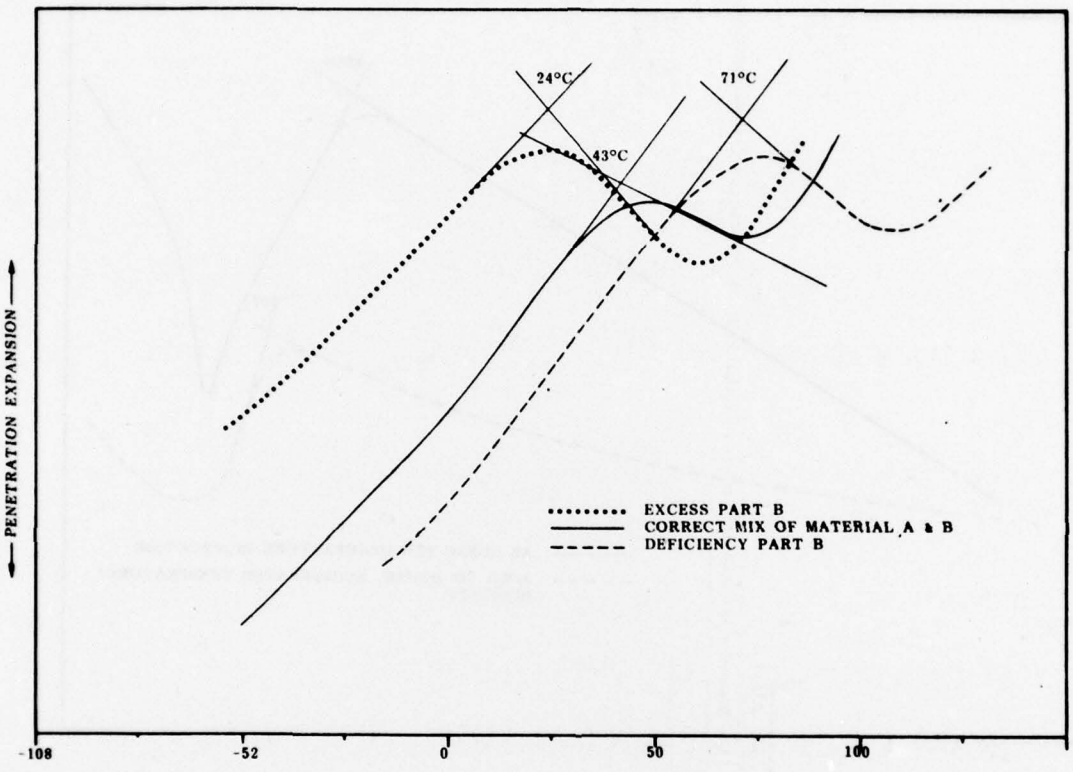

Figure 5. Change in softening point as mix ratio changed.

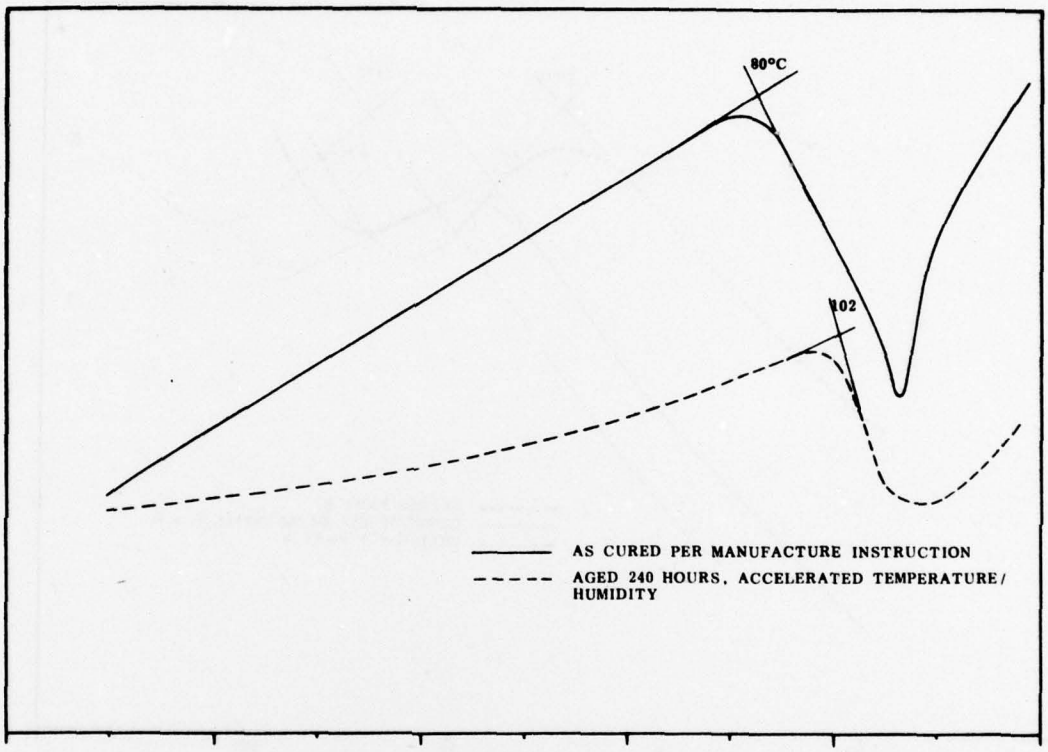

Figure 6. Epoxy encapsulating material exposed to 240 hours accelerated aging.

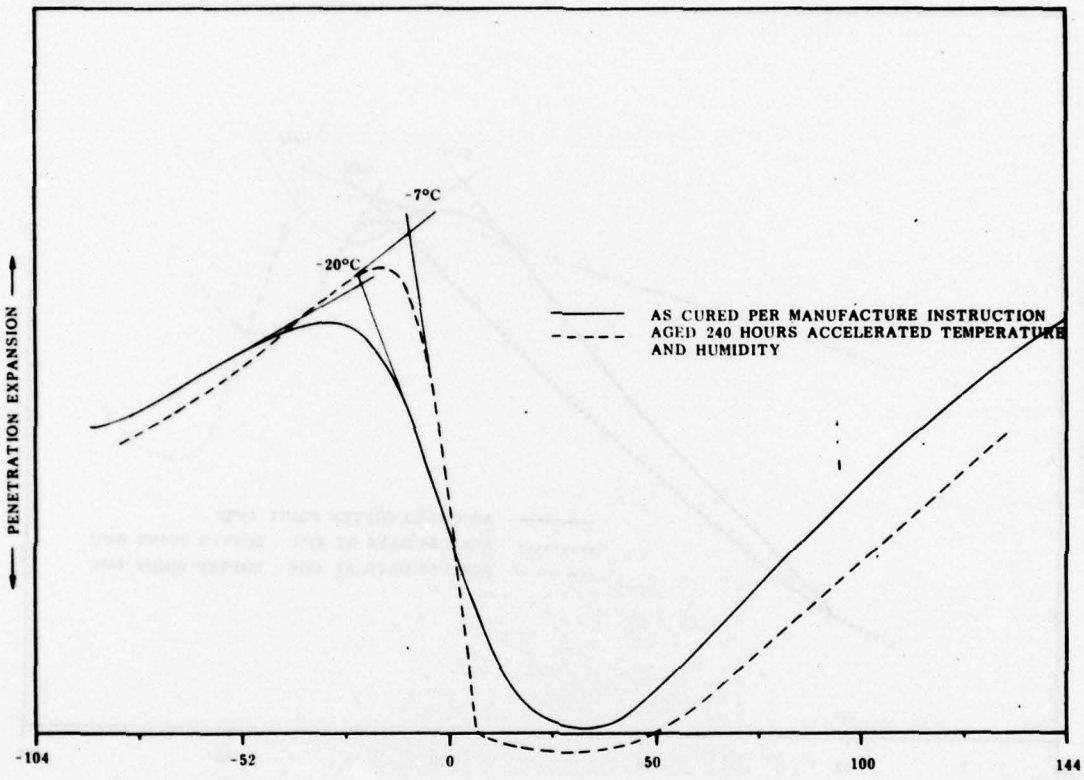

Figure 7. A polyurethane potting material exposed to 240 hours accelerated aging.

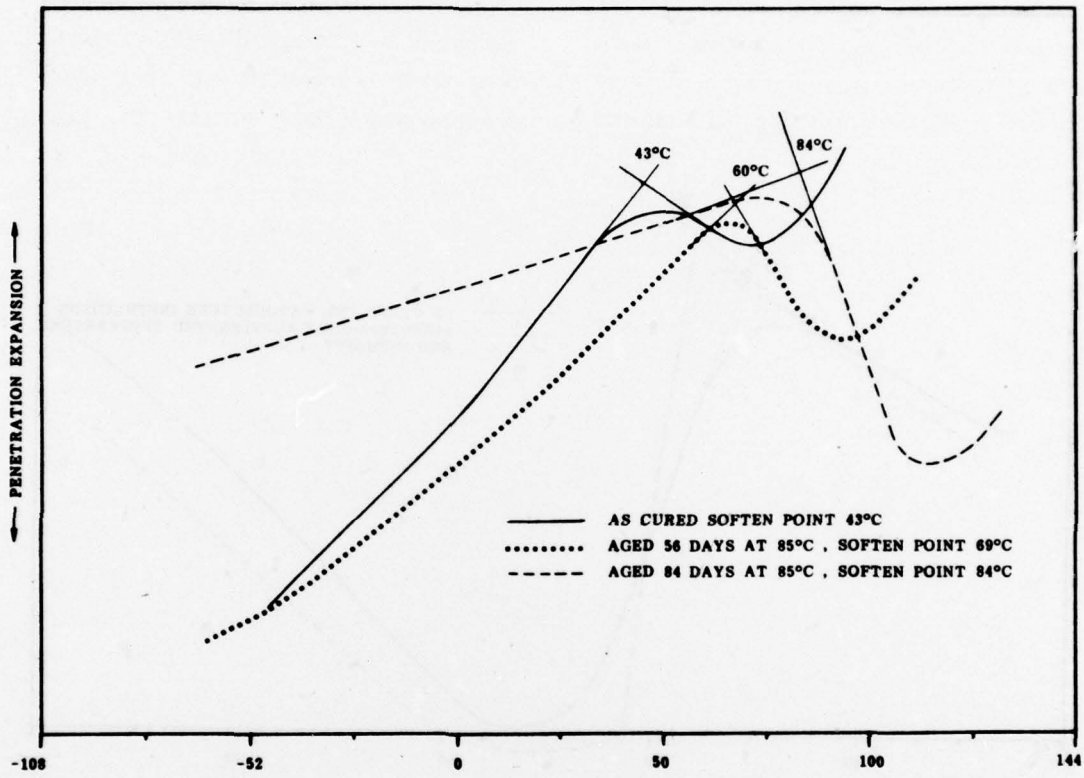

Figure 8. Most of the samples exposed to the 84 day temperature — humidity aging displayed increased curing. This would indicate that the manufacturer's recommended cure cycle was inadequate.

materials are exposed to high humidity and temperature.

7. CONCLUSIONS

The data obtained by the thermomechanical test method indicates this method is a more quantitative measurement and provides more information concerning change in the encapsulating material and rearrangement of the structural elements of the polymer when compared with data from the indentation hardness test method (*Tables 4, 5,* and *6*). The softening point temperature was more sensitive than the changes that occurred in the sample material subjected to the temperature-environmental aging and improper mixing ratio variance (*Figure 5*). The thermomechanical test method is very rapid, requires a small amount of sample *specimen (5-10 mg), is nondestructive* to the manufactured item in that only a small specimen is required and the item can be repaired if necessary. Most of the materials used in this test program displayed increased curing when exposed to the temperature/humidity aging process. This would indicate that the manufacturer's recommended cure cycle was inadequate (*Figures 6, 7, 8*).

8. RECOMMENDATIONS AND IMPLEMENTATION

The softening temperature property data is useful information to the design engineer regarding the general utilization of plastic encapsulating materials. It has been recommended (*Table 6*) that the glass transition temperature point or the softening point temperature property of the cured resin compound be a specified property listing for materials meeting the requirements of plastic encapsulating, molding and coating specification documentation. It has also been recommended that the thermomechanical analysis (TMA) be utilized as a test method for softening point temperature measurements of cured plastic encapsulating materials. Currently MIL-P-55617 calls for glass transition temperature property as a quality control measure for the resin preimpregnated glass cloth. A thermomechanical analytical (TMA) test method is used to measure the Tg of the B-stage resin.

TABLE 6. A LISTING OF PLASTIC ENCAPSULATING MOLDING AND COATING SPECIFICATION DOCUMENTATION

SPECIFICATION NUMBER	NAME OF DOCUMENT
MIL-P-47104	Potting compound, epoxy resin thermosetting
MIL-P-47199	Potting compound, low viscosity silicone rubber
MIL-C-47247	Coating, protective, resin, silicone
MIL-C-47255	Coating, protective, for printed wiring boards
MIL-C-47256	Coating, for printed wiring boards, application of.
MIL-P-47298	Polyurethane molding compound chemically cured (polyether base)
MIL-I-46058	Insulating compound, electrical (for coating printed circuit assemblies)
MIL-I-16923	Insulating compound, electrical, embedding
MIL-M-24041	Molding and potting compound, chemically cured, polyurethane
MIL-I-46879	Insulating compound, electrical epoxy base resin
MIL-P-46838	Potting compound, silicone rubber room temperature vulcanizing
MIL-P-83455	Potting compound, two-component, RTV, fluorosilicone

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