PROJECT INITIATION

Date: May 25, 1973

Project Title: Study of Thermal Coefficients of Expansion in Potted Devices

Project No.: A-1537

Project Director: Mr. W. H. Burrows

Sponsor: Radiation, A Division of Harris-Intertype Corporation

Effective: May 15, 1973

Estimated to run until: Open

Type Agreement: Purchase Order No: 151751

Amount: $1,000

Initial Authorization for first Phase

REPORTS: Report of findings as they occur
Final Report - upon completion of all work

CONTACT PERSON: (technical)
Mr. L. J. Sillay
Associate Principal Engineer
Systems Engineering Dept.
Radiation, A Division of Harris-Intertype Corporation
Post Office Box 37
Melbourne, Florida 32901

(Administrative)
Mr. R. Storum
Subcontract Administrator
Radiation, A Division of Harris-Intertype Corporation
Post Office Box 37
Melbourne, Florida 32901

Assigned to TECHNOLOGY APPLICATIONS GROUP

COPIES TO:

Project Director
Director
Assistant Director
GTRI
Division Chief(s)
Service Groups
Patent Coordinator
Photographic Laboratory
Security, Property, Reports Coordinator
EES Accounting
EES Supply Services
Library
Rich Electronic Computer Center
Project File
Other
PROJECT, TERMINATION
Date: November 27, 1973

PROJECT TITLE: "Study of Thermal Coefficients of Expansion in Potted Devices"

PROJECT NO: A-1537

PROJECT DIRECTOR: W. H. Burrows

SPONSOR: Radiation, A Division of Harris-Intertype Corporation

TERMINATION EFFECTIVE: November 30, 1973

CHARGES SHOULD CLEAR ACCOUNTING BY: November 30, 1973

TECHNOLOGY APPLICATIONS GROUP

COPIES TO:
Project Director
Director
Associate Director
Assistant Directors
Division Chief
Branch Head
Accounting
Engineering Design Services

General Office Services
Photographic Laboratory
Purchasing
Report Section
Library
Security
Rich Electronic Computer Center
Radiation
A Division of Harris-Intertype Corp.
P. O. Box 37
Melbourne, Florida 32901

Attention: Mr. Lou J. Sillay, Associate Principal Engineer,
Systems Engineering Department

Subject: Interim Report, Project A-1537, "Study of Thermal Coefficients of Expansion in Potted Devices"

In accordance with the plan of investigation outlined in our proposal of May 28, 1973, under subject title, we have investigated the problem of failures in potted subassemblies via the following specific studies:

1. DSC studies of the kinetics of resin-curing agent reactions in various stoichiometries.

A number of DSC runs have been conducted with Stycast 2651 resin and Curing Agent 11A in various ratios, but primarily in the recommended ratio of 22 phr. Two Perkin-Elmer DSC-1B instruments were employed; one located in the School of Chemical Engineering; the other located in the Engineering Experiment Station. In most runs there was virtually no evidence of an exotherm.

In order to improve the sensitivity of the instrument by reducing the heat capacity of the resin, the aluminum oxide filler was separated from the resin for further studies. Even these failed to produce readable exotherms. A fresh sample of curing agent provided slight improvement, but we had to conclude that the sensitivity of the instruments being used was inadequate for this task.

Arrangements have been made to use a Mettler TGA-DTA when it becomes available through courtesy of the School of Textile Engineering. This instrument should provide one order of magnitude greater sensitivity than those we have used, and is expected to become available next week.

In the meantime, we have assurance of the presence of a measurable exotherm through experiments run with larger samples in which thermocouples were embedded. We would prefer not to make any computations based upon these results, since the mass of material is such as to provide poor heat transfer, with resulting distortion of the thermal response curve.
2. Identification of resins and curing agents.

A portion of the resin of Stycast 2651 was separated from the filler, cast as a film on sodium chloride and examined by infrared spectroscopy. The IR absorption spectrum is shown in Figure 1. This spectrum is characteristic of a bisphenol A-butyl glycidyl ether epoxy resin, and is similar to that shown by Dow's D.E.R. 331 or 334, and Shell's Epon 828 or 834:

Infrared spectra of curing agents 11 and 11A were run in the same manner, with results as shown in Figure 2. Curing agent 11 appears to consist primarily of an aliphatic tetramine, while 11A has the characteristics of a mixture of diamamines with a fatty acid polyamide, such as linoleic. This blend resembles Union Carbide's ZZLA-0315 epoxy curing agent.

3. Thermal cycling of finished components.

Samples of resin/curing agent mixtures in ratios of 13, 16, 19, 22 and 25 phr have been prepared. From these mixtures, potted sub-assemblies have been prepared, two for each ratio. Simultaneously, blocks of the same mixtures have been cast into polycarbonate boxes, identical with those used for potting subassemblies, two for each ratio. All have been cured on the schedule of 1/2 hour at 62°C and two hours at 100°C. One set of blocks was utilized for the experiments described in study no. 4, below. One set of blocks and one set of potted subassemblies is now undergoing thermal cycling on the following schedule: one hour at -65°C, one hour at room temperature, one hour at +80°C, one hour at room temperature, and repeat, for n cycles. At the conclusion of the cycling, the specimens will be sectioned and studied according to the experiments described in study no. 4, and others, if indicated.

4. Check for cure.

Uniformity of Mix

Potted modules supplied by the sponsor were sectioned by cutting out transverse planes parallel to the base. Sections were approximately 1/8 inch thick. Cutting disks used were ACM Products Company 4 Cut-120-15; passes were made at successive depth increments of 1/16 to 1/8 inch. The operation was thoroughly water cooled. Sections were then polished on one face, using water cooled metallurgical grinding and polishing wheels.

Polished faces were examined under 7+ power magnification, then immersed in acetone for several hours. The acetone was kept in continuous circulation against the polished face. The sections were then removed, dried and reexamined. In no case was any etch pattern observed, as would have been the case had there been pockets of unmixed resin or curing agent.
No evidence was found to indicate that resin and curing agents were not uniformly mixed in preparation of the potting material.

**Stoichiometry**

Sections prepared as above were exposed to methylene chloride for etching purposes; however, attack by the solvent was so severe that the sections were disintegrated into fragments. Dissolution in the solvent did not occur; hence, the fragmentation was a consequence of mechanisms other than solvation.

Other sections were exposed to methylene chloride vapor at room temperature, whereupon the fragmentation occurred as before, but at a rate and under conditions permitting better observation. There was a peripheral failure, causing splitting off of an approximately 1/16 inch section around the outer edge. In addition, the resin separated from the components via transverse splitting. Also, areas of continuous resin showed peripheral splitting extending from their outer edges towards their centers; the centers appeared to be relatively unaffected.

In consideration of the heterogeneity of these sub-assembly sections, it was not possible to propose a mechanism for this type of failure. We prepared samples of Stycast with Curing Agent 11A in ratios of 13, 16, 19, 22 and 25 phr, and cast these into polycarbonate boxes identical with those used for the sub-assemblies. There were cured at 62°C for 1/2 hour, then at 100°C for two hours. After several days at room temperature, these samples were sectioned in the same manner as the sub-assemblies, to a thickness of 1/8 inch, then exposed to methylene chloride vapors at room temperature for a period of eight hours. Observations were as follows:

At two hours, the 13 phr sample showed thin sections split in masses from the upper surface of the specimen. These splinters stood like stalagmites over a large portion of the surface. To a very small degree, the same phenomenon was observed on the 16 phr sample, although the splinters were much smaller and very scattered. No effect was observed on the remaining specimens.

At four hours, the 13 phr sample showed increased stalagmiting. In addition, the entire periphery of the specimen was split off in a jagged line about 1/8 inch from the outer edge. The fragments were 1/2 inch to 3/4 inch in length. The 16 phr sample also showed slightly increased stalagmiting, and its entire periphery was split off in full length jagged fragments approximately 1/8 inch in thickness.

At six hours, the 13 phr sample showed no increase in stalagmite formation; however, fragmentation had proceeded to the point that several layers of material, up to 3/16 inch in thickness, had separated around the entire periphery. There were also some transverse cracks through the central portion of the wafer. The 16 phr sample showed the same effects to a lesser degree, except that there was no transverse splitting. In the 19 and 22 phr samples, the outer layer had split off full length throughout the periphery, and a second layer was separating in the form of chips up to 1/2 inch length. The 25 phr sample showed splitting off of full length fragments, about 3/32 inch thick, along each side.
After eight hours exposure, fragmentation of the 13 phr sample was both multidirectional and peripheral, to the point that the sample showed almost complete disintegration. The 16 phr sample showed continued splitting and chipping inwardly from the edges to a depth of about 5/16" on the ends, 1/4" in the middle. The 19 phr sample showed these effects to a lesser degree; the 22 phr sample, to a still lesser degree, but still quite marked. The 25 phr sample showed failure only in the peripheral splitting off of a 1/16" layer; the remainder of the wafer was still solid. The eight-hour results are shown in Figure 3, a through e.

Results obtained with these wafers, in comparison with the sections cut from subassemblies, are significant from the standpoint of both stoichiometric cure ratio and stress patterns. That the fragmentation which was observed in the five stoichiometric ratios is a consequence of incomplete cure is apparent from the fact that the most severely affected was the wafer cut from the 13 phr sample, and that severity of MeCl2 attack decreased with increasing ratio. Actually, a fully cured epoxy resin should not be attacked at all by this vapor, and the 25 phr system almost met that criterion. The fact that fragmentation did occur in the 25 phr system and to a greater degree in the 22 phr system indicates that the ratio specified for CA 11A (22 phr) is inadequate for complete cure.

The pattern of the fragmentation, which is primarily peripheral, with transverse cracking appearing only in the last stages, can be understood by laying an unexposed chip alongside the exposed chip (Figure 3f). It is apparent that the phenomenon has occurred through absorption of solvent vapors by the slightly uncured resin, causing expansion, which places high radial stress upon the mass. At the same time, penetration by MeCl2 molecules serve to weaken intermolecular bonds of the resin, giving rise to failure in a direction perpendicular to the stress vector; i.e., more or less parallel to the edge. This directional effect is observed in the shape of the jagged edges of the splits and especially in a "beveling" effect seen in the remaining edges of the specimens.

The effect of heat is similar to that of methylene chlorine vapor; however, over the range covered in thermal cycling, this effect is much milder and does not approach the level required for fragmentation to occur. Nevertheless, thermal expansion does produce a similar stress pattern and does cause some weakening of intermolecular bonds. It might well be anticipated that repeated thermal cycling would in time cause structural weaknesses to develop along the lines of failure observed in the MeCl2 exposure samples, although to a degree not noticeable to the naked eye.

Sections of potted subassemblies submitted by the sponsor were exposed to methylene chloride vapor and observed over a period of five hours. One sample was taken at random from those initially supplied by the sponsor;
its history was not known. The other sample was one which had been submitted to repeated thermal cycling and testing by the sponsor and identified by him as a reject. Whether rejection was caused by failure of a solder joint, a glass diode, or other feature is not known.

These sections were examined at the end of two hours, at which time there was no noticeable effect on the random sample, while the "reject" showed slight warping. After four hours, the appearance of the random sample was still unchanged, while the "reject" had separated into several fragments, with some peripheral chipping. The experiment was concluded at the end of five hours, when the random sample showed splitting in the vicinity of some components (Figure 3g). At this time, fragmentation of the "reject" was severe (Figure 3h).

In view of the preceding observations relating fragmentation to cure, it is evident that the "reject" was less fully cured than the random sample. Whether cure failure in this instance was a result of improper mix ratio, decreased activity of the curing agent, improper curing cycle, or other cause is not known. However, the initial experiment with MeCl₂ vapor does indicate that the 22 phr ratio might be too low for the sample of curing agent employed in our preparations.


Because of the difficulties described above, exotherms of the curing reaction have not been measured; however, we hope to obtain suitable results with the Mettler instrument.

6. Hardness of cured resin.

Hardness measurements are being made, using the Shore Durometer, on resins cured under the various stoichiometries. Results will be included in the final report.


Attempts to etch polished sections of potted subassemblies and cast blocks with various solvents were described above. No evidence of inhomogeneity in mixing was found in these studies. Consequently, incomplete mixing has been ruled out as a contributory cause in the failure of the potted units.

8. Microscopic studies.

Solder joints exposed by sectioning have been examined microscopically. The mechanical effects on these joints experienced during the sectioning, however, are sufficiently severe that it has been impossible to relate
observations to stresses that might have developed within the subassembly. A number of solder joints in unpotted subassemblies have also been examined, but no instance of discontinuity has been observed.


Mixes of resin and curing agent in the 22 phr ratio have been prepared from resin and curing agent that have previously been exposed to ca 100% relative humidity for a period of several days. There has been no indication of moisture deterioration from the standpoint of the cure rate and ultimate cure of the mixture.

10. The Alpha report.

We have studied the Alpha report No. TC-007-3C, "A Technical Evaluation of KW-7 Module Design and Workmanship Requirements," and will be willing to comment in detail upon the findings of this report in the light of our own findings in the laboratory. The conclusions of the Alpha report place prime responsibility for failure of soldered joints upon (1) design and workmanship requirements for lead staking, (2) the lack of lead stress relief, and (3) the use of thick RTV coating.

Our findings on expansion effects strongly support items 1 and 3 as contributory factors. The problem of lead stress relief is a complex one, as it is difficult to provide relief in one direction without inviting stress in another direction. That stress relief is needed in lead configuration cannot, however, be argued.

Effect of stress on diode characteristics.

We are enclosing a copy of the paper, "Use of p-n Junction Semiconductor Transducers in Pressure and Strain Measurements," by M. E. Sikorski. Mr. Sikorski, formerly of Bell Telephone Laboratories, is now a member of the Engineering Experiment Station Staff.

This paper may aid in the interpretation of results obtained in the measurement of mother board and subassembly electronic characteristics under conditions of expansion and contraction.

Reference materials on DSC measurements and interpretation.

Dr. Muzzy has provided us with the following papers on DSC measurements and their interpretation. If you do not have copies readily available, we shall be glad to furnish them.


Conclusions

Since this is an interim report, conclusions drawn from the foregoing experiments and results should not be considered final. Within that limitation, however, our experimental results lead to the following factors as contributing to the failure of solder joints in the submitted subassemblies:

1. Design of the module is such that solder joints are made between lead and interior section (apex) of notch, with virtually no support between lead and edge of board (a point made in the Alpha report). Consequently, these joints might be expected to withstand an inward pressure against the joint much more strongly than an outward pressure.

2. Expansion resulting from temperature changes operate to produce stresses against the interior surfaces of the leads and joints and to push away from the joint that portion of the plotting compound which lies between the joint and the edge of the board. This, in effect, weakens the support of the joint on the exterior side, while stress builds up on the interior side.

3. This expansion is increased by the pressure developed in the RTV coating, since the RTV under these circumstances behaves as a completely enclosed and incompressible liquid under thermal expansion.

4. Mechanical failure of the potting compound under thermal expansion is aggravated by incomplete cure.

Future work

This research project will be concluded in the near future by completion of several tasks under way: (1) measurements of exotherms by DSC to determine reaction kinetics, optimum resin/curing agent ratio, optimum curing cycle and completeness of cure, (2) measurement of coefficients of thermal expansion, (3) measurements of compressive and flexural moduli, and (4) effects of thermal cycling.

Respectfully submitted,

[Redacted]
Principal Research Scientist
REMARKS
Like Dow

Move like
DER 334 Bisphenol A/Butyl Glycidyl Ether epoxy

ORIGIN
Mr. Beertma

PER: KIN-ELMER
MODEL 700

PREP: MR. Beertma

PHASE
Liquid

CONCENTRATION
100%

THICKNESS
Film on NaCl

DATE
July 2, 1973

OPERATOR
SRH

PERKIN-ELMER
MODEL 700

SPECTRUM NO.

SAMPLE 1
Hydrazoic Acid

SAMPLE 2

FREQUENCY (CM⁻¹)

TRANSMITTANCE (%)

0 10 20 30 40 50 60 70 80 90 100

2400 2000 1800 1600 1400 1200 1000 800 650

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

0.5 1 2.5 4 5 6 7 8 9 10 11 12 13 14 15

micron

C-N
C=O
C-H
C=O
C=O
REMARKS

Fig 2

Formula

Amide

Acid > p-anisidine

Formedill Block, probably

c-Tetramine, aliphatic

PERKIN-ELMER

MODEL 700

SPECTRUM NO.

SAMPLE 1

Sample 2

PHASE

CONCENTRATION

THICKNESS

NaCl Film

DATE

July 13, 1972

OPERATOR

DRH

ORIGIN

Mr. Gyrrows

R&D Labs

PURITY

SAMPLE 1

IIA Red

SAMPLE 2

II Black

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

TRANSMITTANCE (%)
Use of p-n Junction Semiconductor Transducers in Pressure and Strain Measurements

M. E. SIKORSKI
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

I. Introduction ........................................... 238
II. Semiconductor Diodes .................................... 238
   A. Ordinary Diodes ..................................... 238
   B. Zener Diodes ....................................... 245
   C. Esaki Diodes ....................................... 246
III. Effect of Hydrostatic Pressure on the I-V Characteristics of Tunnel Diodes, Theory ........................................... 251
IV. Operation of Esaki Diodes ................................ 254
   A. Switching Mode ..................................... 254
   B. Amplifier Mode ..................................... 257
V. Experimental Results on Tunnel Diodes ..............
   A. Silicon ........................................... 264
   B. Germanium ........................................ 269
   C. Gallium Arsenide .................................. 273
   D. Gallium Antimonide ................................ 274
VI. Temperature Effects in Tunnel Diodes ..............
VII. Noise in Tunnel Diodes .................................. 284
VIII. Device Applications of Semiconductor Diodes .
   A. Signal Device ..................................... 289
   B. Hydrostatic Pressure Sensor .................... 290
   C. Strain Gage ....................................... 292
   D. Microphones ....................................... 296
   E. Other Applications of Tunnel Diodes ........... 301
IX. Transistor Transducers ................................ 301
X. Discussion ............................................. 318
References ............................................... 319
I. Introduction

The p-n junction devices such as diodes and transistors have found a multitude of applications in the field of electronics, ranging from rectification of electrical currents to amplification of electrical signals. These devices have also been used to convert one form of energy into another, as, for example, in the case of a solar cell in which light energy is converted into electrical energy.

Recently, new applications have been found for the p-n junction devices, namely, the conversion of a mechanical or acoustical signal into an electrical signal, or vice versa. The subject matter of this chapter is related to the conversion from a mechanical to an electrical signal. The reverse problem is treated in Chapter 13.

The usefulness of the p-n junction devices as uniaxial, biaxial, or triaxial stress (pressure) transducers is due to the fact that the current-voltage characteristics of these devices shift as a result of the application of certain sets of stresses. This means that the electrical resistance of a given device for a certain bias condition is a function of the applied stress. The change in the resistance can be used as a measure of the applied stress, or pressure.

The reason why p-n junction devices are of such great promise in the field of pressure and strain transducers is that they have the advantage of the static property measurement, their sensitivity is competitive with that for other signal pickup devices, and they are inherently small in size and simple in construction.

It is the purpose of this chapter to describe the effects of stress, or pressure, on p-n junction devices and in particular tunnel diodes. In addition, methods will be presented whereby these devices can be used to measure stresses or pressures. A few applications will be cited.

II. Semiconductor Diodes

A. ORDINARY DIODES

A diode is a nonlinear 2-terminal device. The electrical impedance is low for one applied bias polarity and high when the bias polarity is reversed. Figure 1 shows the current-voltage characteristic of a semiconductor diode.

The electrical characteristic of Fig. 1 is divided into forward and reverse regions. A forward bias always produces a relatively large current at small applied voltages. The application of reverse voltage, however, has little effect on the magnitude of the reverse current. Figure 1 illustrates these effects. From 0 to A, the reverse current undergoes an increase with reverse voltage. This increase is in microamperes or less. From A to B, large changes in reverse voltage produce very small increases in reverse current (this change is exaggerated in the figure). The region from A to B, therefore, is called the saturation region. The break occurs by a factor of approximately 10^6.

The value of the saturation current is given by the term that is shown in the characteristic.
region. Beyond point \( B \), the current increases rapidly. This is called the breakdown region.

In the saturation region (between points \( A \) and \( B \)), the current is fairly constant for relatively large changes in voltage. This region is commonly utilized in the performance of rectification. In the breakdown region (between points \( B \) and \( C \)), a large increase in current is the result of a small increase in reverse voltage. This can be classified as a constant voltage region and is normally used for voltage regulation. Both of these regions can be utilized to advantage for sensitive strain measurements.

\[ I = I_s e^{(qV/kT)} - 1 \]

where \( I_s \) is a constant in the absence of mechanical stress, \( q/kT \) has a value of 38.6 \( V^{-1} \) at 27°C, and \( V \) is the applied potential. For forward voltages in excess of 50 \( V \), the current rises exponentially and increases by a factor of 10 for every 60 \( V \). For reverse voltages, the exponential term quickly approaches zero, and the current is equal to \(-I_s\). This is shown in Fig. 1 by a dotted line passing through point \( A \) on the diode characteristic and drawn parallel to the voltage axis.
Fig. 2. Forward current-voltage characteristics of a silicon diode:
(a) condition of no stress; (b) uniaxial stress applied in the direction perpendicular
to the plane of the junction.
Fig. 3. Reverse current-voltage characteristics of the silicon diode of Fig. 2: (a) no stress; (b) uniaxial stress of the same magnitude and direction as in Fig. 2.
Actual p-n junctions fail to obey the above constant saturation current condition predicted by the simplified theory which neglects surface effects. The fact that the junction reverse current (between A and B in Fig. 1) is higher than calculated from Eq. (1) is generally attributed to surface recombination and surface leakage across the p-n junction (7).

The physical principles of semiconductor diodes have been discussed at some length in Chapter 10; hence, we will proceed directly to the study of the effect of stress on the diode I-V characteristics.

![Diagram of a p-n junction and ohmic contact](image)

**Fig. 4.** Variation of reverse current with stress for three silicon diodes. Data correspond to a constant voltage bias point of -20 volts.

Figure 2 shows forward I-V characteristics of a silicon diode. Curve (a) was obtained when the diode was not stressed and curve (b) is a characteristic of the same diode under stress. The compressive stress was applied in the direction perpendicular to the plane of the junction. The shift in the characteristic as a function of stress was found to be reversible. If we consider a constant voltage line corresponding to a bias voltage of 0.3 volt, it is about 50 times.

The reverse current was found to be exponential in the same stress and a little over one order in the reverse current in Fig. 3 corresponds to the reverse of stress, for a 100% effect of stress.

The increase of the reverse current is exponential in the same stress. For example, curve (a) provides an ohmic contact in the silicon disks of the entire device.

The stress in the device was made by pressing the assembly uniaxial stress silicon disks. Curves (b) and (c) show the I-V characteristics of the diodes. The constant bias and stress are due to a small pressure of 8000 psi on the silicon disks, and then a rise to occur. This corresponds to the larger change of the device when the strain is applied.

Before remark about the differences in stress stresses present. The pressure was made by pressing the device, and then a rise to occur. This corresponds to the larger change of the device when the strain is applied.
of 0.3 volt, it is clear from the figure that the current increased by about 50 times on account of stress.

The reverse I-V characteristics of the same diode subjected to the same stress as above are shown in Fig. 3. Notice that whereas the exponential rise in current in the forward characteristic corresponds to a little over 0.4 volt, the sudden rise (in absolute value) of the current in the reverse bias occurs at about 50 volts. Again curves (a) and (b) in Fig. 3 correspond to no stress, and stress conditions, respectively. In the reverse characteristic the changes in the current on account of stress, for a given constant voltage, are even more pronounced. These effects are shown in a different manner in Fig. 4.

The insert in Fig. 4 illustrates how the p-n junctions were mounted. The assembly consists of two disks of silicon on which small mesas were made. The p-region was formed in one of the mesas by a diffusion process. This is indicated by a blackened region in the top mesa (pointing down). The top surfaces of the mesas were metallized to provide an ohmic contact on assembly. As shown in the figure, the two silicon disks are separated by a glass spacer. The overall height of the entire device is about 0.014 inch and the diameter is about 0.030 inch.

The stresses were applied to the junctions by putting the devices in a pressure vessel and applying hydrostatic pressure. By the construction of the device the hydrostatic stresses were converted into nearly uniaxial stress, perpendicular to the plane of the junction, the two silicon disks acting as diaphragms.

Curves (a), (b), and (c) of Fig. 4 were obtained for three different diodes. They represent the variation of current with pressure for a constant bias point of -20 volts in the reverse characteristic. Notice that for diode (a) the current started to rise rapidly when a relatively small pressure was applied to the device, whereas it took about 4000 psi of pressure in the case of diode (b) for a substantial current rise to occur. For diode (c), a decrease in the current was first noted and then a rapid rise took place from about 17,000 psi on. These differences in behavior may be due to different amounts of residual stresses present in the device after assembly.

Before we proceed to the next section it is of interest to make a remark about the orders of magnitude of changes in resistance occurring for these diodes on account of stress. Let us consider curve (a). For a pressure range between 2000 and 6000 psi, a change in the current occurred from a value of about 10^-7 ampere to about 10^-3 ampere. This corresponds to a change in resistance on the order of 10^4. Even larger changes of resistance take place for larger negative biases, as can be easily verified by looking at Fig. 3. It goes without saying that these effects could be utilized for very sensitive strain, or force, measurements. Since changes in resistance on the order of micro-ohms can be detected with bridge methods, it should be possible to measure very small strains indeed.
Devices as described in connection with Fig. 4 would also make sensitive hydrostatic pressure transducers.

Recently, very large shifts in the I-V characteristics of germanium diodes under stress were reported in the literature (2-7). In this work diodes were stressed by means of a diamond needle, which was applied in the direction perpendicular to the plane of the junctions. Although the stress field was quite different between this case and ours, in both instances large effects were observed. It is worth noting that in both cases, i.e., for both silicon and germanium diodes, an increase in the current with stress was observed. As will be seen later, in connection with the discussion of pressure effects on tunnel diodes, different effects are observed for silicon and germanium tunnel diodes. For silicon tunnel diodes the current increases with pressure, whereas it decreases for germanium diodes. These effects are related to the different signs of the pressure coefficient of the energy gap for both materials.

We will recall that the diode of Figs. 2 and 3 had a breakdown voltage of about -50 volts. Different applications require different breakdown voltages, hence diodes have to be made in such a way as to give the desired I-V characteristics. The potential at which the breakdown occurs can be regulated by the amounts of impurities in the n- and p-regions of the manufacture.

Figure 5: Typical current-voltage characteristics for silicon and germanium junctions made from materials of different resistivities. [After Chynoweth et al. (5).]

It was at the discovery of the breakdown avalanche mechanism of the Esaki diode that the Zener diode was recognized. As was seen earlier, the breakdown voltage of the silicon and germanium Zener diodes is also called the breakdown voltage of the avalanche breakdown associated with the breakdown of the junction. The avalanche breakdown is characterized by an increase in the voltage across the junction, whereas that of the Zener diode is characterized by a decrease in the voltage across the junction. In the case of the Zener diode, the breakdown voltage is determined by the properties of the materials used, whereas in the case of the avalanche breakdown, the breakdown voltage is determined by the properties of the impurities in the n- and p-regions of the manufacture.
12. p-n Junction Transducers

p-regions of the semiconductor material introduced at the time of manufacture.

Figure 5 shows the I-V characteristics of several diodes made of silicon and germanium material of different resistivities. It is quite clear that as the resistivity of the material decreases, or the doping level increases, the breakdown voltage shifts to lower negative values. This is of interest from the point of view of the physical mechanism of breakdown that occurs for diodes of different doping levels. A. G. Chynoweth et al. (5) have shown that if the breakdown occurs at a low voltage, the mechanism is that of tunneling or internal field emission. If the breakdown occurs at a relatively large negative voltage, it is due to the process called avalanche breakdown. This will be treated in more detail in the section that follows and will lead us logically into the field of Esaki diodes.

B. ZENER DIODES

"Zener diode" is a term which covers voltage regulator, stabilizer and reference diodes. They depend for their operation on the large current rise (Fig. 1, line BC') of a silicon diode in its well-defined breakdown region. The breakdown characteristics are remarkably sharp, the voltage increasing only by a fraction of a volt over several decades of current. The temperature coefficient of voltage changes sign from negative to positive as the breakdown voltage is increased, going through zero in the 5-6 volt region. Voltages of this order are suited to transistor circuits, and Zener diode are used to provide reference voltages.

The change in the sign of the temperature coefficient of voltage in the 5-6 volt region for silicon diodes is related to the change in the mechanism of breakdown in the same voltage range.

It was at first thought that the mechanism of all junction breakdown phenomena was that described originally by Zener (5) and which is also called "tunneling," or "internal field emission." It is now recognized that two distinct mechanisms exist, depending on the thickness of the junctions. In the case of very narrow junctions, those that have breakdown voltages of less than 5 volts for silicon, primarily Zener breakdown seems to occur, and in the case of wider junctions, avalanche breakdown predominates (5). Hence, the breakdown of junction A in Fig. 5 can be considered to be mainly due to avalanching, whereas that of diodes C, D, E, and F is due mostly to tunneling. The unit marked with a letter B breaks down at about 5 volts, and undoubtedly exhibits a mixture of the two breakdown mechanisms.

In the case of the tunneling mechanism, an increase in the temperature causes the forbidden band to become narrower, and hence the tunneling probability increases and the breakdown takes place at a lower voltage.

The avalanche breakdown mechanism involves ionizing collisions of electrons with the lattice which result in electron-hole pair production.
At the time of our preparation of subject Interim Report, there were several facets of the study which were not quite complete. These have now been completed, and are included in this Addendum, together with our conclusions and recommendations concerning the devices under study.

1. Hardness

Hardness of cured samples, prepared with a ratio of 22 parts of curing agent CA-11A to 100 parts resin, was checked with the Shore Durometer. Five readings were taken on each sample at each temperature; Table 1 presents the averages of the five readings.

<table>
<thead>
<tr>
<th>Sample No.:</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C:</td>
<td>22 62 100</td>
<td>22 62 100</td>
<td>22 62 100</td>
</tr>
<tr>
<td>Shore Hardness:</td>
<td>90.2 86.0 63.3</td>
<td>90.4 84.2 63.6</td>
<td>90.2 85.0 64.0</td>
</tr>
</tbody>
</table>

Shore hardness was also determined on a sample prepared at 22 phr and cured at 63 ± 1°C for 1/2 hour, without the 100°C postcure. Average of five readings was 89.4 at room temperature (22°C).
Maximum deviation of readings on any sample at room temperature and at 62°C was 2 points. At 100°C, maximum deviation was 18 points.

2. Coefficient of Thermal Expansion

Linear coefficients of thermal expansion for cured resins prepared with ratios of 13, 16, 19, 22 and 25 phr were measured on the versatile testing device in the Micromechanics Laboratory. Samples used were rods cast by pouring the resin-curing agent mix into test tubes of 3/8" I.D. These rods were cut into lengths of approximately 2-1/4" for insertion into the device. Expansion was measured over a temperature range of -150°C to +60°C using a displacement transducer. Table 2 shows the values of the coefficients for rods cast from the 5 curing agent-to-resin ratios:

<table>
<thead>
<tr>
<th>Curing Agent Ratio, phr:</th>
<th>13</th>
<th>16</th>
<th>19</th>
<th>22</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient x 10^-5 in/in/°C:</td>
<td>4.95</td>
<td>4.82</td>
<td>4.63</td>
<td>4.38</td>
<td>4.197</td>
</tr>
</tbody>
</table>

By contrast, the coefficient of thermal expansion of the glass-filled epoxy circuit board is ca. 2.2 x 10^-5 in/in/°C; the two differ by a factor of 2.

3. Flexural Modulus

Flexural modulus was measured using specimens of rectangular cross section, cut from blocks of the cured resin. Specimens were approximately 0.11" x 0.226" x 2.2". Force measurements were made with a load cell. Curves for force versus deflection were obtained for each catalyst-to-resin ratio at temperatures of 40°C, room temperature (22°C) and 0°C. Copies of these curves are attached as Figures 1 through 15.

4. Compressive Modulus

Similar curves were developed for force versus compression at room temperature, using specimens of similar geometry to those used above. These curves are shown as Figures 16 through 20.

There is comparatively little variation in the compression curves for the five levels of curing agent. This would indicate that these curves span a transition from highly gelled liquid to partially plasticized solid. The transition would occur mainly between the 19 and 22 phr levels, where a decrease in slope is observed. Above this level, the increase in modulus with increasing degree of cure corresponds to increases in flexural modulus, hardness, resistance to methylene chloride vapor sorption; decrease in coefficient of thermal expansion, etc.
Conclusions

1. The design of this subassembly is such that soldered joints between components and circuit boards are subject to thermomechanical stresses well beyond those which appear to have been anticipated in the design. These stresses arise largely from dimensional changes during thermal cycling. The manner in which these forces operate against the solder joints is described in subject Interim Report.

2. The properties of the epoxy system used in this subassembly and described in this addendum are such as to aggravate these stresses at the critical points. In effect, the solder joint is placed in a position where it is subject to severe forces resulting from shearing type displacements between circuit board and epoxy filling, both of which are quite hard and unyielding. While a factor of 2 in relative coefficients of thermal expansion is not large, it is sufficient under the present circumstances to cause brittle failure of lightly soldered connections under repeated thermal cycling over a wide temperature range.

   It has been demonstrated that one subassembly previously checked by the sponsor and found to be defective contained a less fully cured resin than one more fully cured. Since coefficient of thermal expansion decreases with increased degree of cure, it is possible that degree of cure could have been a factor in the amount of stress developed during cycling. It has also been demonstrated that the less fully cured resin is more subject to internal bond destruction; if such occurs, the resulting expansion of the resin places additional stress against the soldered connections in a direction of least support. Full cure is not obtained at 22 phr under a curing cycle of 62°C for 1/2 hour, 100°C for 2 hours. It is apparently not reached even at 25 phr.

3. Another factor which has been pointed out as contributing to the development of destructive stresses at the solder joints is pressure developed in the RTV coatings of subassemblies, the RTV behaving as a completely enclosed and incompressible liquid under thermal expansion.

4. In addition to the mechanical effects demonstrated in these studies, it appears quite possible that pressure effect upon components, particularly diodes but possibly capacitors as well, may change the operational parameters of these components sufficiently to cause rejection of the subassembly for functional reasons.

Recommendations

In view of the difficulties stemming from the design and construction of the solder joints involved in these subassemblies, it is strongly recommended that modifications in design be contemplated to provide a larger contact surface between component lead and circuit board metal. This could be accomplished by making a bend in the lead to permit a short section (e.g., 1/16 inch) to lie on the metal foil and to be firmly soldered to the foil over that distance. The resulting joint would be so much stronger that the present joint that failures under the stresses developed during thermal cycling would have low probability of occurrence.
In view of the difficulties resulting from the rigidity of the epoxy system now being used, it is recommended that an elastomeric potting compound be considered as a replacement for the rigid epoxy. Such a system may be formulated from a butyl rubber base. Its physical characteristics may be varied considerably to provide the specific properties required for a given application; yet, because of its elastic modulus, it will provide a degree of yield under stress which will serve to protect vital points during thermal cycling.

We are enclosing a copy of material published by Enjay Chemical Company, concerning their LM (low modulus) butyl rubber compounds, and direct your attention particularly to the following properties:

- High dielectric strength
- Low dielectric constant
- Low dissipation factor
- High volume resistivity
- Flexibility to -55°F
- Resistance to water vapor penetration
- Stability of mechanical properties to 250°F, continuous
- Resistance to mechanical shock

We trust that the information provided in this Interim Report and Addendum will serve the need which led to your support of this study. It has been a pleasure to participate in this study with you, and we hope to have further opportunities of similar nature in the future.

Respectfully submitted,

[Redacted]

W. H. Burrows
Project Director

WHB/edh

Enclosure
### A-1537 Flexible Modulus

<table>
<thead>
<tr>
<th>Ratio:</th>
<th>13/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>0°C ± 2°C</td>
</tr>
<tr>
<td>Y-axis:</td>
<td>Force equiv to grams</td>
</tr>
<tr>
<td>X-axis:</td>
<td>Deflection</td>
</tr>
</tbody>
</table>

#### Force Scale
- 9000g full scale
- 2" = 5 mil

#### Length Between Supports
- 3.5cm

![Figure 1](image-url)
A-1537  
Ratio: 16/100  
Temperature: 0°C ± 20°C

Y-axis: Force equi to grams  
2000g full scale

X-axis: Deflection  
2" = 5 mil

FIGURE 2
<table>
<thead>
<tr>
<th>A-1537</th>
<th>FLEXURAL MODULUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio:</td>
<td>19/100</td>
</tr>
<tr>
<td>Temperature:</td>
<td>$0^\circ C \pm 2^\circ$</td>
</tr>
<tr>
<td>Y-axis:</td>
<td>Force equ to grams 2000g full scale</td>
</tr>
<tr>
<td>X-axis:</td>
<td>Deflection 2&quot; = 5 mil</td>
</tr>
</tbody>
</table>

FIGURE 3
A-1537  FLEXURAL MODULUS

Ratio:  22/100
Temperature:  0° C ± 2°

Y-axis:  Force equiv. to grams  
        2000g full scale

X-axis:  Deflection  
        2" = 5 mil

FIGURE 4
A-1537
FLEXURAL MODULUS

Ratio: 25/100
Temperature: 0°C ± 2°C

Y-axis: Force equiv to grams 2000g full scale
X-axis: Deflection 2" = 5 mil

FIGURE 5
A-1537 FLEXURAL MODULUS

Ratio: 16/100

Temperature: 22°C

Y-axis: Force equal to grams
2000g full scale

X-axis: Deflection
2" = 5 mil

FIGURE 7
A-1537

FLEXURAL MODULUS

Ratio: 10/100

Temperature: 20°C

Y-axis: Force eqv to grams 2000g full scale

X-axis: Deflection 2" = 5 mil

FIGURE 8
FIGURE 10

<table>
<thead>
<tr>
<th>A-1537</th>
<th>FLEXURAL MODULUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio:</td>
<td>25/100</td>
</tr>
<tr>
<td>Temperature:</td>
<td>250°C</td>
</tr>
<tr>
<td>Y-axis:</td>
<td>Force equiv to grams 2000g full scale</td>
</tr>
<tr>
<td>X-axis:</td>
<td>Deflection 2&quot; = 5 mil</td>
</tr>
</tbody>
</table>

△ 25° of 5 mils deformation

25-12  7.0
11-17  12.0
15-12  15.5
16-13  22.0
<table>
<thead>
<tr>
<th>A-1537</th>
<th>PLEXURAL MODULUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio:</td>
<td>13/100</td>
</tr>
<tr>
<td>Temperature:</td>
<td>40°C ± 1°C</td>
</tr>
<tr>
<td>Y-axis:</td>
<td>Force equiv to grams</td>
</tr>
<tr>
<td></td>
<td>2000g full scale</td>
</tr>
<tr>
<td>X-axis:</td>
<td>Deflection</td>
</tr>
<tr>
<td></td>
<td>2&quot; = .5 mil</td>
</tr>
</tbody>
</table>

FIGURE 11
A-1537  FLEXURAL MODULUS

Ratio:  16/100
Temperature:  40°C ± 1°C

Y-axis:  Force equal to grams
        2000g full scale
X-axis:  Deflection
        2" = 5 mil

FIGURE 12
A-1537

FLEXURAL MODULUS

Ratio: 19/100

Temperature: 40°C ± 1°C

Y-axis: Force equiv. to grams 2000g full scale

X-axis: Deflection 2" = 5 mil

FIGURE 13
A-1537  Flexible Modulus
Ratio:  22/100
Temperature:  400 C ± 19
Y-axis:  Force equiv to grams
         2000g full scale
X-axis:  Deflection
         2" = 5 mil

Figure 14
A-1537
FLEXURAL MODULUS

Ratio: 25/100
Temperature: $40^\circ C \pm 1^\circ$

X-axis: Deflection
$2'' = 5$ mil

Y-axis: Force equ. to frame
2000g full scale

FIGURE 15
A-153T  COMPRRESSIVE MODULUS

Ratio:  13/100

Temperature:  220 C

Y-axis:  Force equiv to grams
        12kg full scale

X-axis:  Compression
        1.5" = 1 mil
        l_o = 5.94 cm

FIGURE 16
A-1537
Ratio: 16/100
Temperature: 22° C

Y-axis: Force equiv to grams
12kg full scale
X-axis: Compression
1.5" = 1 mil
l₀ = 5.63 cm

FIGURE 17
<table>
<thead>
<tr>
<th>A-1537</th>
<th>COMpressive MODULUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio</td>
<td>19/100</td>
</tr>
<tr>
<td>Temperature</td>
<td>22°C</td>
</tr>
<tr>
<td>Y-axis</td>
<td>Force-eqv to grams</td>
</tr>
<tr>
<td></td>
<td>12kg full scale</td>
</tr>
<tr>
<td>X-axis</td>
<td>Compression</td>
</tr>
<tr>
<td></td>
<td>1.5&quot; = 1 mil</td>
</tr>
<tr>
<td></td>
<td>l₀ = 6.11 cm</td>
</tr>
</tbody>
</table>

**FIGURE 18**
A-1537  COMRESSIVE MODULUS

Ratio: 22/100
Temperature: 22°C

Y-axis: Force equiv to grams
12kg full scale

X-axis: Compression
1.5" = 1 mil
l_0 = 5.77 cm

FIGURE 19
A-1537  COMPRESSIVE MODULUS
Ratio:  25/100
Temperature:  22°C
Y-axis:  Force equiv to grams
        12kg full scale
X-axis  Compression
       1.5" = 1 mil
       1.0 = 5.53 cm

FIGURE 20
SEALANTS

Butyl LM can be formulated into two part, room temperature curing sealant compounds. These can be used in insulated window manufacture, and for architectural, marine, highway and aircraft sealants. The primary performance features of Butyl LM sealants are:

Outstanding moisture vapor transmission resistance
Butyl has long been regarded as the standard against which elastomer barriers are compared. Its close packed molecular structure prevents the passage of liquids and gases.

High resistance to polar chemicals
Butyl compounds can be immersed in salt solutions, acids, bases, esters and vegetable oils with negligible changes in physical properties.

Long service life
The low level of unsaturation of the butyl polymer has resulted in a long record of outdoor durability and good heat resistance.

Effective vibration damping
Butyl LM sealants possess the same damping ability that has made butyl so useful to automotive manufacturers in auto body mounts and similar structures.

ELECTRICAL POTTING COMPOUNDS

Butyl has long been used for high voltage electrical insulation because it combines good dielectric properties with durability. Butyl LM compounds can be formulated so that they are pourable and can be cured in place. These Butyl LM compounds maintain good insulating properties after aging and demonstrate marked advantages over potting compounds based on other polymers. The major advantages are:

Environmental resistance
Butyl LM has excellent durability, even in hot, humid environments where other potting compounds are not as effective. Butyl LM compounds will not hydrolyze.

Flexibility
Rigid potting compounds cannot tolerate the physical and thermal shocks that have no effect on Butyl LM compounds.

Low moisture vapor transmission rate
Potting compounds are usually expected to protect valuable components from moisture. Butyl LM compounds are twenty to several hundred times better in resistance to penetration by water vapor.

COATINGS

Coatings based on butyl rubber have been used for years in a wide range of critical applications. Butyl LM and Chlorobutyl LM compounds extend the range of coating formulations due to their ease of application. The uses include fabric laminating, dipped goods, roofing, waterproofing, tank lining, maintenance coatings and vapor barriers. LM polymers offer many advantages:

High solids at low viscosity
Butyl LM and Chlorobutyl LM can be formulated to have double the solids content of a compound with the same viscosity containing regular butyl.

Outstanding chemical resistance
Acids, alkalis, aqueous salt solutions and polar solvents have little effect on properly formulated LM polymer coatings.

Low moisture vapor transmission rate
Butyl LM has one of the lowest moisture vapor transmission rates of the elastomeric barrier coatings.
ELECTRICAL POTTING AND ENCAPSULATING

Enjay Butyl rubber has been used for over 30 years in high voltage cable insulation. Butyl and Butyl LM provide excellent insulating properties.

Properties of Butyl LM Based Insulation Compounds

- High dielectric strength: up to 800 volts/mil
- Low dielectric constant: 2.5 to 3.5
- Low dissipation factor: 0.005 to 0.01
- High volume resistivity: $10^{15}$ ohm-cm

An outstanding advantage of Butyl LM (and of butyl) is its resistance to the effects of water. Formulated Butyl LM has outstanding resistance to moisture vapor transmission and will not hydrolyze. It provides protection for delicate electronic components in hot, humid environments and effectively insulates and protects high voltage transformers in contact with ground water (URD). The superiority of Butyl LM’s resistance to water vapor transmission is illustrated in Table VIII.

Butyl LM formulations are rubber like and flexible, eliminating problems of stress cracking and mechanical damage. Compounds can be formulated with physical properties ranging from a soft gel such as is needed in cable flooding compounds to strong dense rubber compounds such as are used in transformer encapsulants. Properly formulated compounds are:

- Resistant to moisture vapor transmission
- Castable
- Curable at room temperature (two part system)
- Curable at elevated temperature (one part system)
- Flexible to −55°F
- Odorless
- Able to retain mechanical properties at environmental temperatures of 250°F continuous and 350°F intermittent

TABLE VIII

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>MVTR (1)</th>
<th>MVTR Relative to Butyl LM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enjay Butyl LM (2)</td>
<td>0.04</td>
<td>1</td>
</tr>
<tr>
<td>2 part room temp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 part room temp.</td>
<td>8.31</td>
<td>208</td>
</tr>
<tr>
<td>cure</td>
<td>8.00</td>
<td>200</td>
</tr>
<tr>
<td>2 part room temp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 part room temp.</td>
<td>2.16</td>
<td>54</td>
</tr>
<tr>
<td>cure</td>
<td>2.80</td>
<td>70</td>
</tr>
<tr>
<td>Polysulfide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 part room temp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) g of H$_2$O/24 hrs/100 sq. in. at 100°F and 90% RH differential normalized to 20 mil thickness.
(2) All Butyl LM formulations tested thus far fall in the range of 0.02 to 0.4 MVTR depending upon formulation.
Able to absorb vibration and sound effectively—high mechanical damping
Inert to copper catalyzed oxidation non-corrosive to copper
Resistant to soil bacteria
Resistant to chemicals and oxidation
Resistant to hydrolysis

These properties suggest the following applications:

**Transformer encapsulants**
Provides electrical and moisture protection

**Cable flooding compounds**
Allows controlled flow of compound through punctures

**Conformal coatings**
Electronic components and circuit boards are protected from moisture

**Transformer coatings**
Prevents metal corrosion from the environment

**Battery coatings**
Resistant to acidic and alkaline chemicals

When compounding Butyl LM for these electrical properties the ingredients used play an important role. Fillers, plasticizers and solvents are discussed in the following paragraphs specifically for electrical compounds.

**PLASTICIZERS**

**Oil**

*Hydrocarbon transformer oil* - A recommended oil for service under 200°F is Univolt 33, with a viscosity of 60 SSU at 100°F. This results in compounds that are pourable at room temperature when the oil is used at the 75 phr level.

**Wax**

*Microcrystalline wax* - To produce hard compounds that are pourable, a high melting wax, e.g., Microvan 1604, can be used. This necessitates an application temperature above the melting point of the wax as well as an elevated temperature cure system. Hardness is in the 40 to 50 Shore “A” range.

**SOLVENT**

For very low viscosity compounds, a solvent for the polymer, e.g., toluene, can be used. Where external dimensions are not critical, such as in conformal coatings, these formulations are ideal since the compound will shrink around the part for a better fit. The shrinkage of the compound is limited to the loss of solvent only. Compound hardness varies from 20 to 60 Shore “A” depending on the fillers.