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PRESSURE-TOLERANT DEVICE TECHNOLOGY
STATE OF THE ART

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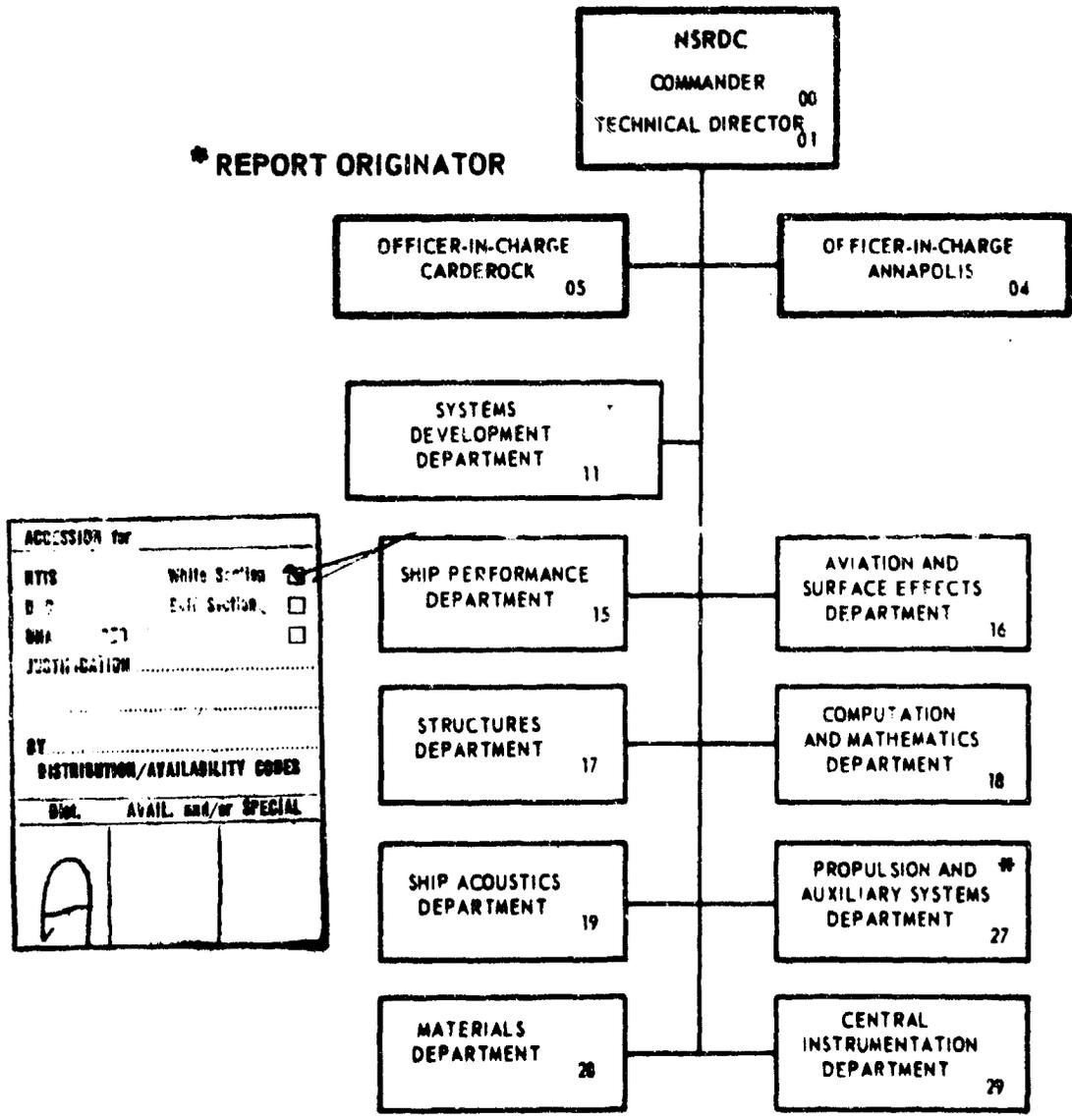
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<p>This report describes the research effort devoted to the study and development of a device and material technology to provide electronic and electrical components, circuits, and equipment that will operate successfully in the ocean environment without the need for pressure shell protection. The work has been concerned with: (1) identification and evaluation of device problem areas, (2) development of technology to be used to prevent</p> <p align="right">(over)</p>		

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device failures, and (3) identification and evaluation of system requirements. The report incorporates excerpts from previous in-house and contractor information and discusses in detail recently completed analyses and experimentation. Its purpose is to document, in a logical manner, the results of the work in determining the influences of an oil/pressure environment on contemporary electronic/electrical components and systems.

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ADMINISTRATIVE INFORMATION

This work was accomplished under the Device Technology for Deep Ocean Applications Program, Task Area XF 54 545 010, Work Unit 2781-514.

LIST OF ABBREVIATIONS

Å	- angstrom
ASW	- antisubmarine warfare
atm	- atmospheres
°C	- degree Centigrade
°C/W	- degree Centigrade per watt
cm ²	- square centimeter
CMOS	- complementary metal oxide semiconductor
cSt	- centistokes
dc	- direct current
DIP	- dual-in-line package
DOT	- deep ocean technology
e.g.	- for example
et al	- and others
etc	- and so forth
ft	- foot
g	- gram
g/cm ³	- gram per cubic centimeter
Hz	- hertz
I _B	- base current
IC	- integrated circuit
I _C	- collector current
I _{CBO}	- collector-base cutoff current
i.e.	- that is

I_E - emitter current
in. - inch
 I_O - cutoff current
 I_S - leakage current
I-V - current-voltage
lb/in² - pound per square inch
mA - milliampere
mg/g - milligram per gram
min - minimum
MOS - metal oxide semiconductor
MOSFET - metal oxide field effect transistor
mV - millivolt
 μ A - microampere
 μ g/g - microgram per gram
 μ m - micrometer
NA - not applicable
NC - normally closed
npn - negative-positive-negative
ohm-cm - ohm-centimeter
p/m - parts per million
p-n - positive-negative
pnp - positive-negative-positive
PTE - Pressure-Tolerant Electrical/Electronic Systems
sec - second
SCR - silicon controlled rectifier
TTL - transistor-transistor logic
TUT - transistor under test

V - volt
V_{BE} - base emitter voltage
V_{CC} - collector supply voltage
V_{CE} - collector emitter voltage
vdc - volts direct current
via - by way of
V_L - load voltage drop
W - watt
yr - year

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INTRODUCTION

BACKGROUND

The need for electronic components which can survive and operate when exposed to hydrostatic pressures of the ocean results from two considerations:

- The ocean bottoms will be explored and the undersea depths used by the Navy for undersea defense and ASW* activity.
- Protection of electronic equipment at shallow and great depths is costly. As structures are designed to withstand the pressure of greater depths, the increase in hull thickness and weight puts a high premium on the use of the available space and buoyancy.

Contemporary electronic components are adversely influenced by ocean pressures, and catastrophic failure has been demonstrated. Electronic components and hardware are usually designed for use in the earth's atmosphere or outer space. Little consideration has been given to the performance of hyperbarically stressed components and hardware. However, electronic hardware which could be placed outside the pressure hull in a liquid environment, in equilibrium with the surrounding sea, and operate satisfactorily on demand would result in the need for less space inside the pressure hull and less buoyant materials with concomitant savings in weight, size, and thickness of hull.

The immediate problem is to determine what electronic technology is available in terms of components, circuits, and packaging for use in a liquid medium and subjected to high hydrostatic pressures and expected noise and shock pressures. A systematic approach using experiment and available theory should identify problem areas, evaluate difficulty, and provide guidelines for construction of equipment capable of successfully operating outboard of submarine pressure hulls.

PAST WORK

As early as 1959,¹ testing was started to determine the effect of deep ocean pressures on both passive and active components. Subsequent tests were performed in the same manner.²⁻⁴ Typically used components were selected, and circuit parameters were monitored to determine their change in value versus pressure. The results included:

*The definitions of all abbreviations used are on page i.

¹Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

- Carbon-composition resistors usually changed value by $-20\%/1000$ to $-30\%/1000$ atm. Wire-wound or film-type resistors usually exhibited little change in resistance with pressure.

- Capacitors of completely filled construction, such as molded or dipped mica, glass, mylar, and impregnated paper types, usually showed small change in capacitance with pressure. Exceptions were traceable to internal voids. The effects of these voids were more noticeable for tantalum and aluminum electrolytic capacitors, which usually exhibited severe case deformation and often failed.

- Inductors and transformers with laminated cores usually exhibited little parameter value change (inductance or voltage ratio). However, porous core structures, such as permalloy dust, tape wound, and ferrites, were found to exhibit large value changes with pressure.

- Transistor cases crushed at various pressure levels. Usually, the larger the case size, the lower the pressure at which it failed.

A few attempts at modification were made. Potting was found to be effective in increasing component pressure resistance, particularly when a flexible silicone rubber undercoat was used prior to the addition of a more rigid outer cover, such as epoxy. Another technique, flooding with oil, was also found successful, at least on a short-term basis.

This previous work has been empirical, generally an attempt to find usable components to fill a particular need. In some cases, the designation and manufacturer of the components tested have been given. In other cases, such information is sketchy or completely absent. The reported results lead to the general maxim, "avoid voids." Other general conclusions are difficult to draw.

More recently, both this Center and NUC, Hawaii Laboratory, Oahu, Hawaii, have entered the field. The effort at NSRDC has been concerned primarily with a review of the total problem of outboarding electronic/electrical systems and, consequently, considered such important problems as selection of the pressurized fluid, identification of failure modes, and techniques to prevent failures.⁵ NUC, on the other hand, has concentrated on evaluating the feasibility of utilizing off-the-shelf components. Numerous devices have been identified as potential candidates for outboard applications.⁶

APPROACH IN PRESENT EFFORT

The basic approach is to classify and separate the various observed effects into physical, physicochemical, and short- and long-term reliability problem areas. More specifically, the approach is to determine: (1) the effect of mechanical stress and deformation on device housing materials; (2) the influence of an oil/pressure environment on device operating parameters; (3) the chemical interaction of oil contaminants on device operation; and (4) system considerations, such as: material enclosures, buoyancy, solubility of materials, heat transfer, and reliability.

SELECTION OF DEVICES AND TEST METHODS

Since a fair amount of work has been reported on passive components, such as resistors, capacitors, and inductors, the emphasis in this area has been concerned only with formulating an analysis that would explain the previous test results. For semiconductor devices, however, a somewhat ambitious program to identify and evaluate problem areas associated with an oil/pressure environment has been undertaken. This has been done for two reasons: first, the amount of past work reported in this area is slight, and second, the recent trend in integration of devices has revolutionized circuit design.

The selection of the specific semiconductor devices to be evaluated was determined by first considering several system types that would possibly be outboarded. Second, a list of components commonly found in these systems was tabulated. The tabulation included a large variety of discrete, IC's, hybrids, and fabricated components. Third, with this listing as a guide, an analysis of the various components, their functions, and possible susceptibility to an oil/pressure environment were performed to ascertain ways to reduce the magnitude of testing required. The following are the conclusions resulting from this analysis.

One of the types of devices that is most likely to be used in power applications is the discrete transistor. Except for relatively rare occurrences, placement of power transistor structures on an IC chip is impractical due to the large area required and because of the heat generated during operation.

Small- or medium-scale IC's are used in relatively simple systems, such as those for sensing and signal processing or those for exercising control. A wide variety of components utilize IC technology, including operational amplifiers, digital IC's, bipolar transistor-type logic families, and the MOS and CMOS structures.

The saving grace in the face of the multiplicity of components is that all of these devices are based on a single technology - silicone planar technology. Therefore, only representative samples of such devices need be tested, and the

behavior of these circuit functions under test can be extrapolated to interpret what will happen with the other types of devices.

Representative devices were selected for testing on the following basis:

- Small signal transistors, both bipolar (npn or pnp) and unipolar (field effect) types, would be expected to be sensitive to ionic contamination on their surfaces unless adequate design in fabrication has forestalled such effects through the use of passivation, field plates, "channel stoppers," or similar techniques.

- Silicon power transistors would be expected to be susceptible to mechanical damage because of the relatively large chip area which provides a greater possibility of voids in the chip to substrate bond. In addition, some experience with heat-transfer characteristics of power devices in pressurized oil is needed.

- Germanium devices lack the oxide passivation used on silicon devices. These would be expected to be immediately affected by any ionic contamination in a pressurizing dielectric oil.

- Medium-scale IC's have relatively large chips, typically 50 to 60 mils per side. Therefore, a greater possibility of encountering voids in larger chip substrates than in smaller ones exists. Linear IC's, such as operational amplifiers, would include a variety of component types on one chip, such as resistors, capacitors, diodes, and transistors. In addition, the input transistors operate at low signal levels and would be expected to show up any contamination effects which would be amplified through to the output stages.

A schematic representation of the approach to evaluating representative semiconductor devices in an oil/pressure environment is presented in figure 1. The selected dielectric oil⁵ (a 5-cst silicone-base oil, Federal Specification product VV-D-001078) was used as the media. Maximum pressure to which the devices were subjected was 15,000 lb/in², equivalent to operation at 20,000 ft with a 1.5:1 safety factor. Step (A), in figure 1, characterizes the device environmental capability as received (off the shelf). In this test, either the component housing withstood the pressure or it deformed and developed stresses somewhere in the structure which were beyond tolerable limits. In the first case, no further testing was performed. In the second case, some modification of the structure had to be made, step (B) or (C). In selection of step (B), the device was decapped and exposed to the media (pressure equalized). The device was then evaluated without added passivation, step (B1). If the test results indicated that device operation was hampered by exposure to the media due to possible contamination, the device surface was passivated and reevaluated, step (B2).

An alternative to pressure equalization, although less desirable, was to stiffen or thicken the housing material (potting), step (C), and then to evaluate.

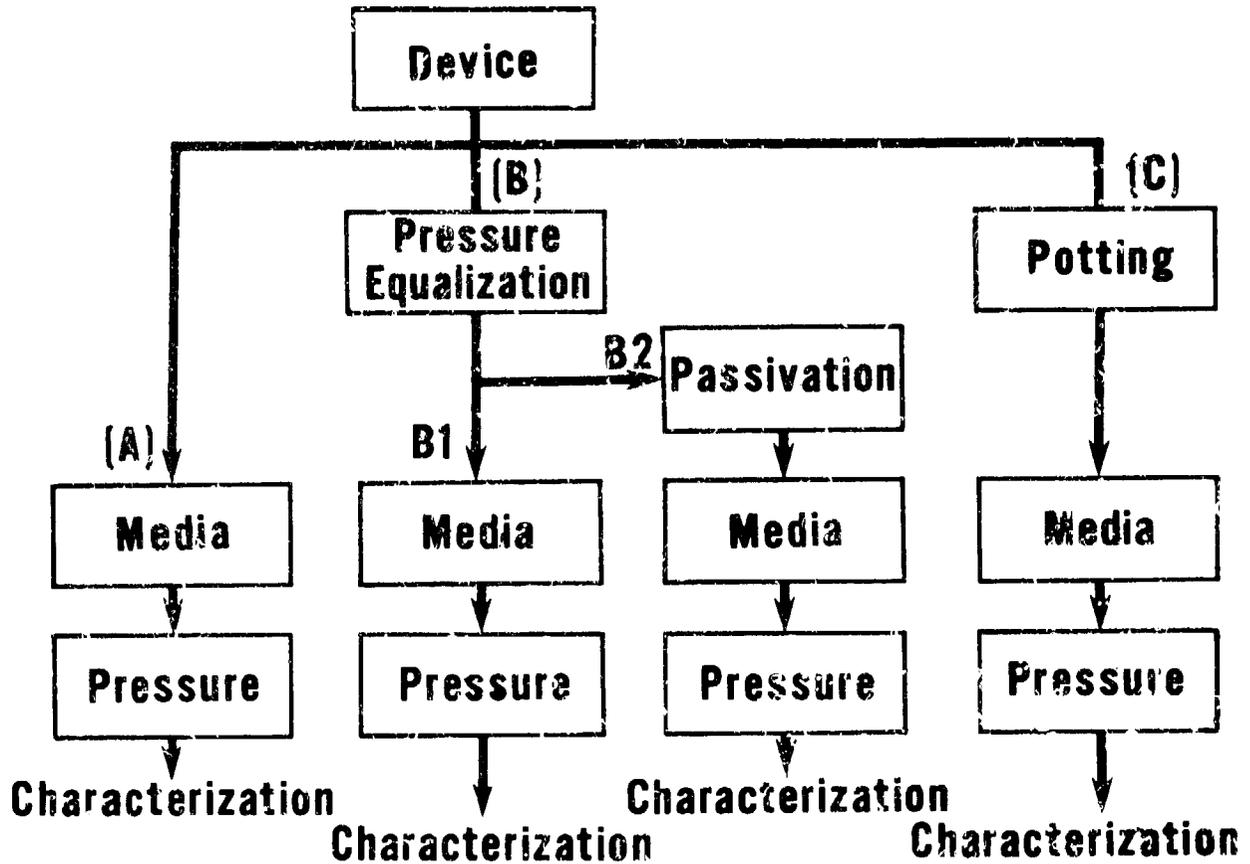


Figure 1 - Schematic Representation of the Approach

PROGRESS

EFFECTS OF PRESSURE ON DEVICE HOUSINGS

Preface

Component housings typically present a large surface area over void regions. Generally, the thickness of the material is sufficient protection under atmospheric pressures but is not sufficient to resist deformation under large hydrostatic pressures. Such deformation may result in damage due to shorting of electrical circuits, catastrophic collapse, or stress amplification that leads to failure of the component internal to the package. These possibilities make it imperative to analyze the deformations that will occur in typical component package configurations (figure 2) and to determine the maximum allowable hydrostatic pressure for a given package type.

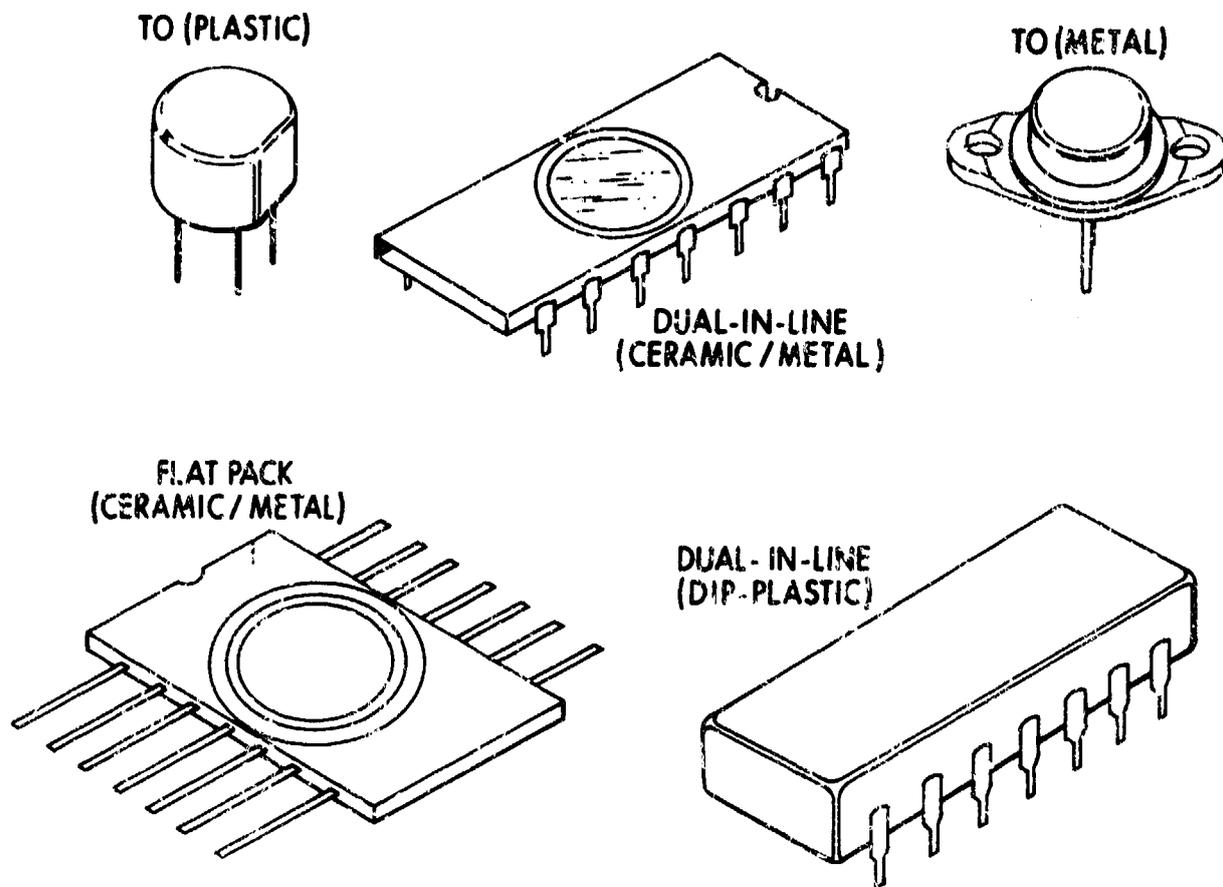


Figure 2
Typical Component Package Configurations

The well-known methods of linear elastic theory were used in the analysis of the mechanical stress distributions which occur in component packages subjected to hydrostatic pressures. The usual assumptions⁸⁻¹⁰ made in such an analysis were employed; namely, that:

- The materials are perfectly elastic.
- The materials are homogeneous and isotropic.
- Superposition of stresses (or strains) is permissible.

These assumptions allow the use of relatively well-developed models to determine at what hydrostatic pressures the limiting value of elastic stress is reached. This is the yield point stress. Beyond this stress, reduced material strength or noticeable permanent deformations occur and the assumptions listed above are no longer valid.

The value of yield point stress is known for most metals and alloys used in component package construction. For ceramic packages where pressure acts on a surface to provide a flexing action (membrane stress), the flexural strength of ceramic materials is analogous to the yield point stress for metals.

The methods of elasticity theory^a are used in facing the general problem of determining the stress distribution $s(x, y, z)$ in model structures which resemble the component packages most generally used. These structures are composed of laminar slab elements. Acting on these elements are the applied pressure (P), reaction forces (R), and bending moments (M_B), as sketched in figure 3.

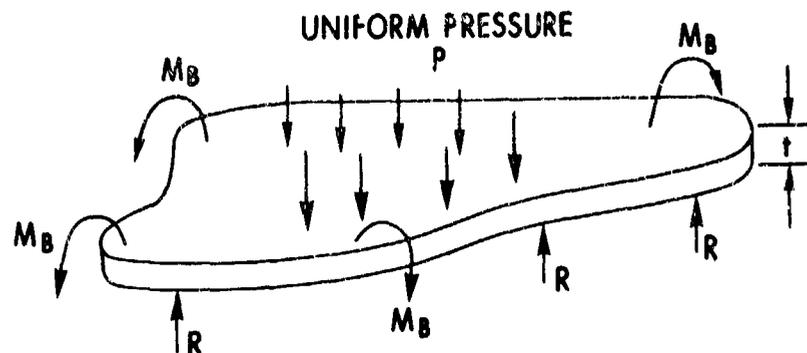


Figure 3
Forces and Moments Applied to Laminar Slab

The maximum stress developed at various points in the structure is then set equal to the yield or flexural strength, as appropriate, and the pressure (P), which produces this stress, is determined. This is converted to an equivalent depth of water and is used to indicate the depth threshold beyond which permanent deformation or fracture can be expected.

In principle, this simplified analysis of the effect of pressure permits the prediction of the maximum usable depth for housings employed by semiconductor devices and circuits as well as passive components.

Semiconductor Housings

Discrete semiconductor devices are housed in a variety of packages. One type, the TO can, comes in various physical sizes which are designated by a TO number, such as TO-18, TO-5, etc. The cans are made of metal, usually kovar, nickel, or aluminum, with a relatively thin shell cover or cap. The headers (bottom cover) may vary from relatively thin disks with a thickness not much greater than that of the cap to a relatively thick plate, as in the case of high dissipation devices such as power devices. It should be noted that at least two different materials are used in the construction of each of these headers. Some insulation, usually glass, is used to insulate feedthrough leads electrically from the metal of the header. In the smaller device packages where heat transfer is not a primary consideration, a large fraction of the header material may be glass.

The TO cans are used to hermetically seal semiconductor devices to prevent contamination. For those applications where ambient conditions do not require such complete protection for the device, it may be covered with one or more plastic materials, such as silicone or epoxy compounds. The physical characteristics of these materials and methods of their application have been discussed by Licari.¹¹

Aside from hermeticity, there is a significant difference between the TO can-type packages and the plastic-type packages. The TO can packages have a significant fraction of the enclosed volume as a void occupied only by a gas. On the other hand, the plastic packages allow intimate contact of the package material with the semiconductor element. Thus, when a pressure is applied to a TO can, there is nothing in the interior of the package to resist the pressure and the forces developed on the surfaces of the can. If these forces are large enough, the can may deform and eventually collapse. On the other hand, a pressure exerted on the surface of an epoxy or a plastic package is transmitted through the plastic directly to the chip. This pressure may be in addition to a pressure which already exists within the plastic package due to such effects as the differences in thermal expansion coefficient between the plastic and the semiconductor device housed within the plastic and shrinkage during curing operations. Early studies^{10,12} have shown that very high mechanical strains may be obtained within a plastic package due to the shrinkage of the plastic following its application at high temperatures.

IC packages come in many varieties. Among these are the TO can types, the flat packs, and the DIP's (figure 2). The DIP's are made both with plastic and with ceramic materials. As in the case of the discrete semiconductor device, the plastic DIP's allow the material of the packages to come in intimate contact with a semiconductor device chip. In the case of the TO can-type, the flat-pack, and the ceramic packages, there is a void inside the package which makes it susceptible to damage by sufficiently high external pressures. For the plastic package, however,

forces developed on the outside of the package are transmitted directly through the plastic to the semiconductor device chip.

A convenient starting point in analyzing the effects of pressure on semiconductor packages which contain voids is to use a simple model for the lids of these packages and to apply standard formulas.⁹ Figure 4 depicts the structures which are to be used.

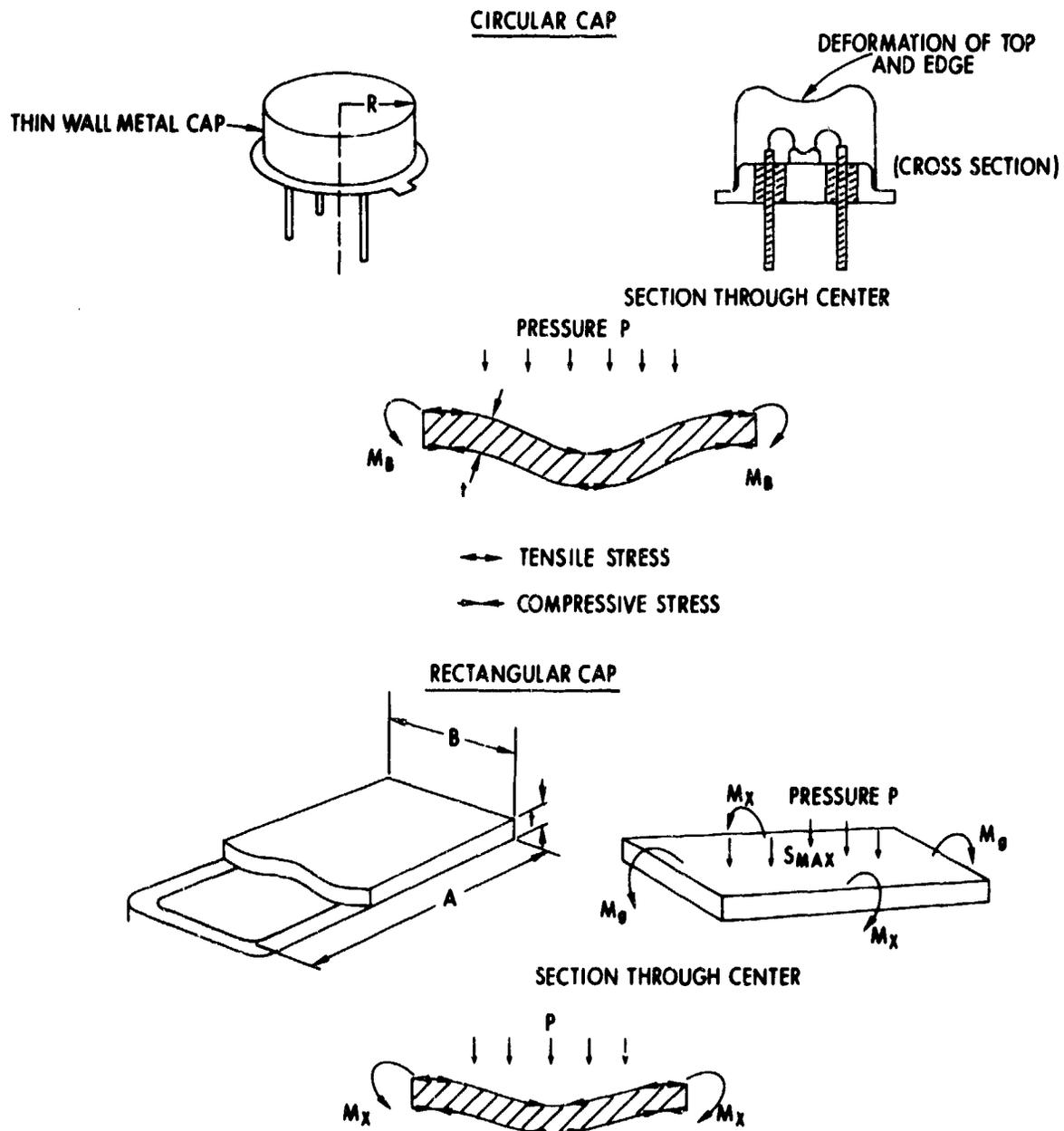


Figure 4
Models for Circular and Rectangular Cap Stress Analysis

In the case of a circular disk which is constrained at the edges (rigid side walls), it can be assumed that the maximum stress that is developed is in the radial direction at the maximum radial distance (r), with the upper surface in tension and the lower surface in compression. This maximum stress in the radial direction ((S_r) maximum) is related to the material thickness (t) and the pressure (P) as follows:*

$$(S_r)_{\max} = 0.750 \left(\frac{r}{t} \right)^2 P . \quad (1)$$

In the case of the rectangular cap constrained at the edges, the maximum stress (S_{max}) is developed at the center of the long edges and is given by:**

$$S_{\max} = \beta \left(\frac{b}{t} \right)^2 P , \quad (2)$$

where the factor (β) in equation (2) depends upon the length-to-width ratio (a/b) of the rectangular surface (for a/b = 1.0, β = 0.3078, and, as a/b approaches ∞, β approaches 0.500), and upon b = the width of the rectangle. Referring to figure 4, M_x is the bending moment developed at the edges about an axis parallel to the long dimension (a), and M_y is the bending moment developed at the edges about an axis parallel to the short dimension (b). Using the simple formulas and the relation between depth (h) in feet and pressure (P) in pounds per square inch for water given by:

$$h = 2.25 P , \quad (3)$$

one may obtain a rough idea of the maximum operating depth for various diameter-to-thickness ratios of disk-type package tops and rectangular top package types. Assuming that the maximum allowable stress is the yield point for the material being used for the tops, values were calculated for typical dimensions and are shown in table 1.

* See reference 9, page 217.

** See reference 9, page 227.

TABLE 1
 MAXIMUM OPERATING DEPTHS
 FOR SOME TYPICAL DEVICE PACKAGES

Circular Top Packages					
Type	R in.	t in.	Top Material	Yield Stress lb/in ²	Maximum Depth ft
TO-18	0.093	0.0095	Kovar	5×10^4	1560
TO-5	0.164	0.0140	Kovar	5×10^4	1090
TO-66	0.250	0.0195	Aluminum	2×10^4	366
TO-3	0.400	0.0205	Aluminum	2×10^4	158
TO-36	0.490	0.0250	Aluminum	2×10^4	162
Rectangular Top Packages					
Type in.	t in.	a/b in.	Top Material	Yield Stress lb/in ²	Maximum Depth ft
1/4 x 1/8	0.005	2.0	Kovar	5×10^4	500
1/4 x 1/4	0.005	1.0	Kovar	5×10^4	290
3/8 x 3/8	0.010	1.0	Kovar	5×10^4	405

Although the simple analysis indicates the main factors in the determination of pressure resistance of the top areas of flat packs and of TO cans, it does not include all of the factors which influence the strength of these members. A more thorough theoretical analysis^{1,3} is required to offer some insight into how the packages actually respond under conditions of external pressure.

The relatively thin lids used for flat-pack construction appear to be the most pressure sensitive. An analysis of typical flat-pack lids was performed.^{1,3} Table 2 gives the result of these calculations assuming kovar (metal) lids.

TABLE 2
 MAXIMUM OPERATING DEPTHS FOR SOME COMMONLY
 USED FLAT-PACK STYLES

Type in.	a in.	b in.	Lid Thickness in.	Lid Material	P _{max} lb/in ²	Maximum Depth ft
1/4 x 1/8	0.217	0.107	0.005	Kovar	218	490
1/4 x 1/4	0.180	0.180	0.0035	Kovar	63	142
1/4 x 1/4	0.180	0.180	0.005	Kovar	129	290
1/4 x 3/8	0.315	0.200	0.010	Kovar	268	604
3/8 x 3/8	0.300	0.300	0.010	Kovar	180	405

Another commonly used semiconductor device package is the DIP. This resembles the flat pack in the use of relatively thin metal lids or ceramic coatings. The ceramic material is usually fairly thick, on the order of 50 mils, above a fairly small cavity, 100 to 150 mils in width. For a typical ceramic flat pack, assuming the material is 94% Al₂O₃ with a flexural strength of 44,000 lb/in², a 2:1 length-to-width ratio ($\beta = 0.497$), material thickness 0.044 in., and material length 0.118 in., the maximum allowable pressure is, by formula (2):

$$P_{\max} = \frac{4.4 \times 10^4}{0.497} \times \left(\frac{0.044}{0.118} \right)^2 = 12,300 \text{ lb/in}^2$$

or an equivalent depth of 27,500 ft. As in the case of the flat-pack lids, the maximum stress at this pressure is developed at the edge of the cavity at the center of the long dimension.

All of the foregoing calculations have been made on idealized models. They provide an estimate of where the package type under consideration will be subjected to stresses in some part of the structure which are above the elastic limit, leading to yielding (in the case of metals) or approaching fracture (in the case of ceramics).

Experimental results of package strength under hydrostatic pressure showed no significant deviation from the calculated results. The aluminum TO-3 caps reached a sizable deflection at less than 200 lb/in² as did the aluminum caps on the TO-36 cans. For a TO-5 can, the permanent deflection starts between 600 and 700 lb/in². With a TO-66 can, the onset is at 400 to 500 lb/in², whereas a TO-18 can does not start deflecting until 1300 to 1400 lb/in² pressure is imposed.

Passive Component Housings

Passive components (resistors, capacitors, inductors, relays, etc) come in a great variety of package types. As with transistor packages, the presence of voids causes trouble at sufficiently high pressures. Resistors and capacitors in molded plastic or vitreous encapsulants will generally be able to transmit applied pressure directly to the internal materials that make up the element. Similar remarks apply to potted, open-frame chokes or transformers. Some discrete components, such as electrolytic capacitors, are housed in relatively thin-walled packages which contain voids and are therefore very susceptible to crushing under pressure. The effects of pressure on the cylindrical package commonly used for many components have been analyzed.¹³ As with TO cans, the regions of maximum stress for a given pressure are at the edges where curvature abruptly changes. This suggests that reinforcement in these regions or rounding would give improved pressure resistance.

Only a few limited experiments on passive component packages were performed to verify previous work by other investigators⁴ which has provided some basis for assessing the problems in these packages. Although extensive testing was done by Anderson, et al,⁴ they did not analyze or comment on the data. The only package types in their investigation, which correspond to cylindrical packages, were housings for electrolytic and solid tantalum capacitors. These were usually found to be grossly deformed or had ruptured end seals. This confirms our analysis which indicates that the greatest stress in the package is developed at the transition from the thin metal cylindrical case to the thick end supports.

Reinforcement or Redesign for Pressure Resistance

When devices must be kept from contact with the pressure transmission fluid and the existent housings are inadequate for the required operating depth, either reinforcement or a redesigned package must be used.

For flat-capped, TO-type cases, the largest stresses are developed at the periphery of the top where the cylindrical side joins the flat top. Rounding of this shoulder reduces the stress level. A minimum occurs when the cylinder makes a smooth transition to a hemispherical dome. Similar stress level reductions could be expected for gradual transitions on rectangular cross-section packages.

Another reinforcement method is to increase the thickness of the material used for the cap. For the curved surfaces, the stress is inversely proportional to the thickness. For flat surfaces, the stress is inversely proportional to the square of the thickness, assuming that in both cases the added material has the same elastic properties as the original material. When the

added material has different elastic properties, a more detailed look must be taken at the relation of stress to applied pressure for a given composite structure.

Experiments were conducted to find a material that would strengthen the housings of semiconductor devices. Several waxes were tried, but all failed to add any strength to the housing. Various epoxies were used to coat TO-5 cans. Due to the epoxy having a tendency to run off the side of the can, it was difficult to obtain a uniform coat. The method of failure in all cases was a collapse of the metal can on the top side. The epoxy on the top adhered strongly during the failure, pulling a plug from the top part of the epoxy shell, indicating a shear failure of this material.

The results of the experiments and analysis for flat-top, TO-type cases of kovar, flat-top kovar with 50-mil epoxy added and hemispherical dome kovar, appear in figure 5.

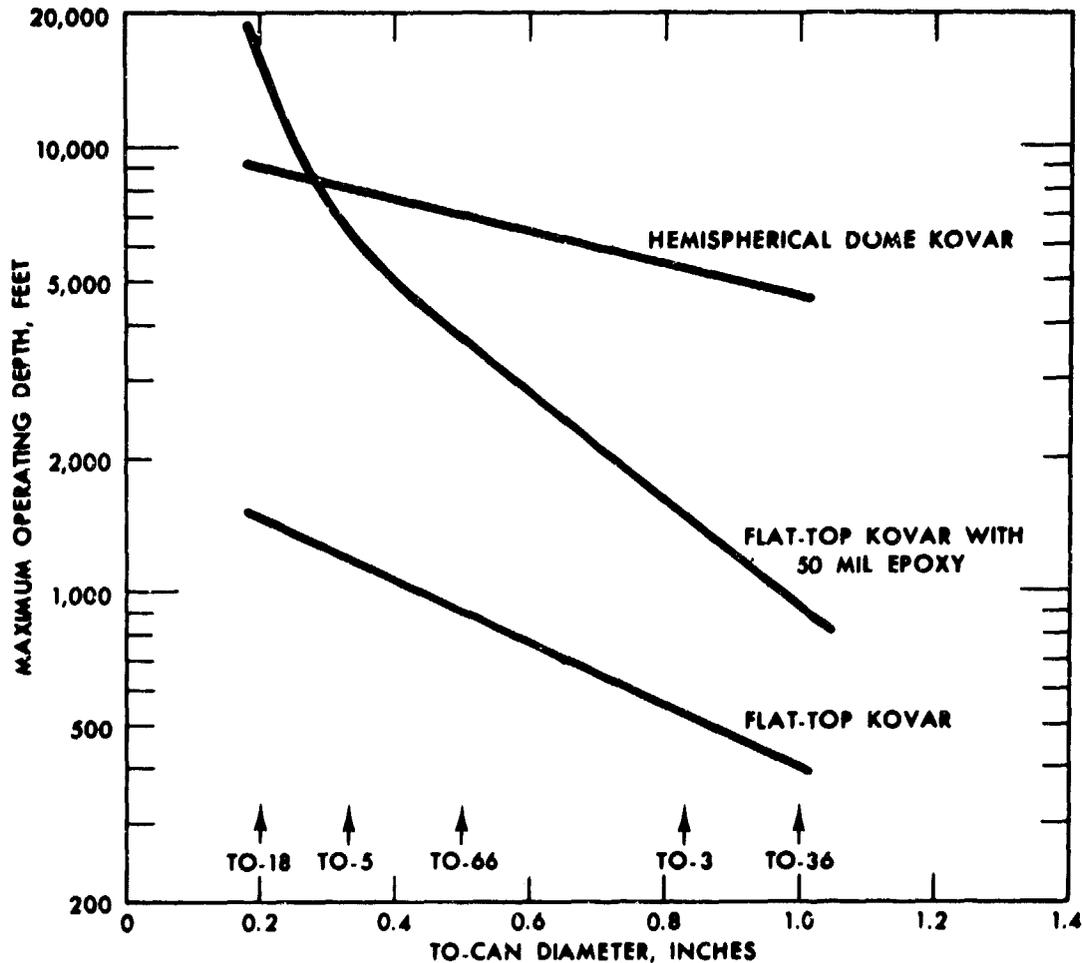


Figure 5 - TO Can Depth Capability

Conclusions

Both cylindrical and rectangular metal housings are very vulnerable to deformation above several hundred pounds per square inch. Wherever possible, these should be replaced by conformal encapsulants (void free) or filled with an inert liquid to allow pressure compensation.

The reinforcement of some semiconductor device packages offers a method of qualifying some devices for operation to moderate depths. The increase in package strength depends upon the thickness and the mechanical properties of the reinforcing material. The possibility of achieving a 4- to 5-fold increase in strength has been demonstrated with epoxy. Reinforcement by metallic materials could drastically improve the operating depths.

It should be pointed out that the use of such reinforcement drastically alters the heat transfer properties of the package. Only those devices which are limited heat dissipators are likely to be alterable by plastic reinforcement.

INFLUENCE OF OIL/PRESSURE ENVIRONMENT ON DEVICE OPERATING PARAMETERS

Preface

In most cases, it is not desirable to modify a component package sufficiently to achieve the desired pressure resistance. This may be due to economic or to operational factors, such as heat transfer limitations. An alternative is to open the package to allow free flooding by a pressure-transmitting dielectric oil. This necessitates consideration of the dielectric oil and introduces two environmental problems which may affect device operation. First, there is the effect of pressure, and second, there is the effect of possible ionic contamination. This section deals with the effect of pressure on device operation. The problem of ionic contamination will be considered in the next section, entitled "Contamination Effects on Exposed Semiconductor Devices."

Dielectric Oil Selection

The desire to traverse the ocean depths has created new requirements for pressure-compensating dielectric oils. The hostility of the environment and the sophistication of the equipment have placed new demands on oils. The oils will have to withstand exposure to ambient temperatures ranging from -2° to 150° C, cycling pressures to $15,000$ lb/in², and a chemically corrosive environment. The oil will be expected to shield solid-state components from the environment and prevent electronic failures due to energy transfer and contamination.

In order to select the best oil, it was necessary to establish a rationale. First, to achieve positive buoyancy for the systems, only those oils whose specific gravity was less than unity were considered. Second, the requirements of such an oil, relative to the environment, were grouped in three categories; namely, chemical, dielectric, and physical. The choice was then based on achieving superior qualifications in all three categories. No one oil possessed the optimum properties in all three categories, but, after careful examination of these properties,⁵ it was concluded that the silicone oil VV-D-001078 was superior.

Exposed Semiconductor Devices

The effect of pressure on the bulk resistivity of silicon and germanium has been examined.¹⁴⁻¹⁶ It was determined that the change in resistivity of the material, due to pressure, depends on the conductivity type, doping level, and doping material. This previous work enables the calculations of the change in resistivity which can be expected for a high hydrostatic pressure of 15,000 lb/in². The change ranges from 0.2% to 0.6% for silicon and from 1.0% to 2.0% for germanium.¹³ This change is negligible in terms of its effect on device operations.

Wortman, et al, have examined the effect of both uniaxial and hydrostatic stress on silicon and germanium p-n junctions.¹⁷⁻¹⁹ It was found that stress levels of 15,000 lb/in² can produce a significant increase in p-n junction current if applied as a uniaxial stress, i.e., along a single axis in the crystal structure. However, these theoretical analyses indicate that a hydrostatic stress of 15,000 lb/in² will cause only a negligible change in p-n junction current.

Representative semiconductor devices of various types, which might be used in a variety of circuit designs, were selected for experiments designed to test these theoretical predictions. All of the devices tested were obtained from commercial suppliers in standard TO-type metal housings. The protective metal TO housings were removed, leaving the devices still mounted on the headers and still connected by the original lead wires from the device bonding pads to the terminal post of the headers. This allowed the devices to be exposed to the laboratory atmosphere and to a hydrostatic pressure when immersed in a hydraulic fluid in a pressure chamber. The pressure effects tests were carried out in a chamber supplied with electrical feedthroughs and

capable of operation at 30,000 lb/in². A 10-cSt silicone-base oil, Federal Specification product VV-D-001078, was used as the hydraulic fluid.

The electrical parameters of the devices were monitored (1) as received with the cap intact, (2) in laboratory atmosphere after opening, and (3) during immersion operation in silicone oil at pressures ranging from atmospheric to 15,000 lb/in². For the transistors, the parameters monitored were the output characteristics (I-V curves) displayed on a Tektronix type 575 curve tracer. For the operational amplifiers, the pulse responses at unity gain, noise voltage, and offset voltage were monitored. These tests were short term. Most were carried out in 1 day.

The results of these tests are shown in table 3. All of the germanium transistors not protected by an oxide or any other passivating covering changed characteristics immediately upon exposure to the laboratory atmosphere and did not recover when immersed in the oil. Under pressure, both germanium alloy power transistors, types 2N1412 and 2N1553, exhibited abrupt irreversible increases in the slopes of the I-V curves (apparent decrease in output impedance). This was not an isolated case; other type 2N1412 germanium alloy transistors tested reacted in a similar manner. In addition, the germanium alloy transistor, type 2N1553, showed evidence of fracture upon completion of the test. Whether this was a latent defect exposed by the pressurization is not known.

Characteristic changes observed in the germanium alloy, type 2N526 transistor, not protected with a passivating covering, occurred on exposure to the laboratory atmosphere. Under pressure, the 2N526 did not indicate the abrupt increase in the slopes of the I-V curves that had been observed with the 2N1412 and 2N1553. It is therefore possible that the changes observed for the 2N526 were due to the lack of passivation as opposed to a pressure effect. As a test of this possibility, one decapped 2N526 was covered with Dow Corning RTV 3144 silicone rubber and found to operate satisfactorily to 15,000 lb/in². This would indicate that the changes observed for the 2N526 may be a result of atmospheric contamination as opposed to a pressure effect. It should be noted, as compared to the 2N1412 and 2N1553 which are high-power devices, the 2N526, a low-power device, is physically much smaller and is supplied by a different manufacturer whose manufacturing techniques may differ.

None of the exposed, passivated, silicon devices was affected by exposure to laboratory atmosphere or to immersion in silicone oil pressurized to 15,000 lb/in².

TABLE 3
EFFECT OF OIL/PRESSURE ON EXPOSED SEMICONDUCTOR DEVICES

Type	Description	Behavior Upon Exposure to Laboratory Atmosphere	Behavior During Pressure Tests in 10-cSt Silicone Oil
2N1412	Germanium alloy pnp 150 watts at 25° C.	Large increase in I_B , I_C versus V_{CE} curves increase slope. Very sensitive to ambient water vapor.	Initial short-term improvement at 1 atm as indicated by an increase in spacing between the I-V curves (increased current gain). Pressure at 6,000 lb/in ² resulted in abrupt increase in slopes of I-V curves (apparent decrease in out- put impedance). Changes were permanent and not reversible at 1 atm.
2N1553	Germanium alloy pnp 106 watts at 25° C.	Same as above.	Same as above plus some evidence of mechanical damage.
2N526	Germanium alloy pnp small signal amplifier and switch.	Same as above	Initial short-term response change at 1 atm as indicated by an increase in spacing between I-V curves (increased current gain) and a rapid increase in current (decreased breakdown voltage level). Pressure to 12,000 lb/in ² did not produce the abrupt change in output impedance noted for the two previous germanium devices.
2N526	Germanium alloy pnp small signal amplifier and switch (modified with a covering of Dow Corning RTV 3144 silicone rubber).	No change.	Operated satisfactorily to 15,000 lb/in ² .
2N3740	Silicon planar pnp 25 watts at 25° C.	No change. Device chip covered with polymeric coating by manufacturer.	Slight reduction in spacings between I-V curves (reduction in current gain) upon immersion at 1 atm, apparently due to better cooling. No change to 15,000 lb/in ² .
2N4232	Silicon planar npn 35 watts at 25° C.	Same as above.	Same as above.
2N2107A	Silicon planar bipolar pnp, small signal ampli- fier and switch.	No change.	Same as above.
2N2222A	Silicon planar bipolar nnp, small signal amplifier.	No change.	Same as above.
2N3736	Silicon planar MOSFET, N channel, small signal amplifier.	No change.	No change to at least 15,000 lb/in ² .
M163	Silicon planar MOSFET, P channel, small signal amplifier.	No change.	Same as above.
5B7741393	Silicon planar IC oper- ational amplifier with internal frequency compensation.	No change.	Offset voltage constant to at least 15,000 lb/in ² .
SG777GT	Silicon planar IC oper- ational amplifier, needs external frequency compensation.	No change.	Pulse response and noise voltage in unity gain mode not affected by pressure to 15,000 lb/in ² .

Encapsulated Semiconductor Devices

As indicated in the preceding section, entitled "Effects of Pressure on Device Housings," TO and metal-lidded DIP's cannot be operated below a few hundred feet. However, two other commonly used type housings, the ceramic DIP flat pack and the plastic DIP flat pack, may have sufficient pressure resistance for operation at 15,000 lb/in².

The physical characteristics of the ceramic and plastic DIP's have been discussed by Licari.¹¹ As in the case of the TO can-type package, the ceramic DIP has a void inside the package which makes it susceptible to damage by sufficiently high external pressure. However, the ceramic material is quite thick and the void fairly small. The plastic DIP allows intimate contact of the plastic material with the semiconductor chip. Therefore, forces developed on the outside of the plastic package are transmitted directly through the plastic to the semiconductor chip.

Two representative semiconductor devices, an operational amplifier housed in a ceramic DIP and a digital circuit housed in a plastic DIP, were selected for test. The devices were immersed in a 10-cSt silicone oil, specification VV-D-001078, and subjected to pressure ranging from atmospheric to 15,000 lb/in². For the operational amplifier, the parameters monitored were the pulse response at unity gain, noise voltage, and offset voltage. For the digital circuit, the minimum voltage required for switching was monitored. These were short-term tests, usually carried out within 1 day.

The results of these tests are shown in table 4. Both devices operated satisfactorily, indicating that they were not affected by the oil/pressure environment.

Passive Components

Passive components were not tested under this program because past work has yielded a fair amount of data on such components. A most comprehensive passive component pressure testing report was by Anderson, et al.⁴ The results of the tests are summarized in the Introduction under "Past Work." A theoretical analysis^{5,13} provides some insight into the cause of the parameter variations observed by Anderson, et al.⁴

When component housings would crush at pressure well below those desired for operation, the housing must be pressure compensated. Two types of problems can result - changes in operation due to the presence of an oil of higher dielectric constant, i.e., oil rather than air, and changes due to contamination. Except for the air dielectric variable capacitor, the presence of a higher dielectric oil will probably not significantly change the electrical operating characteristics of the immersed circuits. Contamination, however, must be carefully considered.

TABLE 4
EFFECT OF OIL/PRESSURE ON
ENCAPSULATED SEMICONDUCTOR DEVICES

Type	Manufacturer	Description	Behavior During Pressure Tests in 10-cSt Silicone Oil
μ6A7777393	Fairchild	Silicon planar IC operational amplifier in ceramic DIP, needs external frequency compensation.	Pulse response and noise voltage in unity gain mode not affected by pressure to 15,000 lb/in ² .
SN7473N	Texas Instruments	Silicon planar IC TTL-dual J-K flip-flop in plastic DIP.	At constant clock pulse amplitude (3.0 volts), the minimum voltage for firing on J-K inputs decreased slightly with pressure to 15,000 lb/in ² . This was not significant.

Paper capacitors are constructed with an impregnating oil in the paper spacing between the metal foil electrodes. The impregnant may be a wax, oil, or synthetic material, such as chlorinated naphthalene or chlorinated diphenyl. If the case has an aperture to allow free passage of the pressure transmission oil, the effect of long-term contact of the oil with the capacitor impregnant must be known in order to assess the possibility of deleterious reactions or the generation of contaminants which could be transported to contamination-sensitive components. A similar consideration applies to aluminum foil electrolytic capacitors, which use an aqueous solution of ammonium borate, boric acid, glycol, or similar electrolytic solutions.

Other types of electrolytic capacitors, the wet and solid electrolytic-type tantalum capacitors, are extensively used in circuit construction. The "wet" types use sulfuric acid or aqueous lithium chloride as the electrolyte because of the high conductivity required to reduce series resistance. The miniature-type tantalum-pellet capacitor is inherently pressure compensated if the electrolyte completely fills the interior of the case. The dual cell type could possibly be compensated by having its outer case punctured to allow oil to fill the voids around the interior capacitor cells, assuming that these are filled completely by liquid electrolyte. The solid electrolyte (MnO₂)

tantalum capacitor would require an interior liquid fill for pressure compensation. However, the liquid would have to be inert to the electrolyte, since the presence of any polar liquid contaminant could change the value of capacitance if transported through the oil and accumulated at the capacitor.

Experimental work on the effects of water, methanol, and isopropyl alcohol on MnO₂ solid electrolyte capacitors has shown that these polar liquids can cause an increase of capacitance and of I_g.²⁶ In this experiment, the capacitors were uncased and immersed in the liquids. However, exposure to room air over a period of 30 minutes at 50% relative humidity gave an increase in capacitance of about 6%. These shifts may be due to water vapor in the oil.

Immersed operation of transformers and chokes in oil should introduce no problems provided that the insulation materials are not soluble or softened to the point where turns could be shorted under pressure.

Safeguards

Past analyses and present experimental observations of exposed, passivated silicon devices indicate that parameter variations caused by exposure to laboratory atmosphere and an oil/pressure (15,000 lb/in²) environment have been negligible. However, for the exposed, unpassivated germanium devices, parameter variations observed upon exposure to laboratory atmosphere were excessive. In addition, the two high-power, unpassivated germanium devices tested were sensitive to pressure and therefore not usable in an oil/pressure environment. As for the one low-power germanium device that was modified by the application of passivation material but functioned satisfactorily, no generic conclusions can be reached.

The use of germanium devices in pressure-tolerant systems should be avoided by the substitution of silicon planar passivated types. This can be done in most cases as the much higher general usage of silicon devices implies. Where substitution of a silicon device is not possible, the germanium device to be used must be evaluated prior to application.

Past analyses and experimental observations of unencapsulated passive components indicate that most of these devices can function in an oil/pressure (15,000 lb/in²) environment. In those cases where pressure, per se, did result in excessive operating parameter variations, the cause was attributed to components with appreciable void content. Other components having an aperture which will allow passage of the dielectric oil must be evaluated as to the long-term effects resulting from such exposure.

The most pressure-sensitive materials were the composition resistors, ferrites, and powdered cores. Wherever possible, these materials/components should be excluded from use in pressure-tolerant systems. If such use cannot be avoided, these materials/components must either be pressure housed or their parameter variations known and compensated for. Wet electrolytic capacitors, which have been known to crush at well below 15,000 lb/in², could be pressure compensated if the electrolyte completely fills the interior of the case.

Conclusions

Experimental results obtained for the exposed, passivated, planar silicon devices confirm the theoretical analyses presented in previous works.¹⁴⁻¹⁸ Pressure to 15,000 lb/in² does not interfere with the operating characteristics of these devices. In addition, exposure to laboratory atmosphere and silicone oil did not affect their operation. Although not tested, visual inspection indicates that damage may occur to nonplanar structures due to material mismatches and construction techniques for these devices. This should not present a problem to circuit designers, since the overwhelming majority of devices utilize planar structures.

All of the germanium alloy devices showed a substantial variation in their operating characteristics when exposed to laboratory atmosphere. In addition, pressure to 6000 lb/in² produced an abrupt increase in the slopes of the I-V curves of the 2N1412 and 2N1553 power devices. In general, the pressure sensitivity is attributed to material compressibility mismatches.

On the basis of experiments conducted on germanium alloy devices, design of circuits for deep ocean applications should exclude their use unless prior qualification tests are conducted. This does not produce any major hardship on the circuit designers, since the overwhelming majority of devices used in present-day design are silicon.

The experimental data⁴ and theoretical analyses^{5,13} of the pressure effects on passive component operation indicate that many materials used for passive component construction exhibit little change in parameter values with pressure to 15,000 lb/in². This includes the materials used in wire-wound resistors, film resistors, capacitor dielectric materials (except air), and certain laminated ferroelectric cores for inductors and transformers. The use of molded or vitreous encapsulants without voids, which are capable of transmitting stress directly to the internals, should provide devices which will not fail due to pressure. Fabrication materials with appreciable void content are likely to exhibit large changes in parameter values with increasing applied pressure. These include: composition resistor material, tapes, ferrite, and powdered cores. This group of materials must either be protected from stress or their change in parameter values must be known and compensated for in some manner if they are to be used.

CONTAMINATION EFFECTS ON EXPOSED SEMICONDUCTOR DEVICES

Preface

It has been long known that ambient conditions have a marked effect on semiconductor device performance. Theoretical and practical studies were made of the effects of various ambient conditions on semiconductor device reliability.²¹ Both oxygen gas and water vapor were found to have considerable effect on the reverse saturation current, junction breakdown voltage, and the current gain of both npn and pnp alloy junction germanium devices. The changes in operational parameters could result from ion accumulation at the semiconductor device surface due to environmental contamination. It is possible, with sufficient positive charge on the surface, to accumulate a large concentration of electrons in the germanium just underneath the surface. When this happens, we call it an inversion layer; in other words, an accumulation of carriers of the same type as the doping of the bulk germanium. On the other hand, if sufficient negative charge accumulates adjacent to the semiconductor surface, the conductivity type may be changed from n to p type, in which case the surface of a semiconductor may influence the electronic properties of the semiconductor surface. Charge of like sign as the majority carriers in the semiconductor will tend to repel these carriers and attract minority carriers. Charge of opposite sign to that of the majority carriers will tend to cause an accumulation of majority carriers near the surface.

Sensitivity to ambient conditions of germanium devices is understandable, since under normal conditions of surface preparation, these devices have only a thin layer, 10 to 50 Å, of native oxide covering the bulk germanium. This thin insulating layer allows ionic charges, which accumulate on the outer surface of the oxide, to exert strong electrostatic attraction on free charge carriers in the bulk material. With the advent of silicon planar, diffused device technology, the possibility of using relatively thick layers of SiO₂, an amorphous, high quality insulator, became apparent. These could be grown on the device surface in an oxidizing atmosphere at temperatures near 1000° C during the diffusion process. The ability of these "thermal" SiO₂ layers to provide stable operating characteristics for silicon devices was reported by Atalla, *et al.*²² A range of thicknesses from thin (150 to 300 Å) to thick (4000 Å) was used. With surfaces protected in this manner, the silicon devices were found to exhibit stable characteristics, at least on a short-term basis, when exposed to a variety of different ambient conditions, such as wet nitrogen gas, wet oxygen gas, dry nitrogen, dry oxygen, ammonia, and ozone. A subsequent report by Atalla, *et al.*,²³ clarified the conditions under which stability could be expected. The thermal silica provided very stable characteristics in a wet atmosphere (gaseous ambient with water vapor present) for junctions without electrical bias or with forward bias. However, reverse-biased junctions caused the current to increase over a period of a few hours until it reached

a saturation value determined by the relative humidity, applied voltage, and oxide thickness. The investigations proposed that the cause of this behavior was the ability of ions on the oxide surface, made mobile by the presence of water vapor, to be sorted out in the electric field fringing the junction where it intersected the surface. Removal of the high field due to the reverse bias allowed the ions to recombine. As would be expected on the basis of such a model, the thicker the oxide over the junction, the higher the reverse bias and relative humidity required to obtain a given saturation current level.

In pressure-tolerant electronic systems, immersed devices are exposed to the dielectric oil and its contaminants. The solubility of some ionic substances in these oils has been determined and evaluated in terms of semiconductor devices and appears in the next section under the subtitle "Solubility of Materials." Certain substances were found to dissolve appreciably in the oils. Some of these substances disassociated into ions and affected the electrical properties of the oils. From the measured ion mobilities, calculations indicated that:

- Appreciable concentrations of ions will accumulate within hours at device surfaces and invert certain device surfaces in pressure-tolerant electronic systems.

- Galvanic corrosion is negligible.

- Electrolytic plating and deplating is negligible for the normal voltages applied.

The question of greatest interest is whether or not the presence of ions in a given concentration in the bulk of the dielectric oil will lead to an accumulation of ions on the surface of a semiconductor device sufficient to significantly change its manner of operation. A measure of this effect is the ability of the accumulated charge to change the conductivity type (inversion) of the semiconductor surface adjacent to the oil.

Exposed Semiconductor Devices in Pure and Contaminated Oils

To ascertain the magnitude and limits of an ion-induced failure mechanism, such as inversion, the I_{CBO} was monitored while exposed devices were operated in pure and contaminated oils. I_{CBO} is the current that flows through the collector-base junction when reverse biased and the emitter junction is open circuited. Monitoring these characteristics can provide a convenient and sensitive instrument for determining and evaluating the presence of ionic species at the surface of a device.²⁴ This technique lends itself to evaluating the deleterious effect of oil-soluble ions present in an oil that envelops semiconductor devices.

Three silicone oil baths were prepared. The silicone oil used was a 5-cSt, Federal specification product VV-D-001078, whose chemical composition, dielectric properties, etc were analyzed and appear in the next section under the subtitle "Solubility of Materials." The first bath consisted of just the oil as received from the manufacturer, the second bath was saturated with chemically pure sodium chloride (0.15 $\mu\text{g/g}$ of oil), and the third bath was saturated with hydrochloric acid (0.78 mg/g of oil). The containers of the three baths were then immersed (close to their respective rims) in a petroleum-base oil whose temperature was maintained at $48.61^\circ \pm 0.25^\circ \text{C}$.

Three types of semiconductor devices packaged in TO cans were selected for evaluation in the oils; namely, 2N1412 (pnp germanium medium-power alloy), 2N3740 (pnp silicon medium-power planar), and 2N4913 (nnp silicon medium-power planar). The 2N1412 type was chosen because, once the kovar cover was removed, an unprotected junction with no oxide or organic coating would be exposed to the oil. The 2N3740- and 2N4913-type devices were selected to evaluate the ionic effects on a protected junction. The collector-base junction of both of these devices was formed similarly in an epibase process; the emitter junction was diffused. The semiconductor junctions were covered with a silicon dioxide layer. A coating, 1-mil-thick, was placed over the silicon dioxide, consisting of a silastic for the 2N3740 and a varnish for the 2N4913.

Lead wires were connected between the transistor terminals and quick-disconnect plugs to facilitate application of operating biases or the Tektronix type 576 curve tracer for tests of whether or not any characteristics had changed.

The initial characteristics of each device were checked prior to opening the hermetically sealed housing. After the housing was removed, the device was subjected to the following conditions:

- Step 1 - The device was immersed in pure silicone oil with no bias voltage until it became temperature stabilized. Then, the I_{CBO} was measured.
- Step 2 - A reverse bias of 40 volts was applied across the collector-base junction until a steady-state condition was achieved, the steady-state attainment time being 1 to 2 weeks.
- Step 3 - The device was removed from the pure oil and immersed in silicone oil saturated with sodium chloride. The 40-volt reverse bias was maintained until a steady-state condition was reached.
- Step 4 - The 40-volt reverse bias was removed, and the device was forward biased with a voltage sufficient to current limit the collector-base current to 6 mA. This voltage was applied until a steady-state condition was attained.

● Step 5 - The 40-volt forward bias was disconnected; the device was removed from the silicone oil saturated with sodium chloride and cleaned. The device was first cleaned with electronic-grade trichloroethylene and then with electronic-grade acetone.

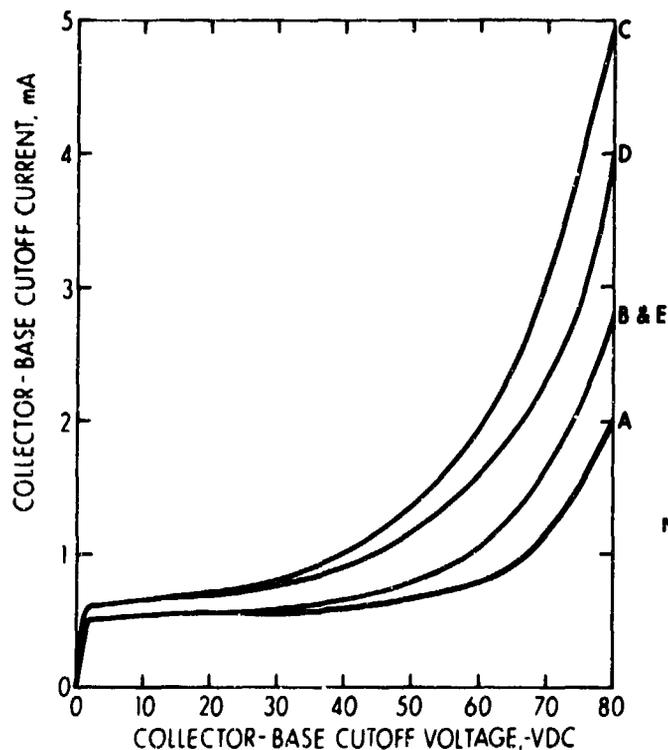
● Step 6 - The cleaned device was immersed in pure silicone oil and reverse biased until a steady-state condition existed.

● Step 7 - Steps 1 through 6 were repeated, except that in step 3, the device was immersed in hydrochloric acid saturated silicone oil.

Note: After steps 1, 2, 3, 4, and 6, each of the three devices was disconnected from its steady-state condition and connected to a Tektronic type 576 curve tracer, where its I_{CBO} was displayed and photographed with either 60- or 80-volt reverse bias applied, as indicated in figures 6, 7, and 8.

Figure 6 contains the collector-base cutoff characteristics of a decapped, germanium-type 2N1412 power transistor in pure and sodium chloride saturated silicone oil. The curves were obtained after disconnecting the transistor leads from their steady-state conditions and connecting them to the curve tracer. Referring to the steps indicated above, the display was obtained as follows:

- Curve A - result of step 1.
- Curve B - result of step 2.
- Curve C - result of step 3.
- Curve D - result of step 4.
- Curve E - result of step 6.



Curve A - In Zero Bias Circuit Immersed in Pure Oil
 Curve B - In Reverse Bias Circuit Immersed in Pure Oil
 Curve C - In Reverse Bias Circuit Immersed in Silicone Oil Saturated with Sodium Chloride
 Curve D - In Current-Limited Forward Bias Circuit Immersed in Silicone Oil Saturated with Sodium Chloride.
 Curve E - In Reverse Bias Circuit Immersed in Pure Oil After Having Been Previously Operated in Silicone Oil Saturated with Sodium Chloride and Cleaned

Note: The device was disconnected from the bias circuits to measure the cutoff currents on a curve tracer.

Figure 6
 Steady-State Collector-Base Cutoff Characteristics of a Decapped Germanium-Type 2N1412 (PNP) Power Transistor in Pure and Sodium Chloride Saturated Silicone Oils at 48.61° C

Examining figure 6, we can conclude that:

- In pure oil (curve A), the I_0 drifts to a steady-state value (curve B).
- In the oil contaminated with sodium chloride, the I_0 increases from its pure-oil value (curve B) and attains a new steady-state value (curve C).
- Forward biasing the collector-base junction (curve D) does not completely restore the I_0 to its pure-oil, steady-state value (curve B).
- Cleaning the contaminated device surface restores the I_0 to its steady-state value in pure oil (curve E).

Restoration of the I_0 to its pure-oil, steady-state value is significant. It indicates that the ions do not diffuse into the unprotected junction material but rather form a surface leakage path, thereby increasing the value of the I_0 . The fact that forward biasing the junction did not completely restore the I_0 to its pure-oil, steady-state value is interpreted to indicate that van der Waals forces, in addition to the electric field flux near the device surface, are retaining ions near the surface.

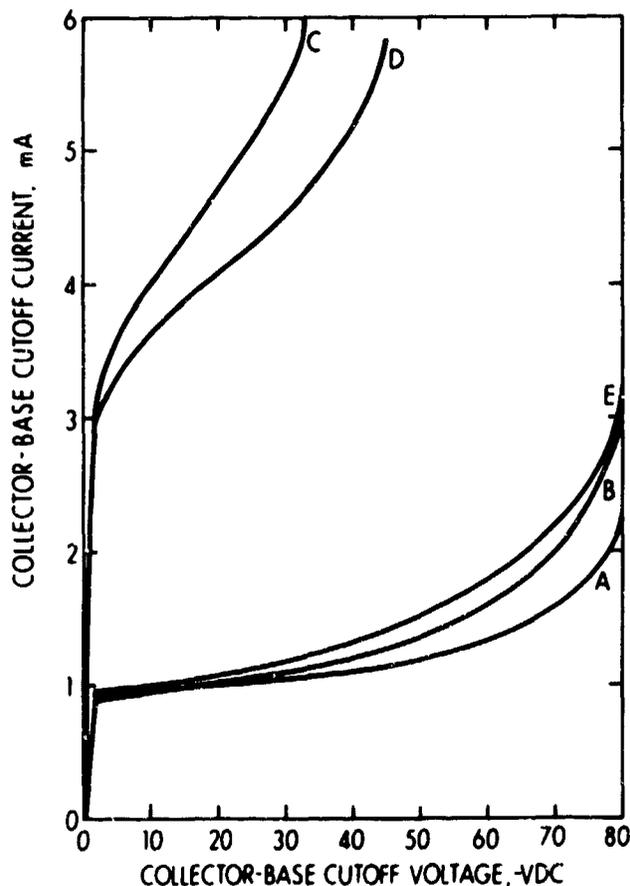
Figure 7 contains the collector-base cutoff characteristics of a decapped, germanium-type 2N1412 power transistor in pure and hydrochloric acid saturated silicone oil. The curves were obtained, as before, after disconnecting the transistor leads from the steady-state conditions and connecting them to the curve tracer. Referring to the steps indicated previously, the display was obtained as follows:

- Curve A - result of step 1.
- Curve B - result of step 2.
- Curve C - result of step 3.
- Curve D - result of step 4.
- Curve E - result of step 6.

The behavior of the I_0 of the device immersed in oil saturated with hydrochloric acid is analogous to that of the device immersed in oil saturated with sodium chloride. We conclude that:

- In pure oil (curve A), the I_0 drifts to a steady-state value (curve B).
- In oil saturated with hydrochloric acid, the I_0 increases from its pure-oil value (curve B) and attains a steady-state value (curve C).
- Forward biasing the collector-base junction (curve D) does not restore the I_0 to its steady-state value (curve B) in pure oil.
- Cleaning the device surface returns the I_0 to a value (curve E) close to its steady-state condition (curve B) in pure oil.

Near restoration of the I_0 to its pure-oil, steady-state value by cleaning the device surface is interpreted to indicate that the ions do not appreciably diffuse into the unprotected junction material but rather form a surface leakage path, thereby increasing the value of the I_0 . The fact that forward biasing the junction, when compared with cleaning, had little effect on restoring the I_0 to its pure-oil, steady-state value is interpreted to indicate that the van der Waals forces at the surface are stronger than the corresponding electric field flux.



- Curve A - In Zero Bias Circuit Immersed in Pure Oil
- Curve B - In Reverse Bias Circuit Immersed in Pure Oil
- Curve C - In Reverse Bias Circuit Immersed in Silicone Oil Saturated with Hydrochloric Acid
- Curve D - In Current-Limited Forward Bias Circuit Immersed in Silicone Oil Saturated with Hydrochloric Acid
- Curve E - In Reverse Bias Circuit Immersed in Pure Oil After Having Been Previously Operated in Silicone Oil Saturated with Hydrochloric Acid and Cleaned

Note: The device was disconnected from the bias circuits to measure the cutoff currents on a curve tracer.

Figure 7 - Steady-State Collector-Base Cutoff Characteristics of a Decapped Germanium-Type 2N1412 (PNP) Power Transistor in Pure and Hydrochloric Acid Saturated Silicone Oils at 48.86° C

Figure 8 contains the collector-base cutoff characteristics of decapped, silicone-type 2N3740 and 2N4913 power transistors in pure silicone oil, silicone oil saturated with sodium chloride, and in silicone oil saturated with hydrochloric acid. The curves were obtained, as before, after disconnecting the transistor leads from their steady-state condition and connecting them to the curve tracer. Referring, once again, to the steps outlined previously, the display was obtained as follows:

● Curve A

• For 2N3740 (pnp) and 2N4913 (nnp) in pure silicone oil, result of steps 1 and 2.

• For 2N3740 (pnp) and 2N4913 (nnp) in sodium chloride saturated silicone oil, result of step 3.

• For 2N4913 (nnp) in hydrochloric acid saturated silicone oil, result of step 3.

• For 2N3740 (pnp) in hydrochloric acid saturated silicone oil, result of step 6.

● Curve B - for 2N3740 (pnp) in hydrochloric acid saturated silicone oil, result of steps 3 and 4.

Note: Since no change was observed for the 2N3740 and 2N4913 in sodium chloride saturated silicone oil (step 3), steps 4 and 6 were not required. Since no change was observed for the 2N4913 in hydrochloric acid saturated silicone oil (step 3), steps 4 and 6 were not required.

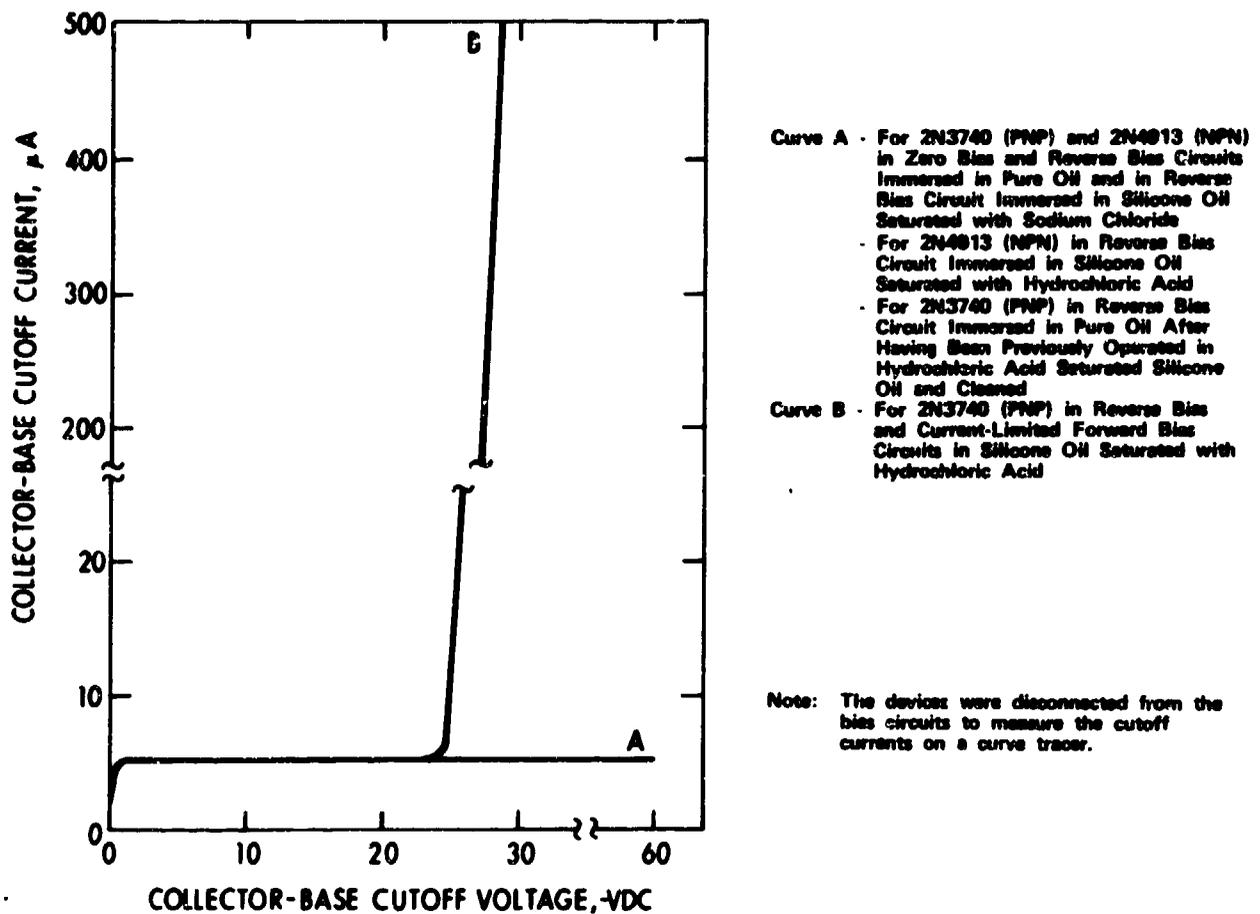


Figure 8
 Steady-State Collector-Base Cutoff
 Characteristics of Decapped Silicon Types
 2N3740 (PNP) and 2N4913 (NPN)
 Power Transistors in Pure and Contaminated
 Silicone Oils at 48.36° C

It is significant to note that, once again, cleaning the device surface restores the I_0 to its pure-oil value. It is not surprising that the contaminant-induced changes in the cutoff characteristics of these silicon devices differ from those of the germanium device, because the collector-base junctions of the silicon devices were passivated with an oxide layer and an organic coating, but it is surprising that the changes in the cutoff characteristics of the two types of silicon devices differ. The difference in the changes in the cutoff characteristics of the silicon devices is attributed to the different collector doping materials. The collector region of the 2N3740-type device

was doped with boron to form a p region; in contrast, the collector region of the 2N4913-type device was doped with phosphorous to form an n region. It is known that, when silicon dioxide is grown over the collector, boron diffuses into the oxide layer, thus depleting the surface of the p region and contaminating the oxide layer with positive charges. It is known also that phosphorous atoms in the n region attract charges and thus deplete the oxide layer over the collector of any charges.

As mentioned earlier, the two types of silicon devices were passivated with different coatings, one coating a varnish and the other a silicone resin. Since both of these junction coatings are the same thickness, it is believed that this difference is not contributing to the different characteristics between the two types of silicon devices.

In figure 9, the changes in the cutoff characteristics of the decapped, 2N1412-type power transistors shown in figures 6 and 7 are plotted as functions of voltage. The changes are the differences between the steady-state I_{CBO} of the transistor in the reverse-bias circuit and its initial I_0 . These changes are plotted for operation in pure silicone oil (curve A), silicone oil saturated with sodium chloride (curve B), and silicone oil saturated with hydrochloric acid (curve C). These curves illustrate that the changes in the I_0 depend on the concentration of ionic species, the concentration decreasing from curve C to A.

The device characteristics expounded on were reproducible in all cases. This indicates that similar behavior can be anticipated in pressure-tolerant systems. Due to the variations inherent in device manufacturing, the exact dependence of current on voltage is not reproducible, as seen by comparing curve A in figure 6 with curve A in figure 7. It can also be seen that the shapes of the two curves are similar. The forthcoming conclusions assume that the reproducibility is limited to the shapes of the device cutoff curves.

Curve A - In Pure Silicone Oil
 Curve B - In Silicone Oil Saturated with Sodium Chloride
 Curve C - In Silicone Oil Saturated with Hydrochloric Acid

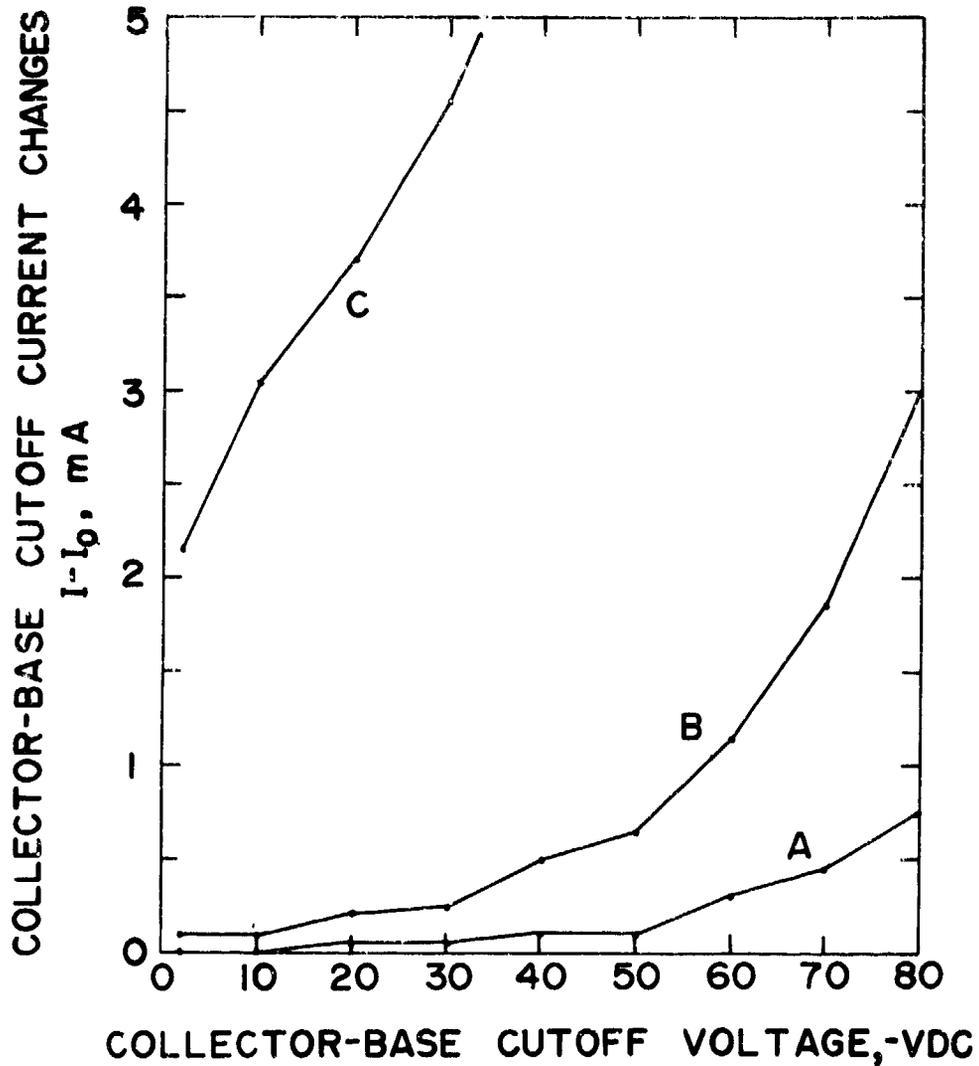


Figure 9 - Changes in the Steady-State Cutoff Current Characteristics of a Decapped Germanium-Type 2N1412 (PNP) Power Transistor in the Reverse Bias Circuit and Its Initial Cutoff Current Plotted as a Function of Collector-Base Voltage

Safeguards

In general, it has been shown that passivated silicon devices are impervious to the oil and that contamination effects are minimal. However, in considering the system, including complete circuits and hardware which may use electrolytic capacitors and batteries that might leak caustic substances into the oil, design safeguards should be considered.

In systems where electrolytic capacitors and/or batteries are used, techniques such as encapsulation or compartmentalization of the devices leaking harmful contaminants could minimize or eliminate their effect on the rest of the circuits. However, precluding their use through substitution of other less harmful devices would be the most sensible first consideration.

Conclusions

In those ocean engineering applications, such as pressure-tolerant electronic systems, wherein semiconductor devices are exposed to dielectric oils containing dissolved ionic species, the induced electric field drift of the species and their resulting accumulation near the surface of semiconductor materials present a possible failure mechanism for certain types of devices. The magnitude and limits of such an ion-induced failure mechanism were ascertained by utilizing the I_{CBO} characteristic of transistors. This technique yielded the following conclusions:

- The change in the I_{CBO} of unpassivated germanium pnp semiconductor junctions increases with the concentration of dissolved ionic species.

- For the silicon devices, the changes in the I_0 of passivated semiconductor junctions depend on the collector doping. For p-type collector regions, the I_0 increases only when the device is operated in oil contaminated with a substantial concentration of ionic species; while for the n-type collector regions, the I_0 is unaffected by operation in oil contaminated with a substantial concentration of ionic species.

- Cleaning the device surface restores the I_0 to its pure-oil, steady-state value.

It can also be inferred that present-day passivation techniques for silicon devices are sufficient to prevent normally encountered contaminants (water vapor and sodium chloride) from interfering with device operation.

PRESSURE-TOLERANT ELECTRONIC/ELECTRICAL SYSTEMS

Preface

Most of the pressure-tolerant electronics developments to date have been the result of efforts to satisfy particular needs in the DOT and related programs. What has evolved from these efforts is both a basic concept and concrete results in terms of devices and hardware. The basic concept is that of the assembly of devices in more or less conventional design and construction, with slight modification in some instances, into equipment that is immersed in an inert dielectric liquid that transmits the ocean hydrostatic pressure directly to the devices. The liquid and equipment are housed so as to provide protection from ocean contaminants, mechanical support, thermal coupling, and acoustic and vibration isolation. Special ports equalize pressures on both sides of the housing. For certain applications, low-density materials may be added to achieve positive buoyancy. This basic configuration is depicted in figure 10.

The utilization of electronic/electrical systems in the environment depicted in figure 10 differs substantially from their usual use in the atmosphere or in outer space. New potential sources of system-type problems are introduced, other than the possible environmental problems for individual devices discussed in the preceding sections. These potential problem areas include:

- Selection of a housing material for oil and devices which will not impede heat transfer nor react chemically in the environment.
- Consideration of the feasibility to achieve positive or neutral system buoyancy.
- The solubility of various electronic/electrical materials and hardware in the dielectric liquid and the resultant impact, if any, on the system operation.
- The environmental influence (oil and pressure) on the system's heat transfer capability.
- Reliability of outboard systems.

Housing Materials for Oil and Devices

Requirements for the housing material include high strength-to-weight ratio, good thermal conductivity, inertness to both seawater and dielectric oil, and the capability to be machined and formed. A recent study of promising metals, alloys, and synthetics revealed that a new titanium alloy (Ti-6Al-2Cb-1Ta/0.8Mo) is the first choice.⁵ Characteristics of this titanium alloy include high strength-to-weight ratio (helping to achieve positive buoyancy); good thermal conductivity; machinability;

weldability; high strength without heat treating after casting or welding; and resistance to pitting, corrosion, and biofouling in seawater when coated. A major disadvantage is its present cost and lack of availability. Therefore, other materials (e.g., certain aluminum alloys) may be considered for pressure-tolerant systems.

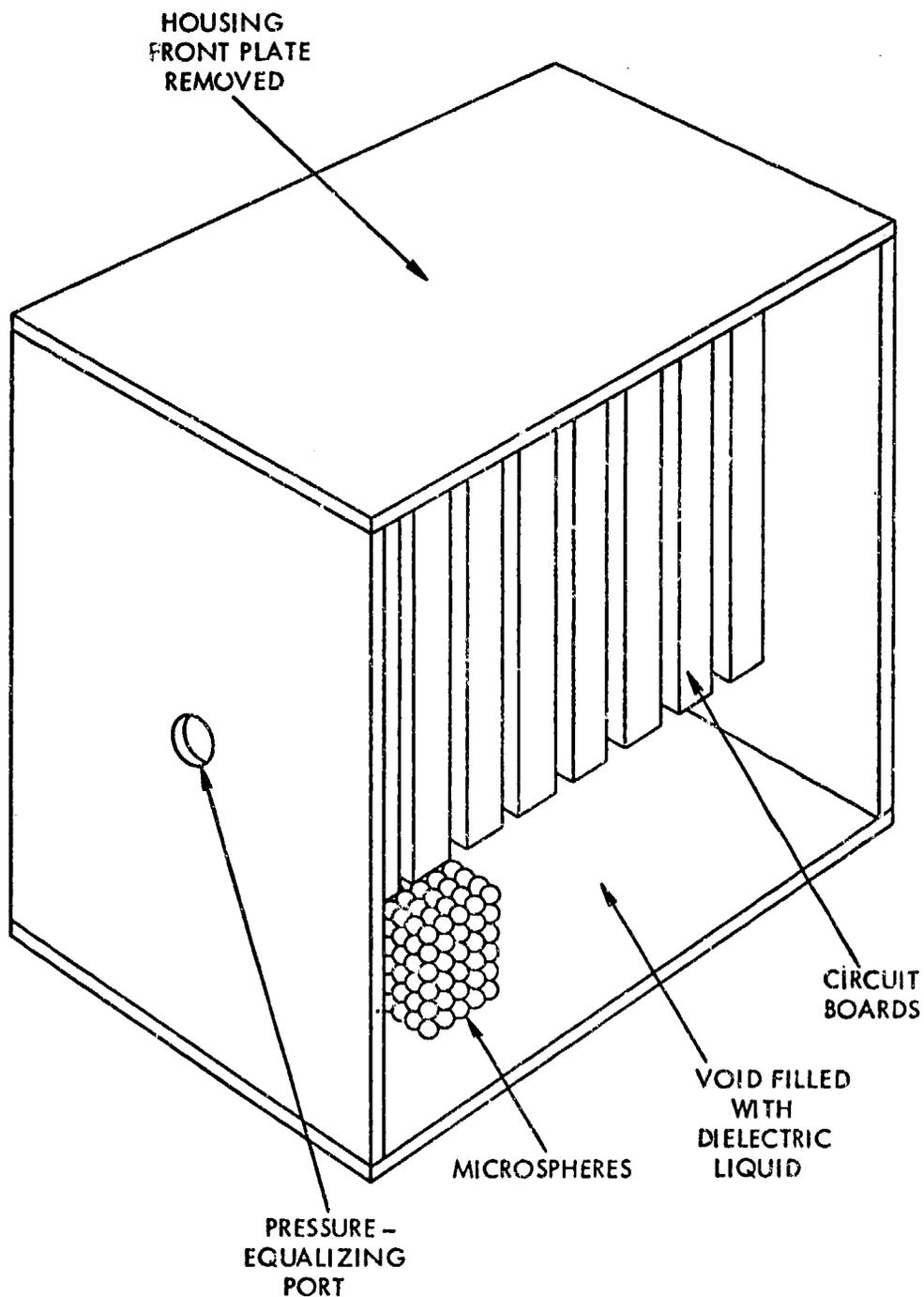


Figure 10 - System Concept

Future efforts should analyze the selected housing material to determine compatibility with the dielectric oils, capability for bonding dissimilar metals, and the resultant effects due to heat and pressure, in addition to design requirements and techniques to be utilized to fabricate the first test vessel.

Buoyancy Consideration

Achievement of overall positive buoyancy is obtained by use of low-density materials to fill some of the void in the equipment housing. At depths of up to 10,000 ft, glass microspheres are the most suitable. At greater depths, a higher density but stronger syntactic foam (microspheres imbedded in resin) may be used. Achievable effective densities in each case can be estimated from the following. The effective density of a pressure-tolerant package of the type described above can be easily shown to be given by:

$$\text{Effective Density} = d_{e1} \times \frac{V_{e1}}{V_T} + d_f \left(1 - \frac{V_{e1}}{V_T} \right), \quad (4)$$

where:

d_{e1} = average density of electronic material

d_f = density of the filler

V_{e1} = displacement volume of the electronics

V_T = total volume.

Typical commercial electronics are packaged so that the packing factor (V_{e1}/V_T) is about 0.2. The average density of the electronic material is about 2.5 g/cm³. If the dielectric fluid were a hydrocarbon of density, 0.8 g/cm³, the effective density of the overall package would be 1.14 g/cm³. Using microspheres with diameters in the range of 30 to 300 μm, a density of 0.33 g/cm³, and a packing factor of 0.65 gives an effective density = $2.5 \times 0.2 + (0.35 \times 0.8 + 0.65 \times 0.33) (1 - 0.2) = 0.89 \text{ g/cm}^3$, thus resulting in positive buoyancy (effective density < 1).^{25, 26}

The use of syntactic foam at depths greater than 10,000 ft yields less promising results. A typical density for the foam is 0.6 g/cm³. Assuming that the packing factor for small, regularly shaped pieces of syntactic foam is 0.6, one can again calculate an effective density = $2.5 \times 0.2 + (0.4 \times 0.8 + 0.6 \times 0.6) 0.8 = 1.04 \text{ g/cm}^3$. At any depth, this method can achieve

positive buoyancy by a small decrease in the electronic material packing factor. For example, a packing factor of 0.15 instead of 0.2 would shift the effective density to 0.95 g/cm³ or positive buoyancy.

Solubility of Materials

A possible source of trouble with electronic/electrical assemblies that are operated in a dielectric oil for pressure-tolerant systems is the solution of ions in the oil environment. The effect of dissolved ionic species on the operation of exposed solid-state devices and certain passive devices was addressed in a previous section. In this section, the question will be addressed: whether immersed electronic/electrical component fabrication materials and their associated hardware will dissolve and/or corrode in the selected dielectric oils.

The approach used was (1) to perform a few preliminary experiments in the selected oils to ascertain whether a complete analysis should be undertaken, (2) if so, continue by reviewing the solubility theory pertinent to the solution of ions, and (3) verify the solubility theory.

The selected oils are two commercially available oils recommended for use in PTE systems; namely, a silicone-base and a petroleum-base dielectric oil. The silicone oil, Federal Specification product VV-D-001078, is a 5-cSt polydimethylsiloxane liquid with an average molecular weight of 680 grams and a dielectric constant of 2.6. The petroleum oil is a 5-cSt paraffinic-naphthenic-aromatic mixture plus a rust inhibitor and an antioxidant. Its average molecular weight and dielectric constant are 250 grams and 2.4, respectively.

In order to determine the need for a complete analysis, the solubility of some cured electrical resins and wire insulating materials was assessed. Tables 5 and 6 indicate the results of these tests. The solubility data, the percent hardness changes of the materials, and resistivities of the contaminated oils were obtained by immersing the resins and wire insulation in the oils at 90° C for 30 days and measuring the quantities at 25° C. This elevated immersion temperature constitutes an accelerated test ensuring extreme limits representative of long-term exposure in a pressure-tolerant system. As shown in table 5, both phenolic and silicone homogeneous polymer resins lose weight in both oils, thus indicating dissolution in the oils. Supporting this hypothesis, the resistivity values indicate that these substances are contaminating the oils with ionic species. It was therefore necessary to consider other materials used in PTE systems and to evaluate their impact on the properties of the oils.

TABLE 5
SOLUBILITY OF CURED ELECTRICAL RESINS AT 25° C⁽¹⁾

Type	% Weight Change in		% Hardness Change in		% Resistivity Change of ⁽²⁾	
	Petroleum Oil	Silicone Oil	Petroleum Oil	Silicone Oil	Petroleum Oil	Silicone Oil
Epoxy	0.18	-0.026	<0.1	<0.1	-50	-81
Phenolic	-4.9	-4.0	<0.1	<0.1	-41	-74
Polyurethane	5.7	-12	<0.1	<0.1	-68	-96
Silicone						
Homogeneous Polymer	-2.0	-2.1	<0.1	<0.1	-14	-84
Butadiene Copolymer	14	6.3	-2	-2	18	-81
Melamine Copolymer	9.5	6.9	-2	-2	0.0	-81

(1) A negative sign indicates that the percentage decreased.

(2) The original resistivities of the petroleum and silicone control oils were 2.2×10^{14} and 1.4×10^{16} ohm-cm, respectively.

TABLE 6
SOLUBILITY OF WIRE INSULATION AT 25° C⁽¹⁾

Type	% Weight Change in		% Hardness Change in		% Resistivity Change of ⁽²⁾	
	Petroleum Oil	Silicone Oil	Petroleum Oil	Silicone Oil	Petroleum Oil	Silicone Oil
Epoxy	-0.028	-0.015	<0.1	<0.1	-23	-84
Neoprene	6.7	-4.7	10	-19	-99	-68
Polyester	-0.14	-0.15	<0.1	<0.1	-94	143
Polyethylene						
Chlorosulfonated	2.2	-1.5	-21	4.2	-99	-100
Terephthalate	2.0	-0.026	<0.1	<0.1	-95	7
Tetrafluoro	1.3	1.4	-4.3	<0.1	-94	21
Polyimide	0.051	0.054	<0.1	<0.1	-96	143
Polyvinyl Acetal	-1.9	-2.0	<0.1	<0.1	-99	-14
Silicone	11	39	-13	-42	-94	-68

(1) A negative sign indicates that the percentage decreased.

(2) The original resistivity values of the petroleum and silicone control oils were 2.2×10^{14} and 1.4×10^{16} ohm-cm, respectively.

Both of the oils used are nonpolar dielectric oils. The solubility predictions which follow apply in general to any nonpolar dielectric oil of a similar molecular structure and composition. Regular solution theory²⁷ predicts that if the chemical composition, structure, or both of these properties of any substance is similar to those of the solvent, then that substance can be expected to dissolve in the given solvent. However, ionic species which have dimensions that are small compared to the molecules of the dielectric oil will not dissolve unless they react chemically with the oil.

The solubilities of chemically pure compounds, which represent several common species, were determined experimentally. The compounds chosen were typical contaminants possible in a PTE system. The chemical species and the contaminants which were studied are listed in table 7, along with a possible source from which each substance might be introduced into a PTE system.

TABLE 7
REPRESENTATIVE PTE CONTAMINANTS

Chemical Species	Contaminant	Possible Source in PTE Systems
Acid (Bronsted)	Hydrochloric Acid	Solder Flux
	Sulfuric Acid	Wet Electrolytic Capacitor
(Lewis)	Aluminum Chloride	Corrosion Product
Base (Bronsted)	Sodium Hydroxide	Wet Electrolytic Capacitor
(Lewis)	Pyridine Water	Processing Seawater
Ester	Dioclyltetrachlorophthalate	Lubricant
Oxide	Aluminum Oxide	Flip-Chip Substrate
	Magnesium Oxide	Corrosion Product
Salt (Monovalent Cation)	Lithium Carbonate	Corrosion Product
	Sodium Chloride (Solid)	Seawater
(Divalent Cation)	Magnesium Sulfate	Corrosion Product
(Trivalent Cation)	Aluminum Naphthenate	Corrosion Product
Other	Saturated Solution of Sodium Chloride in Water	Seawater

The experimental procedure consisted of adding the compounds to the oils to form saturated solutions. These mixtures, then, were refluxed vigorously for 48 hours. After the refluxing was

completed, each mixture was allowed to stand for 24 hours before either filtering with extremely fine borosilicate glass-fiber paper, Reeve-Angle 9-873J, or separating the mixture with a separatory funnel. It was necessary to filter solutions which contained solids to assure that the solubility values would not include values of suspensoids. In each case, the middle fraction of the effluent phase was analyzed quantitatively for a given element or compound according to standard methods.²⁸

Besides measuring the solubilities given in table 8, the resistivity of the ionic species and the dielectric constant of saturated solutions were measured. The dielectric constant measurement was practically insensitive to the presence of ions. The resistivity values were measured on a General Radio D-C Amplifier and Electrometer, type 120-A, which used a Balsbaug 100-3T dielectric measuring coil. A difference in the resistivity values between the pure and contaminated oils indicated that the contaminated oil contained a different concentration of ions or readily ionizable substances.

TABLE 8
SOLUBILITY AND RESISTIVITY RESULTS AT 25° C

Chemical Species Contaminant	Solubility of the Contaminant in a Saturated Solution, µg/g		Resistivity of the Contaminated Oil, ohm-cm	
	Petroleum	Silicone	Petroleum	Silicone
Pure Oil	NA	NA	6.7×10^{13} *	9.5×10^{15} *
Acid				
Hydrochloric	260	776	1.8×10^{13}	1.3×10^{12}
Sulfuric	3.32×10^3	25×10^4 **	3.3×10^{11}	$<10^4$
Aluminum Chloride	34.6	17×10^4	3.9×10^{13}	†
Base				
Sodium Hydroxide	5.74	183	2.0×10^{14}	9.3×10^{12}
Pyridine	25×10^4 **	1.96×10^3	7.2×10^8	2.5×10^{10}
Water	1155	236	1.7×10^{13}	2.6×10^{15}
Ester				
Diocetyl-tetra- chlorophthalate	25×10^4 **	25×10^4 **	6.7×10^{11}	6.4×10^{11}
Oxide				
Aluminum	12.1	<0.02	7.1×10^{12}	6.7×10^{15}
Magnesium	<0.02	<0.02	3.1×10^{13}	7.0×10^{15}
Salt				
Lithium Carbonate	56.4	<0.15	2.4×10^{11}	1.2×10^{15}
Sodium Chloride (Solid)	0.69	0.15	1.8×10^{13}	1.0×10^{16}
Magnesium Sulfate	<0.05	<0.05	9.0×10^{13}	1.8×10^{15}
Aluminum Naphthenate	17×10^4 **	100	†	5.3×10^{11}
Other				
Saturated Solution of Sodium Chloride in Water	<0.05 **	<0.05 **	1.1×10^{14}	1.3×10^{16}

*The standard deviations for four readings are 2.4×10^{13} and 3.7×10^{15} for the petroleum and silicone oils, respectively.
**The value is for a nonsaturated solution.
†A measurement was not possible because the oil gelled.
‡The value is for sodium chloride.

Except for acids, bases, and compounds whose structures and composition are similar to those of the oil, regular solution theory predicts that ionic species should be insoluble in these oils. As seen in table 8, this prediction needs to be qualified. For instance, in petroleum, aluminum oxide is more soluble than the base, sodium hydroxide, which should be appreciably soluble. Some substances, such as sodium hydroxide in petroleum oil and sodium chloride in silicone oil, resulted in an increase in the resistivities of the respective oils. This is probably because these substances react with dissolved water to dry the oils. Consequently, the theory does not predict the relative solubilities of compounds in these oils. From the data in table 8, one concludes that, in these oils, certain substances dissolve appreciably, dissociate into ions, and/or affect the electrical properties.

The results indicate that those components which contain compounds which dissolve appreciably in the oils must either be excluded from use or encapsulated to prevent contamination of the rest of the system. For example, wet electrolytic capacitors and primary and secondary batteries contain acids and bases. The structures of compounds like polyvinyl chloride and silicone rubber resemble those of the petroleum and silicone oils, respectively. In their respective oils, these materials become tacky and eventually dissolve.

In the experiments which measured the solubility of pure chemical species in the oils, it was hypothesized that the resultant solubilities would be maximum values. To verify this hypothesis and to relate the solubility predictions to a real PTE system, a chemical analysis of soluble contaminants was performed on a dielectric oil that had been in service for 2 years on a United States Navy experimental boat. This oil was a 10-cSt petroleum-base oil, Federal Specification product class II VV-I-530. Its average molecular weight and dielectric constant are 280 grams and 2.4, respectively.

This oil enveloped the following devices and circuits which were operated for 10^3 hours: 728 type 741 plastic encapsulated operational amplifiers, 16 type 723 plastic encapsulated regulators, numerous resistors, capacitors, fuses, and transformers. During the 10^3 hours, 15 operational amplifiers failed. The failures have been attributed to lead wire shorts, lifted ball bonds, and deterioration of the metallization. In addition, the oil caused the polyvinyl chloride wire insulation to stiffen.

The oil sample was analyzed by standard neutron activation techniques. The results, listed in table 9, are valid to only two significant figures. The pure oil contained none of the elements listed in this table. It is worthy of note that the analysis shows a substantial amount of polyvinyl chloride in the oil. The water content, resistivity, and dielectric constant of the oil sample were measured. The oil contained 32 p/m by weight

of water. This is 7 p/m higher than that of the pure oil. The resistivity value and dielectric constant of the in-service oil were 5.4×10^{15} ohm-cm and 2.4, respectively, the same as those of the pure oil.

TABLE 9
CONCENTRATION OF ELEMENTS DETECTED IN
THE IN-SERVICE OIL⁽¹⁾

Element	Concentration p/m	Precision + or -
Silver	0.693000	0.140000
Aluminum	0.008270	0.014000
Manganese	0.001280	0.000380
Chlorine	34.400000	6.300000
Gold	0.000072	0.000017
Zinc	0.106000	0.037000
Bromine	0.014000	0.002900
Sodium	0.009320	0.001900

⁽¹⁾ Above results for four data sets.

Corrosion is the other mechanism by which appreciable ion accumulation might influence device operating parameters. From the resistivity values given in table 8, the time that is required for an ion to drift 1 cm in an electric field of unit intensity can be determined. This time is the reciprocal of the ion mobility. The ion mobility (μ_{im}), in units of square centimeter volt⁻¹ second⁻¹, is the velocity of an ion in a uniform electric field of unit intensity. The ion mobility is calculated from the equivalent conductivity (Λ) of the solution according to the following equation:²⁹

$$\mu_{im} = \frac{\Lambda}{2F} = \frac{10^3 K}{2FC} \quad (5)$$

where:

F = the value of the Faraday

K = the value of specific ion conductivity

C = the ion equivalents per liter.

The values of the reciprocal ion mobilities and equivalent conductivities were calculated from the data in table 8 with the

assumptions that the solutions were infinitely dilute, the species were strong electrolytes, and that the species were dissociated only to the first degree of ionization. If no dissolved substance was detected, the minimum detection limit was substituted for the solubility value. The results of these calculations are listed in table 10.

TABLE 10
RECIPROCAL MEAN ION MOBILITIES AND EQUIVALENT
CONDUCTIVITIES AT 25° C

Ionic Substance	$\mu_{im}^{-1} \times 10^{-11}$ sec volt cm^{-2}		$\Lambda \times 10^7, cm^2 ohm^{-1}$ Equivalent ⁻¹	
	Petroleum Oil	Silicone Oil	Petroleum Oil	Silicone Oil
Hydrochloric Acid	280	48	0.07	0.40
Sulfuric Acid	36	0.000052 ⁽¹⁾	0.54	370,000 ⁽¹⁾
Aluminum Chloride	380	NA	0.50	NA
Sodium Hydroxide	45 ⁽¹⁾	74	0.43 ⁽¹⁾	0.26
Pyridine	3.7	1.1	5.4	18
Water	1,900	96,000	0.01	0.0002
Dioclyltetra-chlorophthalate	51	54	0.38	0.36
Aluminum Oxide	15	8.0	13	2.4
Lithium Carbonate	0.58	9.6	33	2.0
Sodium Chloride(s)	0.46	46 ⁽¹⁾	42	0.42 ⁽¹⁾
Aluminum Naphthenate	NA	0.21	NA	92

(1) The value is based on the resistivity value of the contaminated oil.

Assuming a tentative minimum resistivity value of dielectric oils for deep ocean applications of 3.0×10^{11} ohm-cm, calculations³⁰ based on the mean ion mobility of a solution with this tentative resistivity value showed that for aluminum metallization of a semiconductor device, (1) the galvanic corrosion rate is 2×10^{-8} g cm^{-2} yr^{-1} , and (2) its electrolytic dissolution rate in an electric field with an intensity of 100 V cm^{-1} is 3×10^{-6} g cm^{-2} yr^{-1} . Applying these corrosion rates to a square centimeter of aluminum metallization $1 \mu m$ thick, the galvanic

corrosion rate is 0.01% per year, and its electrolytic dissolution rate is 1% per year. Therefore, the corrosion rates of the aluminum metallization on devices should be negligible for the expected conditions.

Heat Transfer

Variations of temperature can cause variations in the operating parameters of semiconductor devices. Leakage current, transistor current gain h_{FE} , and junction forward voltage drop at constant current V_{BE} , are all sensitive to temperature changes. For silicon transistors, typical figures are:³¹

- I_S doubles with a 12° to 15° C increase.
- V_{BE} decreases at about 2 mV per 1° C increase.

The change in current gain with temperature depends upon the way in which the device is made. A recent study³² found that, for an 80° C change (from -55° to 25° C), the change in d-c common-emitter current gain varied over a wide range, from a factor of 1.12 to a factor of 3.04.

Many techniques have been devised by circuit designers to minimize the effects of temperature changes on circuits using semiconductor devices. Large area heat sinks are employed to improve dissipation from power controlling devices, such as rectifiers, SCR's, and power transistors. It is necessary for the system design engineer to know to what extent the heat transfer from semiconductor devices will be altered by immersed operation.

Many large power transformers operating at atmospheric pressure are immersed in a dielectric oil which, among other uses, serves as a heat transfer medium. The heat transfer is usually accomplished by free convection and by conduction through the oil. Generally, the heat transfer rate is significantly greater in a liquid than in air for a given temperature drop between the heated object and the surrounding medium. This fact has prompted a careful look at liquid cooling of high density microelectronic circuits. A recent study³³ has compared free convection cooling in air with free and forced convection cooling in silicone oil, Federal Specification product VV-D-001078. It was determined that free convection cooling by silicone oil dissipates three times as much heat per unit area as occurs in free air.

To determine whether or not this optimistic forecast can actually be achieved, the heat dissipation characteristics of two types of commercial power transistors were evaluated: (1) in air, (2) in a 5-cSt silicone oil, Federal Specification product VV-D-001078, at atmospheric pressure and at 15,000 lb/in², and (3) in a 10-cSt petroleum-base oil, Federal Specification product class II, VV-I-530, at atmospheric pressure and at 15,000 lb/in². The two types of power devices used were: (1) a silicon npn power transistor, type 2N4913, mounted on a TO-3 header, 87.5 watt

nominal power dissipation at 25° C, and (2) a silicon pnp power transistor, type 2N3740, mounted on a TO-66 header, 25 watt nominal power dissipation at 25° C. Three specimens of each device type were tested. The devices were decapped to provide direct physical heat transfer between the junction and air, as well as between the junction and the immersion oils. No external heat sink was used, heat transfer was by natural convection only.

Using an environmental test chamber, calibration values of V_{BE} versus temperature were obtained for each device. The base-emitter current was maintained at 10 mA with the collector open. The V_{BE} versus temperature curves were linear, as indicated in figures 11 and 12. These curves allow for the use of V_{BE} as an accurate indication of junction temperature instead of the more cumbersome thermocouple.

The circuit used for the measurements to determine power dissipation and device temperature, via V_{BE} , is shown schematically in figure 13. The relay RY1 was driven at 60 Hz to provide a 50% duty cycle. The relay switched the device between a power dissipation state and a calibration state, allowing the measurement of V_{BE} under the calibration condition of 10 mA base-emitter current. The variable resistor (R_1) was used to provide the required base drive in order to obtain the desired power dissipation.

The thermal resistance (θ), thermal time constant (τ), and thermal response time (T_r) were measured and/or calculated from measured data per the following definitions:

$$\theta \triangleq \frac{\Delta T}{\Delta P} \text{ (}^\circ\text{C/watt)} - \text{per MIL-STD 750B, method 3126.}$$

ΔT - increase in junction temperature in response to a step change in the forcing function ΔP .

ΔP - Δ change in the average power dissipated by the device under test.

τ - Δ time required for ΔT to reach 63.2% of its final value when responding to a step change in ΔP per MIL-STD-750B, method 3146.1.

T_r - Δ time required for ΔT to reach 90% of its final value when responding to a step change in ΔP per MIL-STD-750B, method 3141.

Table 11 lists the average values of θ , τ , and T_r found for the devices tested.

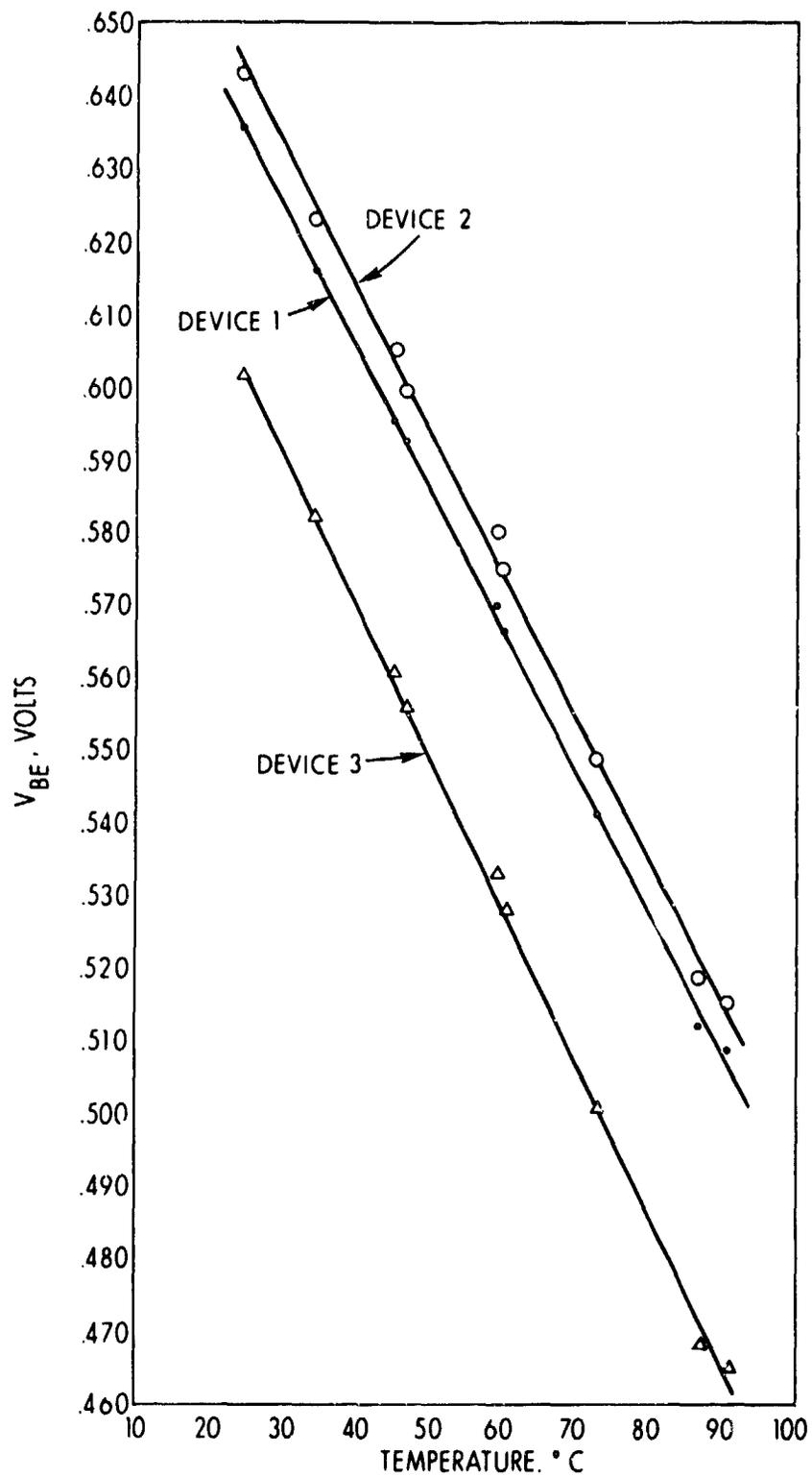


Figure 11
 Temperature Versus V_{BE} of
 Three Decapped 2N4913 Transistors
 ($I_E = I_B = 10 \text{ mA}$; $I_C = 0$)

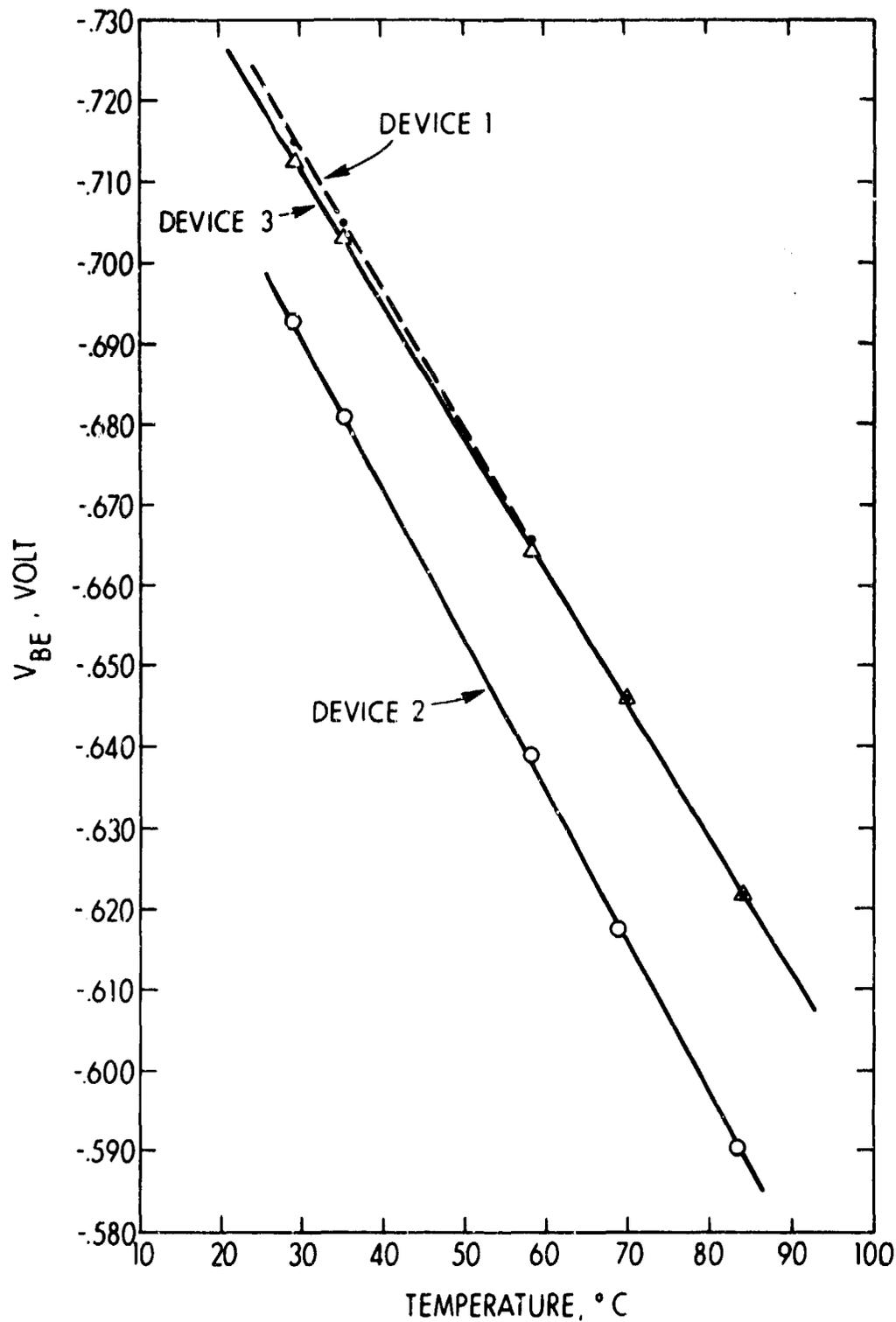


Figure 12
 Temperature Versus V_{BE} of
 Three Decapped 2N3740 Transistors
 ($I_E = I_B = 10$ mA; $I_C = 0$)

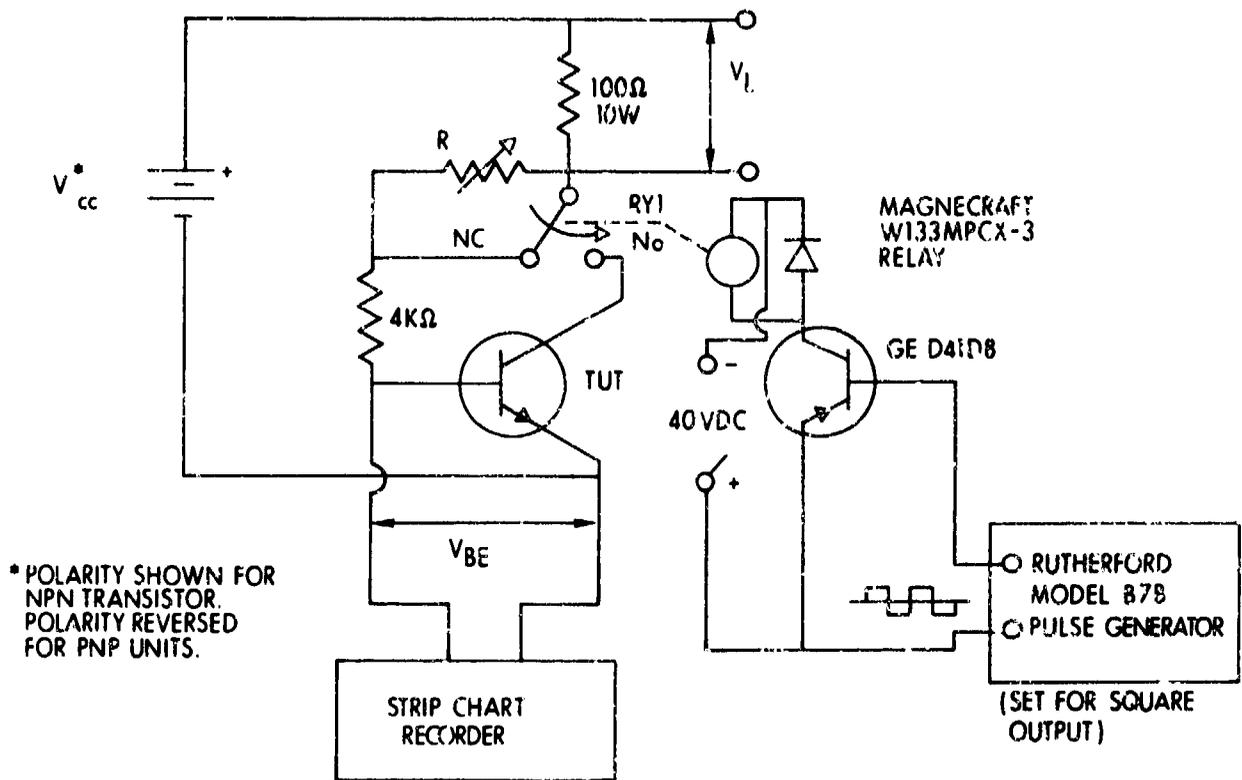


Figure 13
Schematic Diagram of Test Circuit for
Heat Transfer Tests

TABLE 11
THERMAL RESISTANCE, TIME CONSTANT, AND
RESPONSE TIME DATA

	2N4913 - NPN			2N3740 - PNP		
	θ °C/W	τ min	T_r min	θ °C/W	τ min	T_r min
Air	36.2	3.8	8.6	39.1	1.4	2.9
VV-D-001078, 5 cSt						
1 atm	5.0	0.41	1.0	5.5	0.26	0.62
15,000 lb/in ²	5.7	0.55	1.2	6.5	0.30	0.75
Type II, VV-I-530, 10 cSt						
1 atm	7.4	0.54	1.25	9.5	0.29	0.77
15,000 lb/in ²	9.9	1.07	2.59	12.1	0.59	1.47

As shown by the data in table 11, all three thermal characteristics for the devices under test improved when they were immersed in an oil as compared to their respective air values. For example, the thermal response time in the 5-cSt silicone oil and the 10-cSt petroleum-base oil at atmospheric pressure ranged from 5 to 12 times faster than that in air. Increasing the pressure of the oils to 15,000 lb/in² had the effect of slowing the thermal response time anywhere from 10% to 100%. Although this was a decline in the thermal response time in the oils at 15,000 lb/in², it still provided a much better transfer medium than air.

Overall, it can be seen that:

- Oil immersion increases heat transfer capabilities as compared to an air environment at an equivalent pressure.

- Although there is a noticeable drop in the heat transfer of oils at high pressures, the heat transfer is still markedly better than the air medium.

- In general, a silicone base oil is just as efficient a heat transfer medium as a petroleum-base oil.

Reliability of Outboard Systems

No definitive statement can be made on the whole question of reliability of electronic devices for pressure-tolerant electronics at this time. Very few studies have been conducted that have considered enough samples to have any significant statistical value. Almost all investigations, the present study included, have utilized representative devices but often only one or two in each category.

The present study has considered some of the more obvious failure modes. However, subtle failure mechanisms will certainly be identified for all device types. Experimentally, the most common failure mechanisms were those normally encountered in devices, such as voids in the bonding, misplaced leads, and poor metallization. The fluid-pressure environment, like mechanical testing, will sometimes accelerate these failure mechanisms.

It should be emphasized that no significant long-term testing was done in this study to allow statistical evaluations. The most important tests will involve cycling for long periods of time. This approach has been used at NUC, and numerous failures have occurred for some devices.

The whole area of plastic creep and stress relaxation has not been treated and will need much attention. Evaluations of these problems should result in the establishment of needed screening tests for the pressure-induced failures. For example, overpressurization may be an excellent accelerated testing method.

From a reliability view, the fact that devices will be free flooded in an inert liquid could greatly enhance their reliability. This is true for two reasons: (1) for free-flooded devices, the device will often be uncapped or unencapsulated, thereby permitting visual inspection even after assembly into such systems; (2) the inert fluid will likely be more benign than the typical encapsulation atmospheres. The latter should greatly reduce the mobility of such impurities as water vapor. Many failure modes are the result of poor quality control of the encapsulating environment.

SUMMARY OF TYPES OF DEVICES TESTED AND TYPES OF TESTS

A tabulation of the various semiconductor devices tested and the associated test conditions included in this report are presented in table 12.

TABLE 12
TEST DEVICES AND CONDITIONS

Device Designation	Function	Material	Type	Testing Type and Condition
2N4232	Power	Silicon	NPN Planar	Oil/Pressure - Decapped TO Can Oil Contamination - Decapped TO Can
2N3740	Power	Silicon	PNP Planar	Oil/Pressure - Decapped TO Can Heat Transfer, Oil/Pressure - Decapped TO Can Oil Contamination - Decapped TO Can
2N1412	Power	Germanium	PNP Alloy	Oil/Pressure - Decapped TO Can Oil Contamination - Decapped TO Can
2N1553	Power	Germanium	PNP Alloy	Oil/Pressure - Decapped TO Can
2N4913	Medium Power	Silicon	NPN Alloy	Heat Transfer, Oil/Pressure - Decapped TO Can Oil Contamination - Decapped TO Can
2N2222A	Small Signal	Silicon	NPN Planar	Oil/Pressure - Decapped TO Can
2N2907A	Small Signal	Silicon	PNP Planar	Same as Above
2N526	Small Signal	Germanium	PNP Alloy	Same as Above
2N526	Small Signal	Germanium	PNP Alloy	Oil/Pressure - Decapped TO Can (Covered with DC-RTV 3144)
2N3796	Small Signal	Silicon	MOSFET N Channel	Oil/Pressure - Decapped TO Can
M163	Small Signal	Silicon	MOSFET P Channel	Same as Above
SN7473N	Dual J-K Flip/Flop	Silicon	Planar	Oil/Pressure - Plastic DIP
Type 474	Frequency Compensated Operational Amplifier	Silicon	Planar 20 Transistors, 12 Resistors, 1 Capacitor	Oil/Pressure - Decapped TO Can
Type 777	Precision Operational Amplifier	Silicon	Planar 20 Transistors, 4 Diode- Connected Transistors, 11 Resistors	Oil/Pressure - Decapped TO Can Oil/Pressure - Ceramic DIP

HIGHLIGHTS

The following highlights give added credence to the feasibility of achieving PTE systems.

PRESSURE EFFECTS

- Several types of off-the-shelf devices (ceramic, plastic, and epoxy packages) are suitable for use at 15,000 lb/in².

- Basic materials, semiconductors, metals, insulation, etc are insensitive to the pressure environment.

- Pressure-induced device failures have been due to package deformation and/or manufacturing techniques.

- Solid-state devices constructed with voids, TO-type cans, metal-lidded DIP flat packs, etc cannot be operated below a few hundred feet.

- Passive components constructed with internal voids or porous materials, carbon-composition resistors, electrolytic capacitors, ferrite core inductors, etc exhibit large value changes with pressure.

PRESSURE HARDENING

- Reinforcement of housings with epoxy, metallic materials, or redesign to hemispherical domes substantially improves operating depth capability.

- Potting to achieve pressure hardening may drastically alter heat transfer properties.

- Pressure equalization (exposure to the dielectric oil) is the most promising hardening technique.

FLOODING EFFECTS

- Most exposed silicon devices are not affected by flooding with contaminated oil and pressurized to 15,000 lb/in².

- Degraded germanium device parameters can be affected by a contaminated oil.

- Heat transfer rate is improved.

DIELECTRIC LIQUID

- Polydimethylsiloxane, a silicone oil, has been selected as the primary dielectric liquid.

- Device evaluation has been performed in the primary and alternate dielectric liquid, and both appear usable.

- Most basic electronic materials are negligibly soluble in the selected dielectric oil.

- Analysis of a petroleum-base dielectric oil, VV-I-530, in service in a PTE system for over 3 months showed no change in resistivity or dielectric constant. However, neither a theoretical nor a controlled laboratory evaluation has been performed on this oil.

SYSTEM CONSIDERATIONS

- Immersion of exposed silicon devices in a dielectric liquid may provide a more benign environment than their operation, encapsulated, in the atmosphere.

- Substantial cooling occurs due to immersion.

- A new titanium alloy (Ti-6Al-2Cb-Ta/0.8Mo) has been selected as the first choice for the system (oil and components) housing material.

- Long-term reliability predictions are not possible at this time.

- Feasibility of positively buoyant PTE systems has been established.

RECOMMENDATION FOR FUTURE WORK

PREFACE

Prior related efforts in deep ocean technology and recent ONR-sponsored analyses^{3 4} have highlighted the major advantages of PTE systems. These advantages are:

- Reduction in pressure hull volume.
- Reduction in heat load on vehicles' ventilation systems.
- Reduction in heat load on electronic water-cooling subsystem.
- Buoyancy improvement.
- Rapid equipment replacement to accommodate ship mission change.

These advantages of outboard systems are not limited to deep ocean vehicles but include other vehicles and systems, such as submarines, torpedoes, acoustic decoys, bottom installations, and variable depth sonars.^{3 4}

Assuming, then, the desirability of PTE systems in most submersibles, the question must be asked as to what is preventing its widespread use at this point. Its provisional feasibility has been demonstrated by the various circuits and assemblies that have been successfully utilized in the environment. However, what is still lacking is a complete, extensive technology base to support the development, design, fabrication, test, installation, and operation and maintenance of PTE systems.

PROGRAM

The requirements necessary to provide a support technology base for the design option of PTE system development from conceptual phase through system deployment have been prepared.³⁵ It provides for the same level of support technology as current nonpressure-tolerant systems. The requirements can be summarized as follows:

- Define operational environment, constraints, and necessary reliability.
- Establish design specifications, materials requirements, design tradeoff criteria, and data base.
- Develop methods for system installation, operation, and maintenance.

The cost of such an effort would be approximately \$4.8 million over a 4-year period.

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