DEFORMOGRAPHIC STORAGE DISPLAY TUBE (DSDT) MATERIAL STUDY

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13. ABSTRACT

This report describes the investigation into the problem of finding a polymer material to serve as the deformable medium for a light valve display device called the Deformographic Storage Display Tube (DSDT).

The DSDT operates on the principle of generating minute deformations in a deformable material by the establishment of an electrostatic force from charges deposited by a cathode ray beam. The deformations in the material are translated into a visual image by projection through a Schlieren optical system. The DSDT has demonstrated feasibility to be a multipurpose display tube. It exhibits storage, controlled persistence, selectable erase, high resolution, high dynamic range, and display sizes from 6 to 60 inches from a single tube. In order for the DSDT to realize its full potential as a multipurpose device, it must exhibit a combination of characteristics which will allow its use for real-time sensor displays. The particular characteristics are: sensitivity (writing rate), time response, and freedom from residual imagery. In addition, the process of tube fabrication must be sufficiently stabilized to assure manufacturability.

As a result of this study, a material was identified which significantly improved the time response and residual imagery effect for the DSDT. In addition, it was found that the new material was more consistent in its operational parameters. Thus, a significant step has been taken in the performance and manufacturability of the DSDT.

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FOREWORD

This technical report on the Deformographic Storage Display Tube (DSDT) Material Study describes the testing, analysis, and evaluation of a series of silicone polymers for utilization as the deformable medium in the DSDT. The work was performed at the IBM Electronics Systems Center, Owego, New York during the period from July 1971 to March 1972. The work was performed for the Office of Naval Research, under Contract Number N00014-71-C-0270. LCDR H. Lyon is the scientific officer.

Technical contributors to the program were: Mr. E. T. Kozol, Mr. P. Pokrinchak, Mr. G. Nielsen, and Mr. G.W. Manley. Mr. E. J. Ross was the technical program manager and Mr. B. I. Halperin was the project engineer for the IBM Corporation. Mr. Halperin was the principal author, Mr. Ross was a co-author.

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GLOSSARY

Å	Angstrom Unit
°C	Degrees Centigrade
Cm^3	Cubic Centimeter
CRT	Cathode Ray Tube
DSDT	Deformographic Storage Display Tube
E_y	Youngs Modulus
F	Force (or Load)
g	Grams
hr	Hours
ln	Natural Logarithm
lp	line pairs
lb/in^2	Pounds per Square Inch
M_c	Molecular Weight Between Crosslinks
M_n	Number Average Molecular Weight
M_W	Weight Average Molecular Weight
mil	Milliinches
ml	Milliliter
ms	Milliseconds
p	Depth of Penetration
P_h	Density of Hexane
PPI	Plan-Position Indicator
P_r	Density of Rubber

r	Radius of a Sphere
R	Gas Constant
T	Temperature
ΔT	Change in Temperature
TMA	Thermo Mechanical Analyzer
TV	Television
V_e	Moles of Effective Network Chains per Unit Volume of Rubber
v_2	Volume Fraction of Polymer in a Solvent Swelling Specimen
W	Grams of Hexane Absorbed per Gram of Rubber
X_1	Interaction Parameter
μA	Microampere

SUMMARY

The purpose of this program was to perform an investigation into the possibility of improving the characteristics of the polymer material which serves as the deformable medium of a light valve display device called the Deformographic Storage Display Tube (DSDT). The DSDT has demonstrated the capability to be a true multipurpose display device. However, it has shown limitations in certain performance areas which has prevented it from operating across the full spectrum of display applications. The primary areas of concern were: a tendency to build up a latent image under continual regeneration of a fixed image, the lack of sufficient material time-response to follow TV rates, and a variation of sensitivity of the image forming membrane.

As a result of this program a significant advancement has been made in the DSDT material technology. A new material has been identified which has a time-response in excess of that required for TV rates. Test membranes fabricated with this material have shown a significant reduction in the variability of sensitivity. The remnant image effect has shown a marked improvement over that of the material used prior to this program. The performance of this material is such that the DSDT can be applied to prototype display applications.

The experience gained on this program indicates a strong possibility of further improvement in material performance. It is recommended that additional support be devoted to a continuing investigation into the material technology.

Section 1

INTRODUCTION

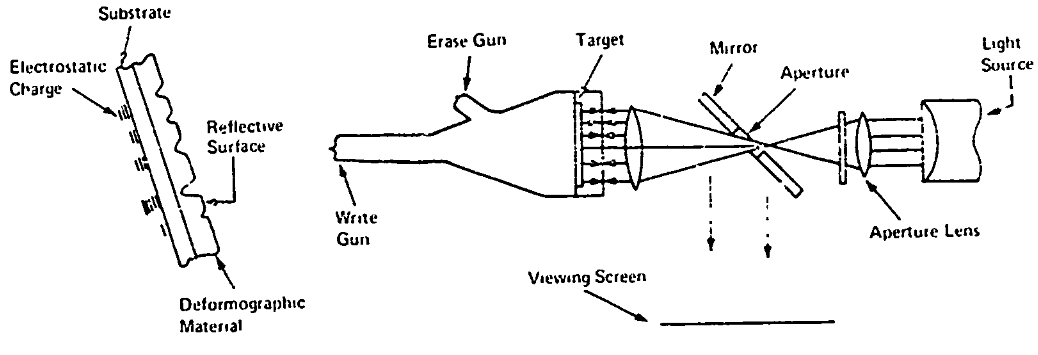
The DSDT is a special type of cathode ray tube (CRT). In a conventional CRT, an image is generated by electron bombardment of a phosphor coating on the faceplate. This results in a visible excitation from which a self-illuminating image is formed. The same type of electron gun is used in the DSDT; however, in this case as shown in Figure 1-1a, it writes an electrostatic image on a storage diaphragm inside the tube. The electrostatic charges cause minute deformations in a thin layer of a special deformable material on the opposite side of the diaphragm. These deformations are converted into a visible image by projection through a schlieren optical system.

The image will last for many minutes without being refreshed, but will ultimately fade as the result of charge leakage from the diaphragm. It can, however, be erased at any time through the use of an erase flood gun. Erase time depends on the flood current used, varying from as little as 10 ms for TV, to several seconds for PPI radar rates.

The write/erase mechanism is based on the secondary emission characteristics of the diaphragm. Writing occurs at an accelerating potential where the secondary electrons emitted are fewer than the primary electrons striking the target. As a result, a negative electrostatic charge is deposited and stored by the diaphragm. The electrostatic field, created between these charges and the conductive coating on the faceplate of the tube, causes the minute "wrinkles" in the deformographic material.

Erasure occurs at an accelerating potential where the ratio of secondary to primary electrons is greater than 1. Therefore, electrons at this potential cause the negatively charged image to be neutralized, bringing the erased area back to the same potential as the faceplate.

Presentation of the visual image requires a schlieren optical system. Figure 1-1b illustrates an on-axis reflective system that should be the basic operational configuration. Light from the source is passed through an apertured mirror, collimated, and transmitted to the target surface. In the absence of a disturbance on the surface, the light returns through the mirror and effectively exits the system, with the aperture serving as a schlieren stop. However, if a surface deformation occurs, light rays in that area are diffracted and return to the mirror surface to be reflected to the viewing screen. Spatial correlation is maintained between charge deposition, material deformation, and screen illumination. Thus, a visual image is obtained from the electronic pattern.



a Target Assembly

b DSDT Display With On Axis Schlieren Optical System

Figure 1-1. Basic Principles of DSDT Operation

The Deformographic Storage Display Tube (DSDT) has been developed at IBM as an advanced display device. It has demonstrated the following features while maintaining relatively simple operational characteristics:

1) Image storage (>5 min)
2) Electronically variable image persistence
3) Small - large scale (6 to 60 in/dia) imagery by optical projection
4) Selective image erase and regeneration
5) High resolution (850 line pairs/dia)
6) High dynamic range (>50:1).

The technology associated with the DSDT has progressed sufficiently that feasibility model sealed tubes have been fabricated and are presently in operation in a demonstration unit at IBM's Electronics Systems Center. To reach this state of development, IBM has invested significant company resources and has received some support from the Air Force. This particular program represents an interest by the Office of Naval Research in determining if deformographic materials can attain the necessary performance for use in cockpit display applications.

1.1 DSDT TARGET TECHNOLOGY

The properties of the DSDT are a result of a unique light valve dielectric membrane (target) utilized in the device. Figure 1-1a illustrates the structure of the target.

The operating characteristics of the target are governed in part by the substrate and the reflective layer; however, the critical constituent of the target is the deformable material. The basic material utilized thus far in the DSDT technology has been a silicone polymer marketed by the Dow Corning Co. under the designation XR 63 493. When polymerized under accepted procedures (base-to-crosslinking agent ratio of 100:10) the resultant material can be used in the DSDT for display and annotation applications involving the medium speed generation of alphameric and graphic data. However, if a wider latitude of capability is desired, such as presenting live video information from active sensors, the polymer must be prepared in an unconventional manner (base-to-crosslinking agent ratio of 100:3.5). In this circumstance, the present polymer has been found to be quite variable in its performance characteristics, i.e., its sensitivity in particular, and has exhibited a tendency toward remnant or residual imagery when an image point is repetitively scanned many times or when a high contrast image is stored for some time; also, in the case of TV formats, the material was too slow in time response. The purpose of this program was to investigate various polymers and their characteristics in order to develop a new polymer which could exhibit the desired operational characteristics without these undesirable effects.

1.2 STUDY APPROACH

The basic problem to be addressed by this program was the identification of an improved material for utilization as the deformable medium of the DSDT. The specific areas of desired improvement were a reduction in residual imagery and less variability in the fabrication of the deformable target.

Because the financial scope of the program was rather small, it was necessary to develop a program plan which would provide the greatest effectiveness for the effort expended. The essential elements of this plan were:

1) Use prior knowledge and experience to select the most likely material candidates
2) Obtain the assistance of polymer experts
3) Use a bracketing technique in order to quickly home in on proper parameter values
4) Compile previous experimental results and conduct new tests, as required, to provide a data base for quantitative determination of material characteristics.

1.2.1 ALTERNATE DEFORMABLE MATERIALS

The basic deformable material which has been used for the DSDT is a Dow Corning product designated as XR 63 493. This compound is categorized as a dimethyl siloxane polymer or sometimes more simply as a silicone polymer.

Approximately six weeks before the beginning of this contract, IBM established an informal working relationship with Dow Corning in which an iterative approach would be taken to testing and defining new materials for the DSDT application. This relationship was the source of alternate materials tested during this program. As a result of our initial discussions with Dow Corning scientists, it was decided that a linear dimethyl siloxane polymer group with a variation in the number of crosslinking sites provided the best hope for improving performance within a limited scope program. This decision was based on two considerations: (1) the basic deformable material being used in the DSDT was a dimethyl siloxane polymer and was providing reasonably good performance, (2) Dow Corning's knowledge of this polymer class and of the DSDT's requirements indicated to them that a satisfactory compound could be found within this basic group.

During the program, six different silicone polymers were evaluated. The compounds differed in molecular weight and in molecular weight distribution. The testing of the compounds included several mix ratios between each polymer base and its crosslinking agent; in addition, various material handling techniques were employed in order to prepare test targets of the various compounds. Thus, considerable effort was expended in evaluating the various forms of these six compounds.

1.2.2 TARGET TESTING

The targets fabricated in this program were tested primarily for improvements in time response, remnant effect, and sensitivity consistency. However, these parameters are significant only if the target retains a reasonable level of performance in other parametric areas such as resolution and dynamic range. Therefore, the targets were judged acceptable only if they attained a minimum resolution of 200 line pairs per inch and a 30:1 contrast ratio.

During the course of the program, it was found to be quite difficult to measure the remnant effect in a quantitative manner. The DSDT utilizes a schlieren optical system to create the visual output image. Schlieren systems are often used to perform analytic measurements of effects that produce small phase changes in transmitted light. The remnant effect existing in the DSDT is sometimes only barely visible or is evidenced by secondary effects; thus, it can be seen that it is difficult to find an alternate measurement technique which will provide significantly better results than simply observing the output image of the DSDT's schlieren system. Thus, the results of the target testing contain a certain amount of subjectivity since comparisons were made visually. It was possible to perform some measurements with an interferometric microscope and with a light measuring photocell which indicated the reasonableness of the results obtained from the visual observations.

The methods of testing employed in this program were as follows:

1) Demountable Testing — Targets were fabricated on sample substrates and inserted in a demountable CRT. The sensitivity of the target was determined by interrogating the output image contrast with a photocell and measuring the beam current required for a 30:1 contrast ratio. Time response was measured by comparing the output of the photocell to an input signal on the DSDT grid.

Resolution was measured by placing a 225-lines per inch raster on the target and inspecting the resultant image both visually and with a photocell. Remnant imagery effect was judged in three ways: (a) by cycling a line at a high rate and watching the output for latent image buildup, (b) writing the image on the tube at an excessive contrast ratio and, after storage and erase, inspecting the output for a latent image, (c) writing a raster on the tube at various contrast ratios, storing and erasing the image; then writing a new raster at a 45° to 90° angle and inspecting the new image for a moire pattern resulting from remnance of the previous image.

These tests were conducted alternately with new materials and with the standard XR 63 493 material in order to provide reasonable correlation in time for the subject viewing conditions and the equipment operation.

2) In-Air Testing - Sample targets were prepared on glass slides which contained variably spaced metallic bus bars for applying a deforming voltage to the target structure. The surface of the glass slide could be viewed with either a schlieren optical system or by an interferometric microscope. The degree and frequency of deformation was determined by the voltage and frequency of the input square wave to the bus bars.

Resolution was determined by viewing the output image as a function of the spatial frequency of the bus bars. Dynamic range was achieved by adjusting the input voltage to produce a 30:1 contrast ratio. Remnant imagery was determined primarily by cycling a glass slide containing a new material simultaneously with a glass slide containing XR 63 493 material. By comparing the remnant image as function of the number of deforming cycles for the two slides, a determination of relative remnant sensitivity was made. This same arrangement was also used to inspect the surface with an interferrometric microscope.

The tests conducted on the in-air tester were the prime source of the remnant imagery results. These tests also provided an indication of the time response and the lifetime capability of the target.

1 2.3 PARAMETRIC ANALYSIS

The parametric analysis portion of this program was devoted to the formulation of a data base which could lead to quantitative measurement and prediction of the performance of potential deformable materials. If a correlation could be shown between certain quantitative measurements and actual target performance, then further investigative work may be simplified. However, it is necessary to be mindful that most parametric tests are conducted with the material in bulk (volume) form while in the actual application the material is used in a thin film form. Therefore, one must be prudent in the interpretation and correlation of results

The major parametric analysis performed during this program are listed below with the rationale for their performance.

1) Gel Phase Chromatography - This analysis was performed in order to ascertain the molecular weight and molecular weight distribution of the candidate materials.

2) Thermo-Mechanical Analyzer and Solvent Swelling Studies - This analysis was performed to determine the crosslink density and elastic properties of the materials.

3) Young's Modulus and Yersley's Oscillograph - These tests were conducted to determine if simple mechanical measurements could be correlated with actual target operation in order to simplify future material investigation.

Section 2

PROGRAM RESULTS

2.1 NEW MATERIALS

Table 2-1 describes nine different dimethyl siloxane base materials which were evaluated during this program. Materials 1 and 2 were two different lots of the XR 63 493 which has been the basic deformographic material utilized in the DSDT up to the time of this program. During this program, these materials served as a standard for comparative performance of the new materials. Materials 3, 4, and 5 differ from the standard materials primarily in their molecular weight; their dispersity index numbers indicate that their molecular weight spectrums are relatively wide. Materials 6, 7, and 8 differ from the standard materials in molecular weight and dispersity index. Material 9 was submitted by error by the supplier and exhibited properties diametrically opposed to those desired for the DSDT.

Table 2-1

DIMETHYL SILOXANE BASE MATERIALS

No.	Material Identification	Molecular Weight		Dispersity Index
		Number Average	Weight Average	
1	XR 63 493, Lot 8	22,200	55,000	2.48
2	XR 63 493, Lot 09091	23.200	63,500	2.72
3	78 060, Lot 707-1	61,000	116,500	1.91
4	78 060, Lot 707-1	62,000	144,000	2.32
5	78 060 Lot 707-2	4,980	14,750	2.96
6	78 060, Lot 09092	29,200	35,500	1.23
7	78 060, Lot 10181	103,000	154,000	1.49
8	78 060, Lot 10182	136,000	232,000	1.71
9	78 060	18,100	103,755	2.15

As previously mentioned, the study was directed towards finding improvements in the remnant imagery effect, greater sensitivity, and better stability in the sensitivity figure; the material was also required to meet minimum standards of resolution and dynamic range.

The results of the alternate material investigation can be summarized as follows:

1) The molecular weight of the final material should fall within a weight average range between 25,000 and 60,000; higher molecular weight materials are difficult to handle and exhibit undesirable resolution and time response characteristics, lower molecular weight materials tend to produce a target which is too insensitive. The optimum molecular weight within this range will require further experimentation.

2) A material having a low dispersity index greatly enhances the performance of the DSDT target. The low dispersity index number indicates that the base material is of greater purity and more homogenous than materials having higher index numbers. These properties are reflected by lower remnant effect, better time response, and greater consistency of the sensitivity characteristic.

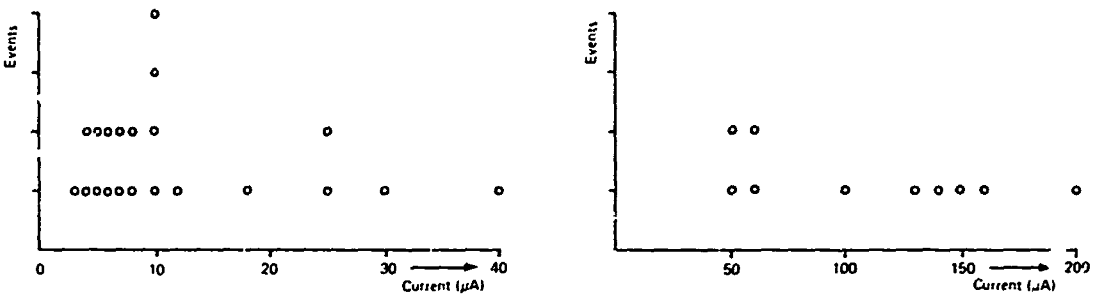
3) Material No. 6 (78 060, Lot 09092) provided DSDT targets which exhibited superior performance relative to the standard XR 63 493 compounds. The specific areas of notable improvement were a reduction in the remnant imagery effect by a factor of 3 to 5, a greater consistency in the sensitivity figure for the new targets, greater resistance to damage from excessive electrostatic charge, and a faster response time. These improvements were attributed primarily to the greater purity of the material and a more uniform and complete crosslinking of the polymer. Material No. 6 maintained resolution and dynamic range characteristics as good as or better than the standard XR 63 493 material.

2.2 TESTING

2.2.1 DEMOUNTABLE CRT TESTING

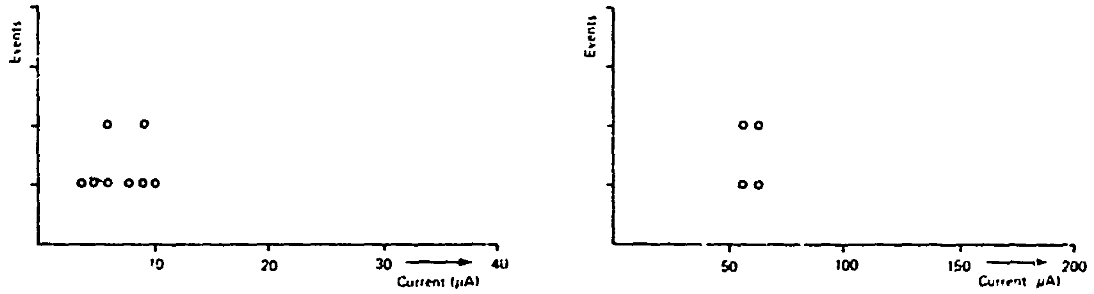
The performance of the materials tested was ascertained by utilizing the methods described in Subsection 1.2.2.

The results of the demountable CRT testing provided excellent data on the improvement in the variation of target sensitivity as a result of using a monodispersed base material. Figure 2-1 illustrates sensitivity data measured for a series of XR 63 493 targets and for a series of 78 060, Lot 09032 targets. The number of targets tested for 78 060, Lot 09092 was not sufficient for extensive statistical evaluation. However, it is felt that the scatter diagrams show a definite improvement in the repeatability for targets made from this material.



a. Targets from XR 63 493 Mix Ratio of 100:3.5

b. Targets from XR 63 493 Mix Ratio of 100:10



c. Targets from 78 060, Lot 09092 Mix Ratio of 100:4

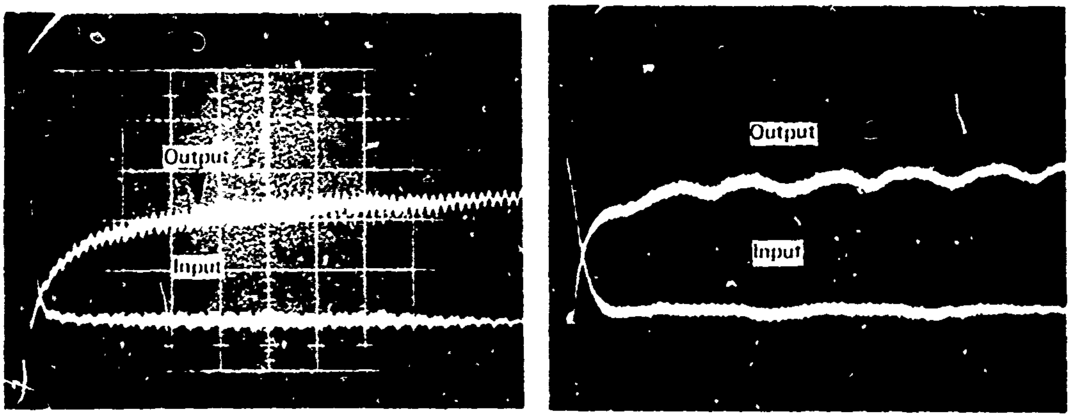
d. Targets from 78 060, Lot 09092 Mix Ratio of 100:10

Figure 2-1. Scatter Diagrams for the Sensitivity Results of Samples of Targets Made From XR 63 493 and 78 060, Lot 9092 Materials

The sensitivity measurements indicated the undesirability of using a material with a molecular weight as low as that of the 78 060, Lot 707-2. This material was found to be too inelastic and therefore too insensitive for use in the DSDT technology.

Light output measurements which were utilized to determine the contrast ratio of the image were also used to determine the development time, i.e., a measure of the response time of the materials. This measurement indicated the undesirability of high molecular weight materials since these materials exhibited excessive time response characteristics. Material 78 060, Lot 09092 showed a significant improvement in time response over the XR 63 493; Figure 2-2 illustrates the improved time response. The significance of this improvement is discussed in Subsection 3.2.4.

The undesirability of high molecular weight materials was also illustrated by a significant loss in resolution for those compounds with a molecular weight average greater than 100,000.



a. Time Response for XR 63 493
Absicissa. 50 ms/div
Ordinate: 30:1 contrast ratio

b. Time Response for 78 060, Lot 9092
Absicissa. 5 ms/div
Ordinate: 30:1 contrast ratio

Figure 2-2. Oscillographs of the Time Response for the Test Deformographic Material

Remnant imagery was evaluated by judging the performance of test targets and reference targets under the same operating conditions. The two observers were experienced in viewing imagery from the DSDT. The evaluation was an average of the subjective judgment of the observers. This assessment was not the primary test for remnant imagery; however, it did supply one source of evaluation and by utilizing experienced observers, the assessments were judged to be reasonably valid. Because of performance characteristics caused by low and high molecular weight, most of the materials were eliminated due to poor resolution, poor response time, or low sensitivity. Only material 78 060, Lot 09092 exhibited performance characteristics sufficiently good to advance to the remnant imagery test. The visual assessment of the targets made from this material indicated a significant improvement. The degree of improvement was judged to range from 3 to 10 times better than the effects viewed on targets made from the XR 63 493 material.

A standard test conducted on demountable targets is to subject the test target to an overwrite condition to determine its resistance to excessive charge. The targets fabricated from the 78 060, Lot 9092 material exhibited an increase in damage resistance relative to comparable XR 63 493 targets by a factor of 3 to 5.

2.2.2 IN-AIR TESTING

The in-air test provides information on sensitivity, time response, resolution, remnant effect, and target life. Since the first three items were addressed quite well by the demountable experiments, the in-air tests for this program consisted primarily of target evaluation for remnant effect and target life.

The method of testing utilized was to subject a glass slide of new material and a glass slide of standard XR 63 493 material to simultaneous deformation via an electronic cycling circuit. The electronic cycler had a nominal frequency of 15 Hz. The voltage of the deforming signal was scaled to produce a 30:1 contrast light output signal at the image plane.

Performance of the material was judged by noting the [illegible] at which each sample first manifested the remnant image effect; beyond that point, subjective judgment was used to differentiate between the magnitudes of the effect at any given total number of cycles. The last observation was aided by the configuration of the bus bars on the glass slides. Certain visual effects (patterns) would arise first on one sample slide and later on the other indicating a progressive degree of remnant imagery.

It was decided to cycle the test slides to destruction in order to achieve some estimate of life capability. Both the XR 63 493 and the 78 060, Lot 09092 targets achieved 18 million cycles without catastrophic failure, that is, their basic physical structure was intact. At this point in time both samples were quite remnant; however, photocell measurements showed that they both retained a deforming capability in response to the cycling waveform.

From the observations based on the onset of a visual indication of remnant imagery as well as comparing the degree of remnant effects visible at any particular time, it was judged that the new material exceeded the performance of the XR 63 493 material relative to resistance to remnant effects by a factor of approximately 5. Thus a significant improvement was achieved with material 78 060, Lot 09092.

Time response measurements of less than 2 ms were observed during these tests. As a result, additional demountable tests were conducted and a significant improvement over the XR 63 493 material was noted.

Section 3

DISCUSSION

3.1 TECHNOLOGY STATUS

At the beginning of this program, the basic deformable material (XR 63 493) was predictable only in a mix ratio between polymer base and crosslinking agent of 100:10. Since the 100:10 material is relatively insensitive, this limited the high confidence application of the DSDT to low to medium speed graphic displays and annotation applications. With the development of material 78 060, Lot 9092, confidence has been extended to a material which exhibits a sensitivity that is 5 to 10 times greater than the 100:10 mix ratio XR 63 493. This means that the DSDT can now be applied to such real-time sensor display requirements as radar, sonar, and possibly TV.

This material study program has resulted in a dialogue between IBM and Dow Corning (the material supplier) regarding the requirements of the DSDT and the properties achievable from various polymers. As a result of this dialogue, Dow Corning feels there exists a strong possibility of further improvement in the deformable material. Areas of potential improvement are in greater sensitivity and greater resistance to remnant effects.

IBM feels that Dow Corning has demonstrated competence during this program and can be expected to produce additional improvements if a joint program is allowed to continue. It is therefore recommended that means be found to continue the work initiated by this study.

3.2 PERFORMANCE IMPROVEMENTS

3.2.1 REMNANT EFFECT

The resistance of material 78 060, Lot 09092 to the remnant imagery effect was judged to be in the order of 5 times greater than that of XR 63 493 under equivalent operating conditions. This improvement was attributed to the greater purity and uniformity of the new material which resulted in a more uniformly crosslinked polymer.

It should be noted that the remnant effect has not been completely eliminated from the sensitive 78 060, Lot 09092 polymer. However, a significant improvement has been attained which will allow the DSDT to be tested in advanced experimental applications; the improvement also indicates the distinct possibility of subsequent improvements as a function of additional investigation. It should also be noted that the material sensitivity may be varied as a function of the application; many applications can be satisfied with less sensitive targets than those tested in this program; in that case the remnant effect can be virtually eliminated.

It should also be noted that the remnant effect appears to be sensitive to the rate of deformation as well as the total number of deformation cycles. It would therefore most probably be erroneous to conclude that the degree of remnant effect noted for 500,000 cycles attained at a rate of 1 Hz would be the same as for 500,000 cycles attained at a rate of 15 Hz. Furthermore, low to medium levels of remnant imagery have been observed to "heal" during inoperative periods of the DSDT. It is therefore quite difficult to visualize or predict just how the remnant imagery effect would manifest itself in an operational situation. In general, it appears that the effect would be less troublesome than it was at first thought.

Because of the time required for the investigation, the dependency of remnant effect versus cycle rate was not explored. However, because this dependency is felt to exist, no special significance has been attached to the value of the total number of cycles required to achieve a remnant effect. Rather these values have been utilized to draw a relative comparison between the test material and the standard material.

A relatively simple explanation of the cause of the remnant effect with the XR 63 493 material can be deduced from Section 6.4 of this report which concerns itself with the variation of crosslink density and elastic properties. At low crosslink densities, the molecules consist of long dangling chains which become intertwined with their neighbors to form the soft and easily deformed polymer associated with the mix ratio of 100:3.5. In this state, a portion of the energy of deformation is dissipated to its environment. This lost energy is associated with the remnant effect.

In contrast, the more highly crosslinked molecule formed from the mix ratio of 100:10 is spacially more segregated. The energy of deformation is transformed to potential energy within the molecule. When the applied electrical charge is removed, the potential energy is transformed into kinetic energy which caused the molecule to assume its original shape.

3.2.2 SENSITIVITY

In the fabrication of sensitive targets from XR 63 493 material, the ratio of basic to crosslinking agent produces a polymer of marginal stability. In addition, this material has a wide molecular weight distribution and contains plasticizers which cause nonuniform polymerization. As a result, targets from this material exhibit a relatively wide range of sensitivity characteristics, particularly when fabricated for high sensitivity.

The new 78 060, Lot 09092 material exhibits a much narrower molecular weight distribution and exhibits greater purity from other materials. As a result, the polymerization process has been more uniform and has therefore produced targets with greater consistency in sensitivity. This consistency of target fabrication is significant when considering the fabrication yield requirements for the DSDT for prototype or production application.

3.2.3 TARGET STRENGTH

Sensitive targets (100:3.5) fabricated from XR 63 493 material exhibited a sensitivity to permanent damage if excessive charge were deposited on the supporting substrate. The less sensitive targets (100:10) fabricated from XR 63 493 material successfully resisted damage from excessive charge. This capability was due partly to the total polymerization of the target in the 100:10 mix ratio.

In the case of the new material (78 060, Lot 9092) it was observed that when mixed to produce a target sensitivity equivalent to the 100:3.5 XR 63 493 target, the new material exhibited a greater resistance to damage from excessive charge. The degree of resistance was approximately 3 to 5 times greater. This resistance to damage was attributed to the greater degree of polymerization for this material.

3.2.4 TIME RESPONSE

In order for the DSDT to be compatible with a TV format it should have a time response (light output to signal input) of 10 to 20 ms and must be sufficiently sensitive to allow writing speeds compatible with TV rates. The standard XR 63 493 material exhibits a time response in excess of 50 ms when mixed in the sensitive 100:3.5 ratio. When mixed in the 100:10 ratio, its time response is in the order of 2 ms; however, because of the resultant target insensitivity, the CRT gun cannot provide sufficient deforming charge at TV writing rates. Material 78 060, Lot 9092 exhibits a development time in the order of 10 to 20 ms and a sensitivity similar to the 100:3.5 ratio of the XR 63 493 material. Therefore, this material has provided a significant step forward in achieving TV compatibility for the DSDT.

3.2.5 ANOMALY

During the preparation of the various test targets, an anomalous situation was encountered. One target of XR 63 493 mixed in the high sensitivity ratio of 100:3.5 exhibited performance parameters superior to all other sensitive targets tested during the program. This particular target was virtually free of remnant effects, exhibited good resistance to damage from excessive charge, and had nominal sensitivity, resolution, and dynamic range capabilities.

This performance was speculated to be the result of the manner of preparing the polymer mixture and possibly a poisoning of the catalytic agent in the crosslinking material. Attempts to duplicate the preparation procedure resulted in some improvement in subsequent XR 63 493 target performance. However, no other target of either test material exhibited the degree of capability represented by this particular target.

3.3 RECOMMENDATIONS

The DSDT technology has shown itself to have significant potential for handling diverse and complex display requirements. The primary need at the present time is the quantification and stabilization of the fabrication processes leading to prototype tubes for system evaluation. This program contributed to the progress in that direction. As mentioned in Section 3.1, it is felt that significant progress can still be attained in the material development area.

IBM would therefore make the following recommendations regarding the DSDT technology:

1) The present material development program should be continued as long as improved performance can be reasonably expected. At the present time it is expected that significant progress is still possible in the material area.

2) A tube development program be initiated to address the unique fabrication processes associated with the DSDT. Progress in the development and utilization of the DSDT requires a supply of prototype tubes and the confidence that the technology is capable of being reduced to production.

3) Specific application programs be initiated which will confirm the advantages of the DSDT. The results of these programs can be used to support decisions regarding either technology development or system configuration philosophy.

Section 4

TARGET PREPARATION

The prepolymers (base and crosslinking agent) as possible substitutes for XR 63 493 were mixed in various base-to-crosslink ratios. The mix ratios were performed in order to determine the approximate ratio of reactants which would yield a relatively soft, easily deformed polymer. The desired mixture of base and crosslinking agent was poured onto a demountable target substrate and spun so a resulting material thickness of 1.0 to 2.0 mils was attained. The entire demountable target was slowly elevated in temperature, 2°C per minute to 165°C, and held at this temperature for 16 hours to obtain the polymerized silicone. The target was then slowly cooled, 2°C per minute, to room temperature. The slow heating and cooling procedure is required to prevent the substrate from fracturing. The reflective coating was then applied and the finished target placed in the demountable DSDT for evaluation.

Section 5

TARGET TESTING

Two types of target testing methods were employed during the program: demountable CRT testing and in-air testing on special glass slides. Each testing method has its advantages; the demountable CRT tests provide sensitivity, dynamic range, resolution and time response results that are completely valid for interpreting into DSDT performance. The in-air slides provide a convenient means for life testing targets and for testing for the remnant imagery effect. In addition, once a valid correlation is established between glass slide operation and DSDT operation, the in-air tester provides the simplest and cheapest method of testing materials.

Considerable difficulty was experienced in fabricating the glass slides to be used in the in-air tester; as a result, more of the testing was conducted in the demountable CRT than originally planned. The glass slide fabrication problem was finally solved and a series of tests were conducted on the glass slides toward the end of the program. The in-air tester is now the prime method of testing materials and will be used for future evaluations.

5.1 DEMOUNTABLE DSDT

The demountable CRT used for our target evaluation is shown in Figure 5-1. It consists of a sealed tube body connected to a vacuum system by means of a 4-inch manifold. The faceplate as well as the electron guns are sealed into the tube with 0-rings. The target to be tested is mounted behind the faceplate by a series of spring clips which can be seen in Figure 5-1. The system is evacuated to the low 10^{-7} torr region, the guns activated, and the target evaluated using a schlieren optical system. Resolution, dynamic range, and time response measurements are performed at the image plane of the optical system. Sensitivity measurements are achieved by the utilization of a Faraday cage for measurement of beam current.

5.2 IN-AIR TESTING

Part of the plan for this program was the design and fabrication of an in-air test device for utilization in evaluating the various deformable materials. The rationale for such a device is that it would eliminate some of the variables associated with the substrate of a normal target and also some of the variables associated with the demountable CRT. In addition, considerable time and effort would be saved with such a device as opposed to the activity associated with testing a target in the demountable CRT.

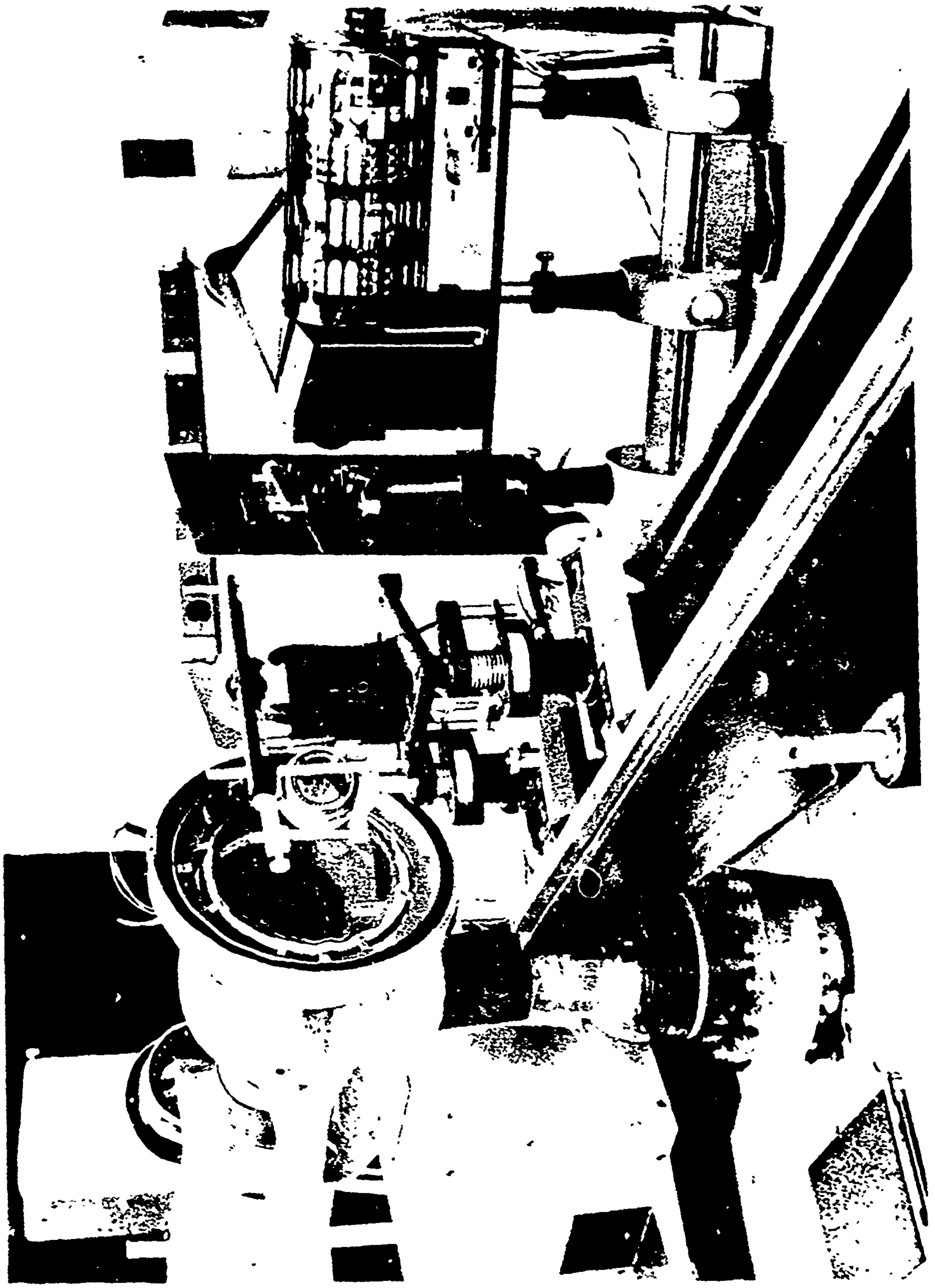


Figure 5-1. Demountable CRT Unit

When using the in-air testing method, the deformographic target material is coated directly onto a glass substrate. The substrates prepared for these evaluations were initially surface coated with 1000 Å of chromium. These were processed so that a series of six sets of 10 chromium lines connected to a common bus bar remained on the surface. These lines have approximately the same width as the beam from the DSDT write gun (1.6 mil). Spacing between the lines of each set is the same. The spacing varies from set to set for resolution determination (see Figure 5-2).

Two different experimental setups were prepared for evaluating the in-air target material. Each employed the same circuit for creating and erasing the deformation (see Figure 5-3).

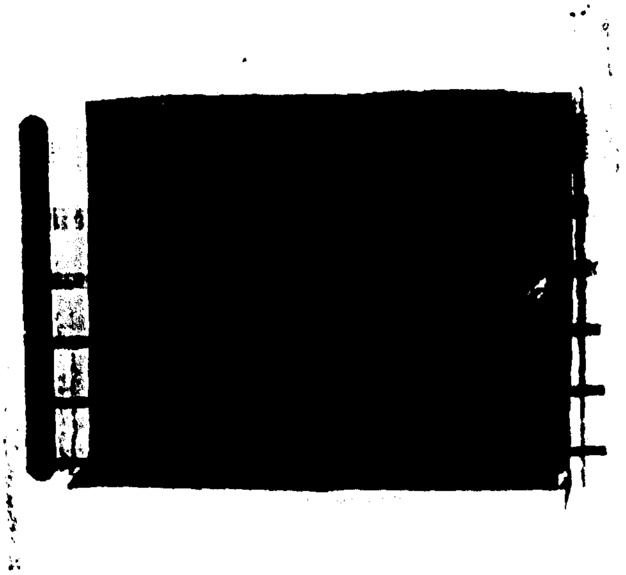


Figure 5-2. In-Air Target With Deformographic Coating and Reflective Layer

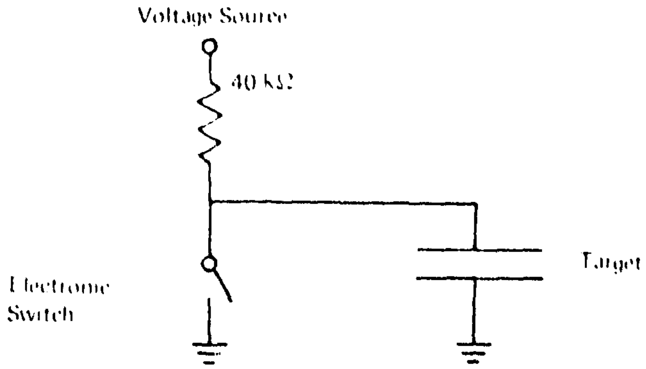


Figure 5-3. In-Air Testing Circuit

The first apparatus was an interferometric microscope on which the in-air test target was mounted (see Figure 5-4). With this, it was possible to actually photograph and measure the deformation which took place on the surface of the polymer as a function of different voltages applied to the bus bars (see Figures 5-5 and 5-6).

The spacing of the lines in these photographs was 8.0 mil. As the spacing between the lines becomes narrower, (Figures 5-7 and 5-8) one line interferes with adjacent lines; this effect enhances the deformation associated with the outermost lines. The effect is obvious in Figure 5-8 where the lines have 3.2-mil spacing. At a finer spacing, according to the interferometric photographs, the resolution of the 1.2- mil thick deformographic layer is lost.

The second apparatus for in-air testing duplicates the schlieren projection system of the demountable tube and uses the same reflective polymer surface on the glass slides as that of the demountable target surface. This setup was used to determine the voltage required to produce various contrast ratios on the glass slide targets. This setup (Figures 5-9 and 5-10) was also used to determine life expectancy of the target material, to measure time response, and to judge the remnant characteristic of each target material.

Figure 5-4. In-Air Tester With Interference Microscope

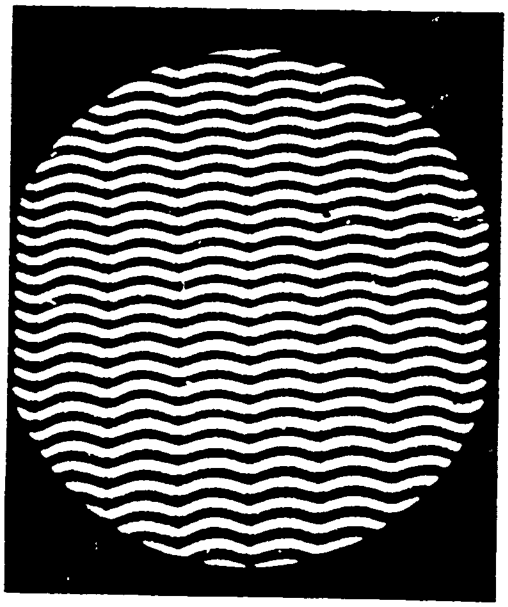


Figure 5-5. Interference Photomicrograph of Depth of Deformation (Voltage - 500 V)

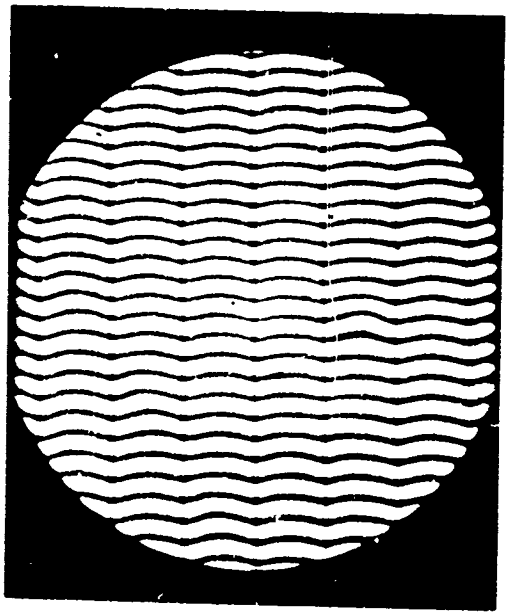


Figure 5-6. Interference Photomicrograph of Depth of Deformation (Voltage - 350 V)

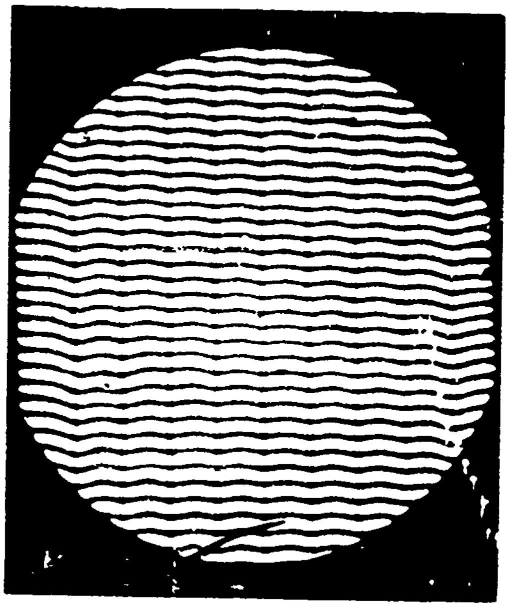


Figure 5-7. Interference Photomicrograph, Line Spacing - 5 mil (Voltage - 500 V)

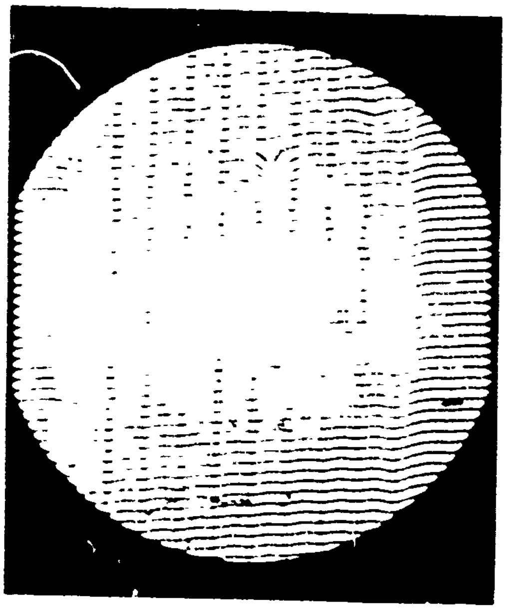


Figure 5-8. Interference Photomicrograph, Line Spacing - 3.2 mil (Voltage - 500 V)

Figure 5-9. In-Air Tester With Schlieren System

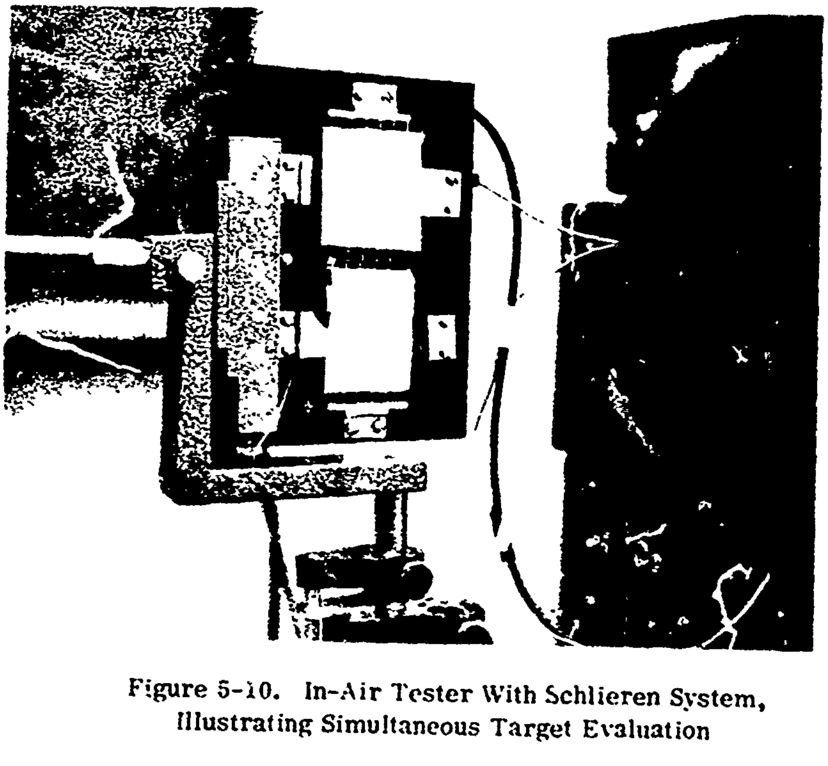


Figure 5-10. In-Air Tester With Schlieren System, Illustrating Simultaneous Target Evaluation

5.3 TEST DATA

This section contains samples of the test data taken during this program.

5.3.1 DEMOUNTABLE TESTS

Table 5-1 is a compilation of data for the performance of deformable targets as tested in the demountable CRT. Targets 161 to 286 are targets fabricated from XR 63 493 material prior to this program. These targets were selected somewhat randomly to serve as a data base for the program. Targets 557 to 666 were targets which were fabricated and tested during this program. Target 607 was the XR 63 493 target which exhibits the anomalous behavior described in Subsection 3.2.5.

5.3.2 IN-AIR TESTS

5.3.2.1 Deformation Calibration

Glass slides containing samples of 100:3.5 mix ratio of XR 63 493 and 100:4.0 mix ratio of 78 060, Lot 09092 materials were prepared and tested on the in-air cycler. It was determined that a 500 V signal on the bus bars would create a 30:1 contrast at the schlieren system's image plane for each sample. Thus, for ensuing remnance and life tests, the degree of deformation would be matched and need not be considered as an additional parameter.

5.3.2.2 Interferometric Microscope Measurements

The in-air test target of 78 060, Lot 09092 material was mounted on an interferometric microscope so the surface behavior could be photographed and evaluated during and after deformation cycling. The voltage amplitudes derived from the previous calibration procedure were used to deform the test material.

The deflection depth of the deformable surfaces can be determined by utilizing the photographs in Figures 5-5 and 5-6 and the relationship:

$$\text{Depth of Deformation} = \frac{\text{fringe deflection}}{\text{fringe interval}} \times \frac{\lambda}{2}$$

In the two cases shown, the measured quantities were:

Voltage 500 V fringe deflection = 18
fringe interval = 55

Voltage 350 V fringe deflection = 16
fringe interval = 55

For the thallium light source utilized: $\lambda = 0.54\mu$, thus

$$\text{Depth of Deformation (500 V)} = 0.09\mu$$

$$\text{Depth of Deformation (350 V)} = 0.08\mu$$

After cycling the test slides for approximately 20 million cycles, the measurements were repeated under a 0 V condition. No discernible deformation was detected.

5.3.2.3 Schlieren Remnant Effect Tests

Table 5-2 is representative of the remnant effect test conducted on the in-air tester with a schlieren viewing system. Observers were given adjectives of none, slight, definite, and heavy to describe the remnant effect as they observed it. They were also asked to attempt to quantify the performance ratio at the time of observation; i.e., the difference between materials A and B. After the test, each observer was also asked to judge the overall improvement ratio of the new material. Because of the quantification intervals defined by the descriptive words and the sample points in the cycle history, there was little variation in the verbal observation results. However, the attempts to quantify the degree of difference between the behavior of the two materials did illustrate a variation in observer opinion.

The test slides were cycled 18 million times. At this point, the remnant effect was quite heavy in each slide; however, deformation was still taking place, and the cycling effect was observable at the image plane. Examination of the target surface revealed no structural failure in the material or the metal surface.

5.3.2.4 Material Time Response

During the course of the in-air testing, the response of the output signal was measured relative to the cycling waveform. It was found that the response was essentially following the rise time of the input wareform; i.e., approximately 2 ms. This was a very significant and somewhat unexpected increase over the XR 63 493 material. Because the demountable experiments had not indicated such a dramatic increase, additional targets (658, 659, 666) were made and tested. It was observed that the charging effects of the target substrate introduced an increase in the time response. In addition, the asymptotic behavior of the light output waveform as well as the interference riding on the signal tended to obscure the definition of the 90% point. It is also felt that a certain amount of preconditioning of the observers relative to the XR 63 493 material caused the original target readings to be high. However, Figure 2-2 illustrates an important result; material 78 060, Lot 09092, exhibits a time response characteristic approximately 5 to 10 times better than material XR 63 493.

Table 5-1

OBSERVATIONS OF TARGET PERFORMANCE UNDER TEST IN THE DEMOUNTABLE CRT

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
TARGETS PREVIOUSLY TESTED						
161	10% XR 63 493	1.5	>190	50	None	-
162	10% XR 63 493	1.5	>190	50	None	-
166	10% XR 63 493	1.3	>190	60	None	-
169	10% XR 63 493	1.3	>190	60	None	-
262	10% XR 63 493	1.2	170	100	Yes	-
244	10% XR 63 493	1.9	---	150	Yes	-
78	10% XR 63 493	1.1	>190	160	Yes	-
79	10% XR 63 493	1.2	>190	130	None	-
80	10% XR 63 493	1.2	>190	140	None	-
81	10% XR 63 493	1.3	>190	200	None	-
131	3.5% XR 63 493	1.8	-	8	Slight	100
136	3.5% XR 63 493	1.7	-	6	Slight	100
202	3.5% XR 63 493	1.8	-	30	Slight	-

Table 5-1. Observations of Target Performance Under Test in the Demountable CRT (cont)

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
TARGETS PREVIOUSLY TESTED						
207	3.5% XR 63 493	1.5	-	12	Slight	60
208	3.5% XR 63 493	1.5	-	40	Slight	-
209	3.5% XR 63 493	1.7	-	50	Slight	-
212	3.5% XR 63 493	2.1	-	25	Slight	-
213	3.5% XR 63 493	2.3	-	25	Slight	-
219	3.5% XR 63 493	1.3	200	10	Slight	100
220	3.5% XR 63 493	1.9	200	18	Slight	-
222	3.5% XR 63 493	1.8	180	10	Yes	60
226	3.5% XR 63 493	1.3	250	7	Yes	80
227	3.5% XR 63 493	1.4	250	10	Yes	-
228	3.5% XR 63 493	1.4	250	6	Yes	100
231	3.5% XR 63 493	1.4	250	7	Yes	100
232	3.5% XR 63 493	1.5	250	8	Yes	-
233	3.5% XR 63 493	1.4	250	10	Yes	-

Table 5-1. Observations of Target Performance Under Test in the Demountable CRT (cont)

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
TARGET PREVIOUSLY TESTED						
263	3.5% XR 63 493	1.3	250	3.5	Yes	100
264	3.5% XR 63 493	1.3	225	4.5	Faint	60
277	3.5% XR 63 493	1.3	250	4.0	Faint	-
285	3.5% XR 63 493	1.2	250	3	Faint	-
286	3.5% XR 63 493	1.2	250	4.5	Faint	-
NEW TARGET MATERIAL TESTED						
557	3.5% 78 060, Lot 707-1	>4.0	Broad	Slow	-	Slow
559	3.5 78 060, Lot 707-2	1.5	< 200	35	Yes	-
560	3.5% 78 060, Lot 707-2	1.5	200	35	Yes	-
561	10% XR 63 493	0.4	Very Poor	160	-	-
562	10% XR 63 493	1.1	< 200	60	Very Faint	-
568	3.5% 78 060, Lot 707-1	2.2	<< 200	10	Heavy	Very Slow

Table 5-1. Observations of Target Performance Under Test in the Demountable CRT (cont)

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
NEW TARGET MATERIAL TESTED						
569	3.5% 78 060, Lot 707-1	0.8	200	15	Heavy	-
576	3.5% XR 63 493	1.1	190	45	None	-
577	3.5% XR 63 493	1.1	190	30	None	-
579	200% 78 060, Lot 707-2	0.7	<190	60	None	-
580	3.5% XR 63 493	1.2	200	6.0	Yes	-
598	4% 78 060, Lot 09092	0.7	220	5.5	Slight	40
599	4% 78 060, Lot 09092	0.8	220	5.5	Slight	80-100
600	3.5% XR 63 493, Lot 09091	1.4	220	4.5	Heavy	-
603	4% 78,060 Lot 09092	1.2	220	4.0	-	50
604	4% 78 060, Lot 09092	1.1	220	4.7	Slight	40

Table 5-1. Observations of Target Performance Under Test in the Demountable CRT (cont)

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
NEW TARGET MATERIAL TESTED						
605	4% 78 060, Lot 09092	1.1	220	8.0	Slight	-
606	3.5% XR 63 493	1.3	200	8.0	Heavy	-
607	3.5% XR 63 493 Lot 09091	1.2	225+	9	Very Slight	-
609	5% 78 060, Lot 09092	1.2	225	10	Slight	-
610	5% 78 060, Lot 09092	1.3	200	17	None	-
612	10% 78 060 Lot 09092	1.2	200	60	None	0.100
613	10% 78 060, Lot 09092	1.2	200	55	None	0.100
614	10% 78 060, Lot 09092	1.1	200	55	None	0.100
615	10% 78 060, Lot 09092	1.2	200	60	None	0.100
618	5% 78 060, Lot 10181	1.2	225	40	-	Very Slow

Table 5-1. Observations of Target Performance Under Test in the Demountable CRT (cont)

Target No.	Material Ratio Crosslinker (per 100 parts base-by wgt)	Material Thickness (mil)	Resolution (lines/inch)	Sensitivity (μA @ 5000 in/sec)	Residual	Develop Time (ms)
NEW TARGET MATERIAL TESTED						
619	5% 78 060 Lot . 0182	1.0	220	25	Yes - Fade Quickly	Very Slow
629	5% 78 060, Lot 10181	1.2	200	20	-	Very Slow
633	10% 78 060, Lot 10182	1.4	200	75-100	-	Very Slow
634	10% 78 060, Lot 10182	1.1	-	20	-	Very Slow
636	10% 78 060, Lot 10181	1.5	200	30	-	Very Slow
637	10% 78 060, Lot 10181	1.4	200	20	-	Very Slow
658	4% 78 060, Lot 09092	1.2	225	9	-	<20
659	4% 78 060, Lot 09092	1.2	200	9	-	<20
666	4% 78 060, Lot 09092	1.1	225	10	-	10-20

Table 5-2

REMNANT EFFECT VS ACCUMULATED CYCLES

Observer	1.6×10^5 Cycles	3.6×10^5 Cycles	1.1×10^6 Cycles	9.5×10^6 Cycles	Overall Improvement Ratio A:B
1	A - None B - Slight A/B = ∞	A - Slight B - Definite A/B = 5:1	A - Definite B - Heavy A/B = 3:1	A - Heavy B - V. Heavy A/B = 3:1	5:1
2	A - None B - Slight A/B = ∞	A - Slight B - Definite A/B = 10:1	A - Definite B - Heavy A/B = 5-10:1	A - Heavy B - Heavy A/B = 2:1	7-10:1
3	A - None B - Slight A/B = ∞	A - Slight B - Definite A/B = 5:1	A - Definite B - Heavy A/B = 3:1	A - Heavy B - Heavy A/B = 2:1	3-5:1
4	A - None B - Slight A/B = ∞	A - Slight B - Definite A/B = 5-10:1	A - Definite B - Heavy A/B = 5:1	A - Heavy B - Heavy A/B = 2:1	5:1

Test Conditions: Material A : 78 060, Lot 09092, Mix Ratio of 100:4
Material B : XR 63 493, Mix Ratio of 100:3.5
Cycle Rate : 15 Hz (500 V)

Section 6

PARAMETRIC ANALYSIS

The formation of the deformable silicone film is an extremely complex process from the chemical viewpoint. It is well known that small amounts of airborne contaminants can adversely affect the polymerization of relatively thick layers of silicone rubbers. In thin layers this effect is greatly pronounced. Variability of the resulting polymer is further increased by a wide molecular weight spectrum of the starting materials of which the XR 63 493 base and crosslinking agent are examples. Polymerization and nonpolymerization of the same mixture of base and crosslinking agent on two similar substrates has been experienced. As discussed in Section 1.1, the DSDT technology requires the use of low base-to-crosslinker ratios. The chemistry of preparation of the silicone rubber formed by less than the suggested amount of crosslinking agent has therefore been the subject of a portion of this investigation. The latter was investigated by differential thermal analysis. The effect of molecular weight and molecular weight distribution within a given starting material also has a profound effect on the properties of the final silicone polymer. This was the object of performing the gel phase chromatographic investigation on each of the materials.

Much of this parametric study was limited to the XR 63 493 material, since it was typical of the compounds which were investigated and the test materials were in limited supply.[1] With the limited amount of the monodispersed samples available, only the Young's modulus and gel phase chromatography tests were run on these materials.

6.1 GEL PHASE CHROMATOGRAPHY

The samples of each base were weighed and dissolved in tetrahydrofuran to produce 1.0% weight/weight solutions. These solutions were injected via the sample loop into a Water's chromatograph with pore-sizes ranging from 2000 Å to 60 Å. The data was recorded on-line through the IBM 1800 Data Acquisition System's analog-to-digital interface using programs developed at IBM Endicott. The chromatograms were normalized to one obtained from Dow-Corning (Figure 6-1) for the XR 63 493 material so that the molecular weights may be regarded as absolute. (Refer to Table 6-1.)

This data indicates the wide range of molecular weight distribution in all the materials with the exception of Lot 09092, Lot 10181, and Lot 10182 which are the monodispersed series of base materials. The chromatograms of Figures 6-2 through 6-10 depict the molecular weight and molecular weight distribution of the samples in Table 6-1.

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[1] The bulk of the data for Sections 6.2 and 6.3 were extracted from work performed by the IBM Research Division under a previous development effort.

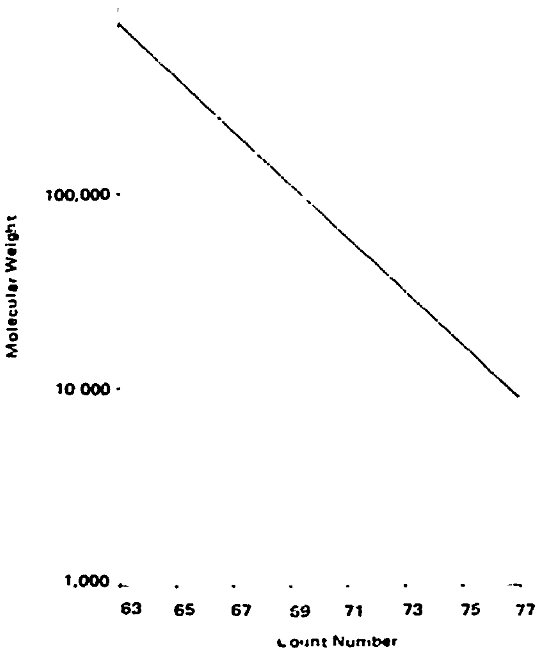


Figure 6-1. Gel Phase Chromatography Calibration Curve

Table 6-1

GEL PERMEATION DATA ON DOW-CORNING DIMETHYL SILOXANE BASE MATERIALS

Base	Molecular Weight		Dispersity Index
	Number Average	Weight Average	
XR 63 493, Lot 8	22,200	55,000	2.48
XR 63 493, Lot 09091	23,200	63,500	2.72
78 060, Lot 707-1	61,000	116,500	1.91
78 060, Lot 707-1	62,000	144,000	2.32
78 060, Lot 707-2	4,980	14,750	2.96
78 060	48,100	103,700	2.15
78 060, Lot 09092	29,200	35,500	1.23
78 060, Lot 10181	103,000	154,000	1.49
78 060, Lot 10182	136,000	232,000	1.71

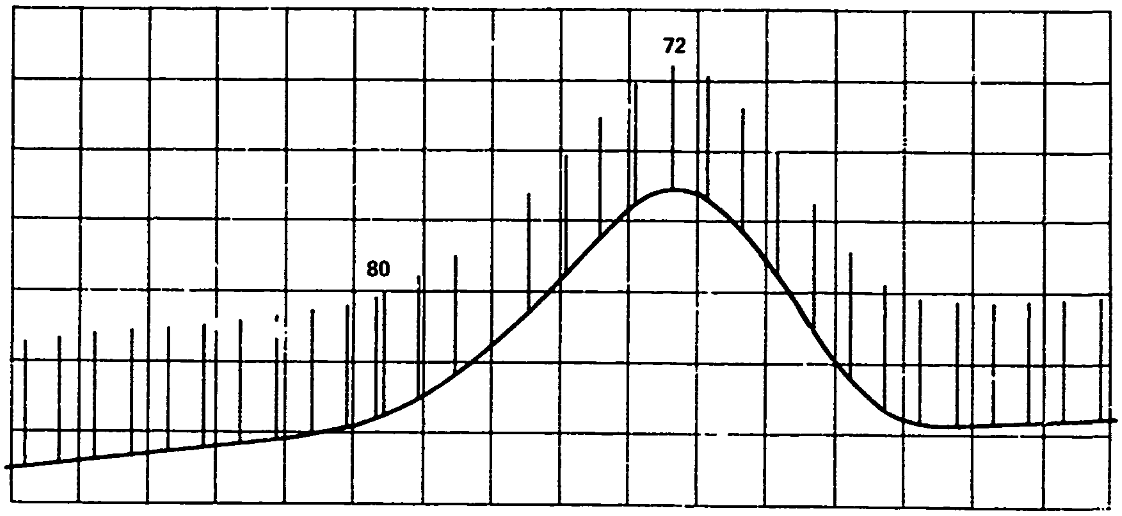


Figure 6-2. Chromatogram of Dow Corning XR 63 493, Lot 8

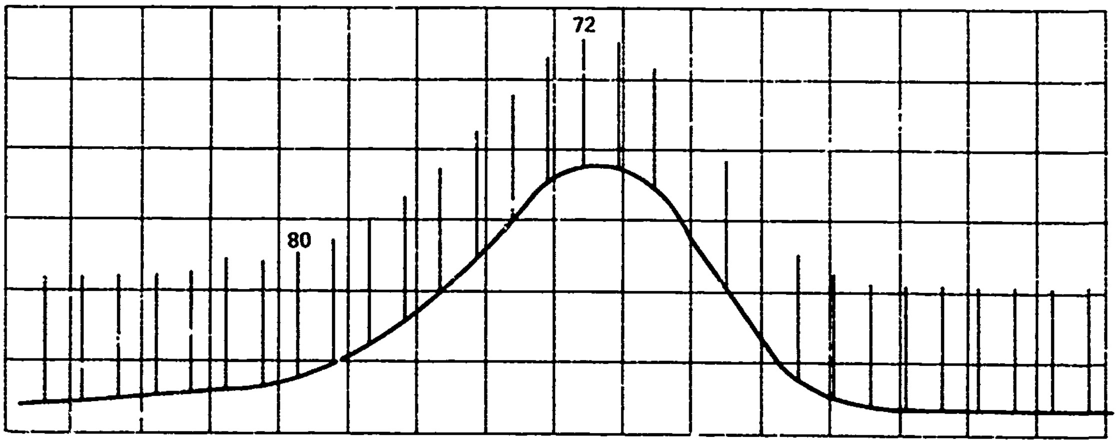


Figure 6-3. Chromatogram of Dow Corning XR 63 493, Lot 09091

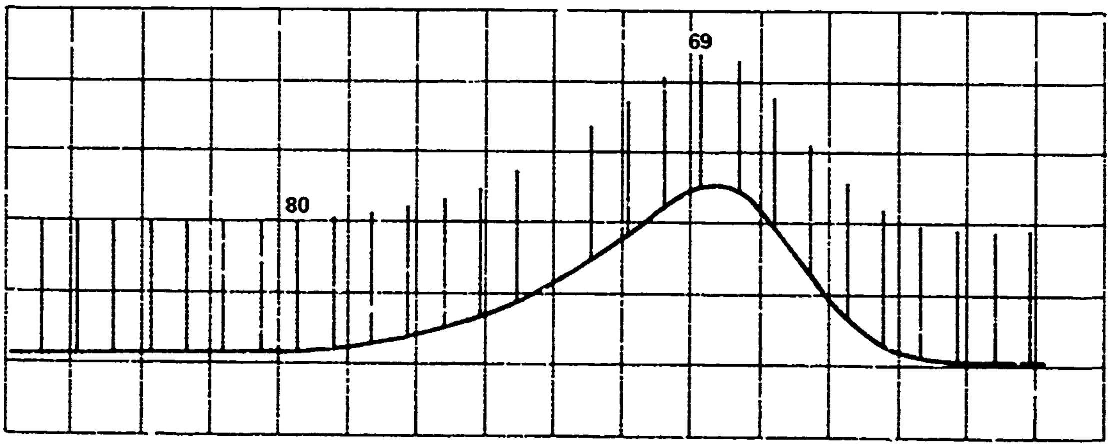


Figure 6-4. Chromatogram of Dow Corning 78 060, Lot 0707-1

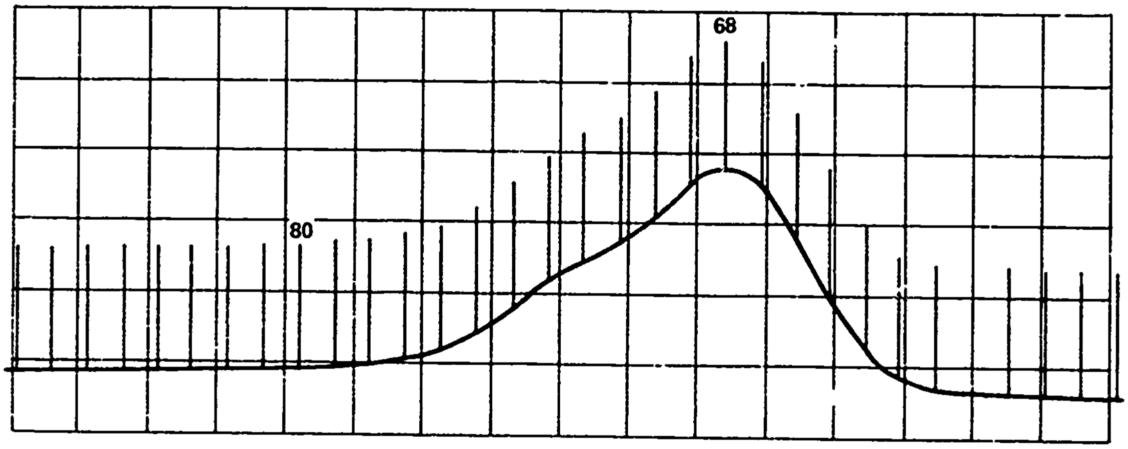


Figure 6-5. Chromatogram of Dow Corning 78 060, Lot 0707-1

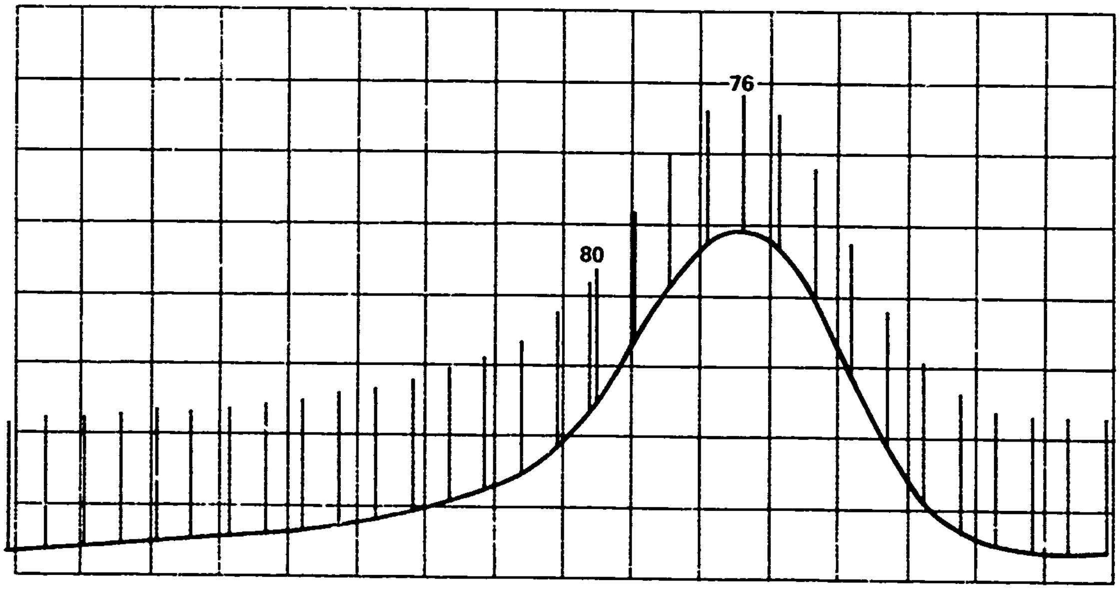


Figure 6-6. Chromatogram of Dow Corning 78 060, Lot 0707-2

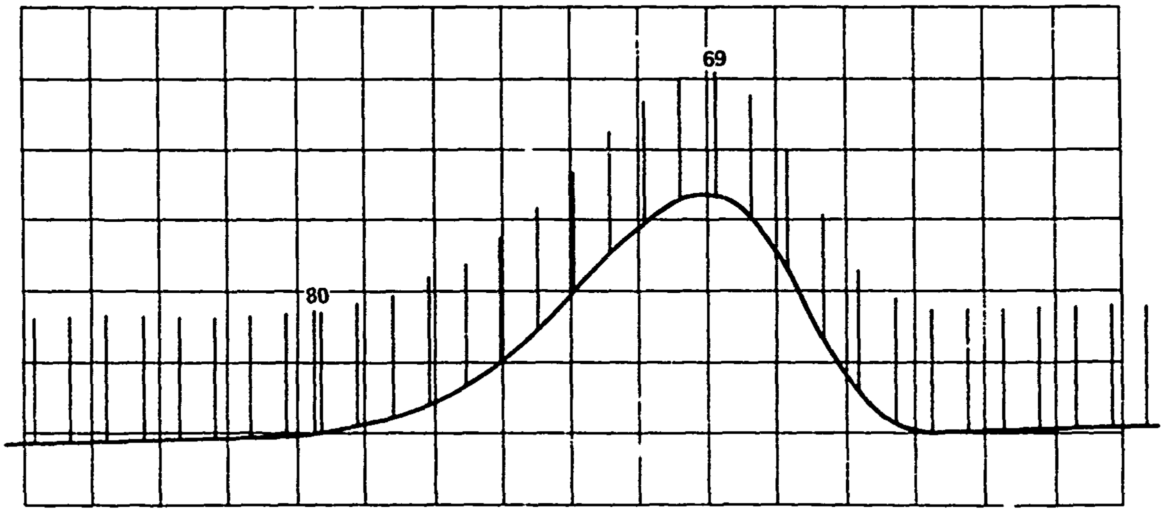


Figure 6-7. Chromatogram of Dow Corning 78 060

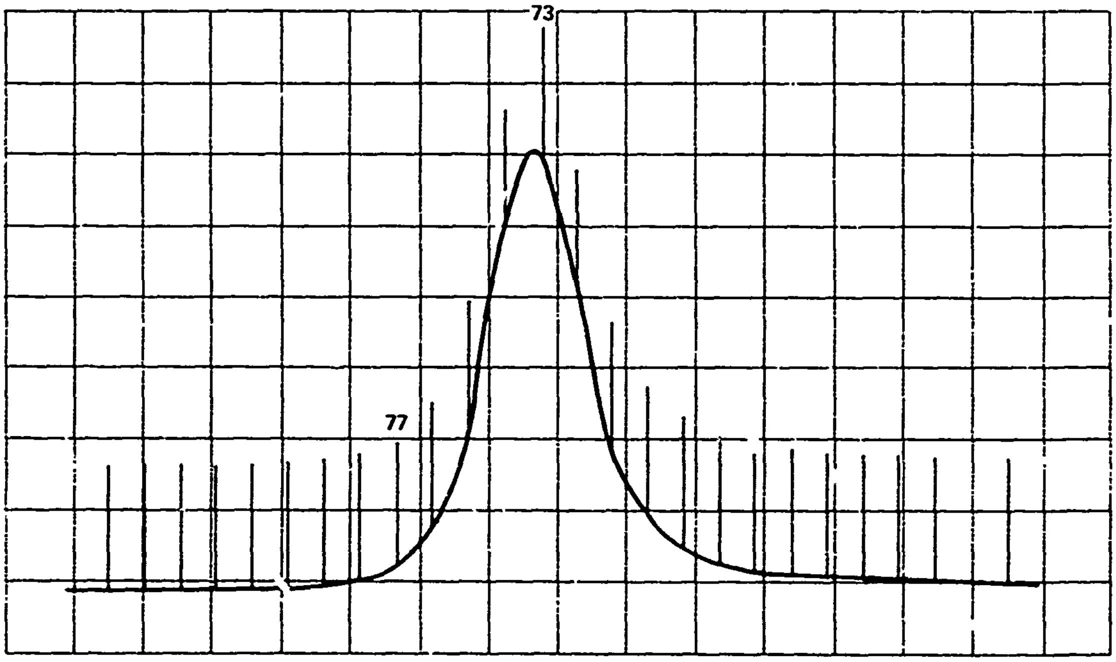


Figure 6-8. Chromatogram of Dow Corning 78 060, Lot 09092

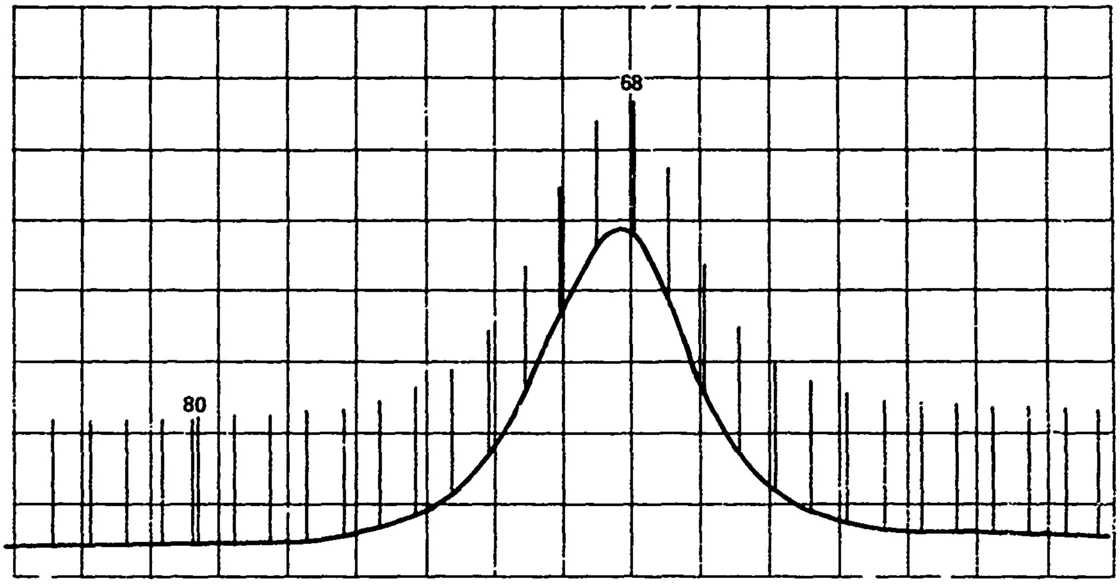


Figure 6-9. Chromatogram of Dow Corning 78 060, Lot 10181

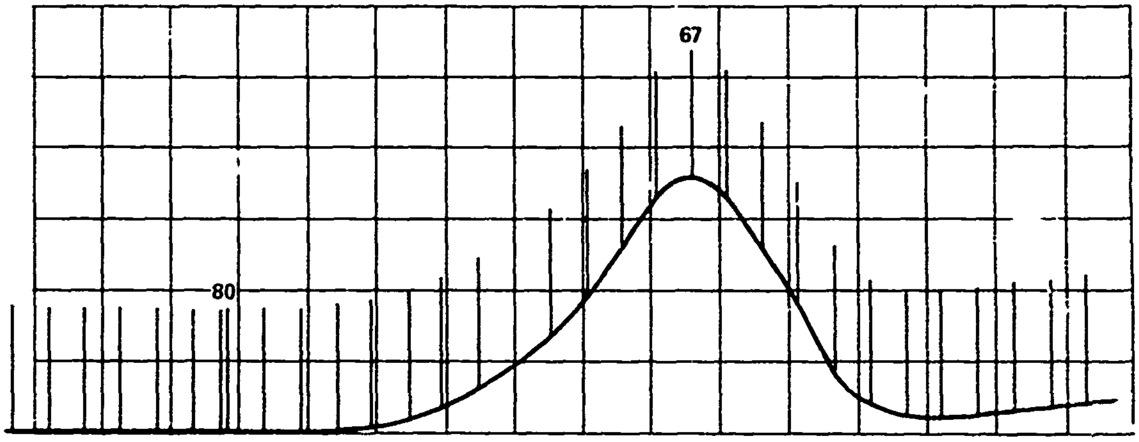


Figure 6-10. Chromatogram of Dow Corning 78 060, Lot 10182

An additional difference in the compounds of Table 6-1 is the absence of cyclic dimethyl siloxane in the monodispersed samples in comparison to the other bases. These cyclic compounds do not undergo polymerization but act as plasticizers when the polymer is formed.

6.2 DIFFERENTIAL THERMAL ANALYSIS

The purpose of this work was to determine the reaction conditions under which the two-part silicone system XR 63 493, would polymerize. This polymerization or crosslinking was attributable to those exotherms which were evidenced in the mixture of base and crosslinking agent and not seen in the individual components. The effect of oxygen on the polymerization was also to be determined.

Samples of XR 63 493 in two mixtures of base-to-crosslinking agent were studied; 42.8% base to 57.2% crosslinker, and 96.6% base at 3.4% crosslinker. The samples were sealed in cold welded aluminum cells under both air and pure nitrogen. The samples were heated at 20°C per minute in a duPont 900 Thermo Mechanical Analyzer apparatus equipped with a differential scanning calorimeter cell. The change in temperature (ΔT) signal was recorded at a sensitivity of 0.008 mV/in and the temperature (T) signal recorded at 0.8 mV/in (nominal 20°C/in). The peaks were positioned along the X-axis with the 5 and 10-inch suppression controls.

6.2.1 XR 63 493 BASE

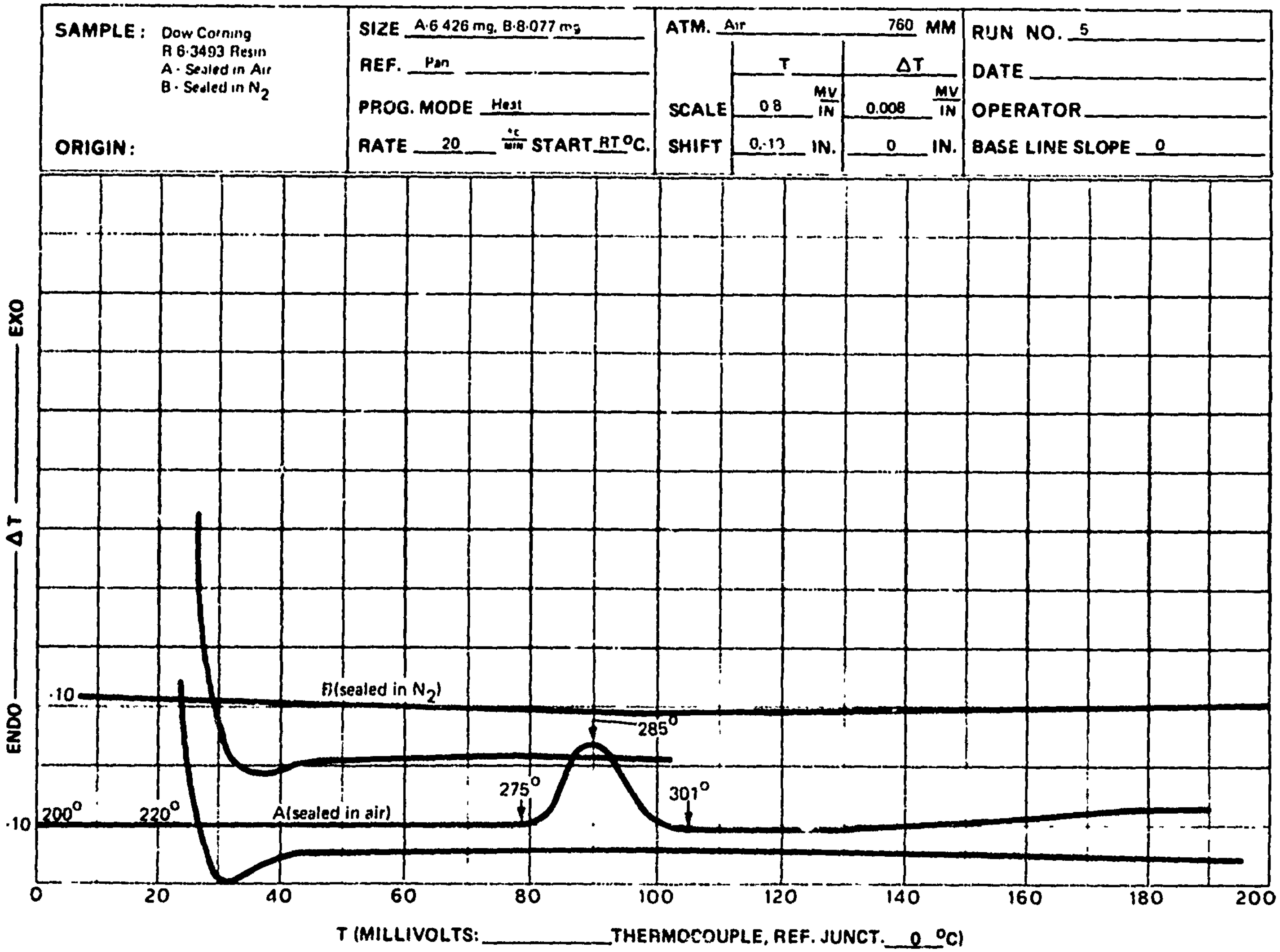
This base material when run in a nitrogen atmosphere with oxygen carefully excluded gave no exothermal reactions from 20°C to 400°C. When sealed with air in the overhead, an exothermal reaction starting at 275°C with a maximum at 285°C and ending at 301°C was noted. It was assumed that this reaction was incomplete, since the only source of oxygen was the 0.05 ml overhead space in the cold welded pan. The product was a gel. See Figure 6-11 for the thermogram.

6.2.2 XR 63 493 CROSSLINKER

The crosslinker sealed in air gave a broad exotherm starting at 185°C with a maximum at 209°C and concluding at 223°C (see Figure 6-12). It was assumed that this reaction was also incomplete for the reasons given in Subsection 6.2.1. A fresh sample sealed in nitrogen showed no reactions up to 400° C. This nitrogen sealed sample was cooled, holes were punched in the hermetic seal and the sample was reheated. A very large exothermal reaction (see Figure 6-13) started at 175°C and continued until the end of heating. The product was a gel. It is obvious that given sufficient oxygen, the crosslinker will react exothermally much more completely than that noted in Figure 6-12.

6.2.3 CROSSLINKER/BASE MIXTURES

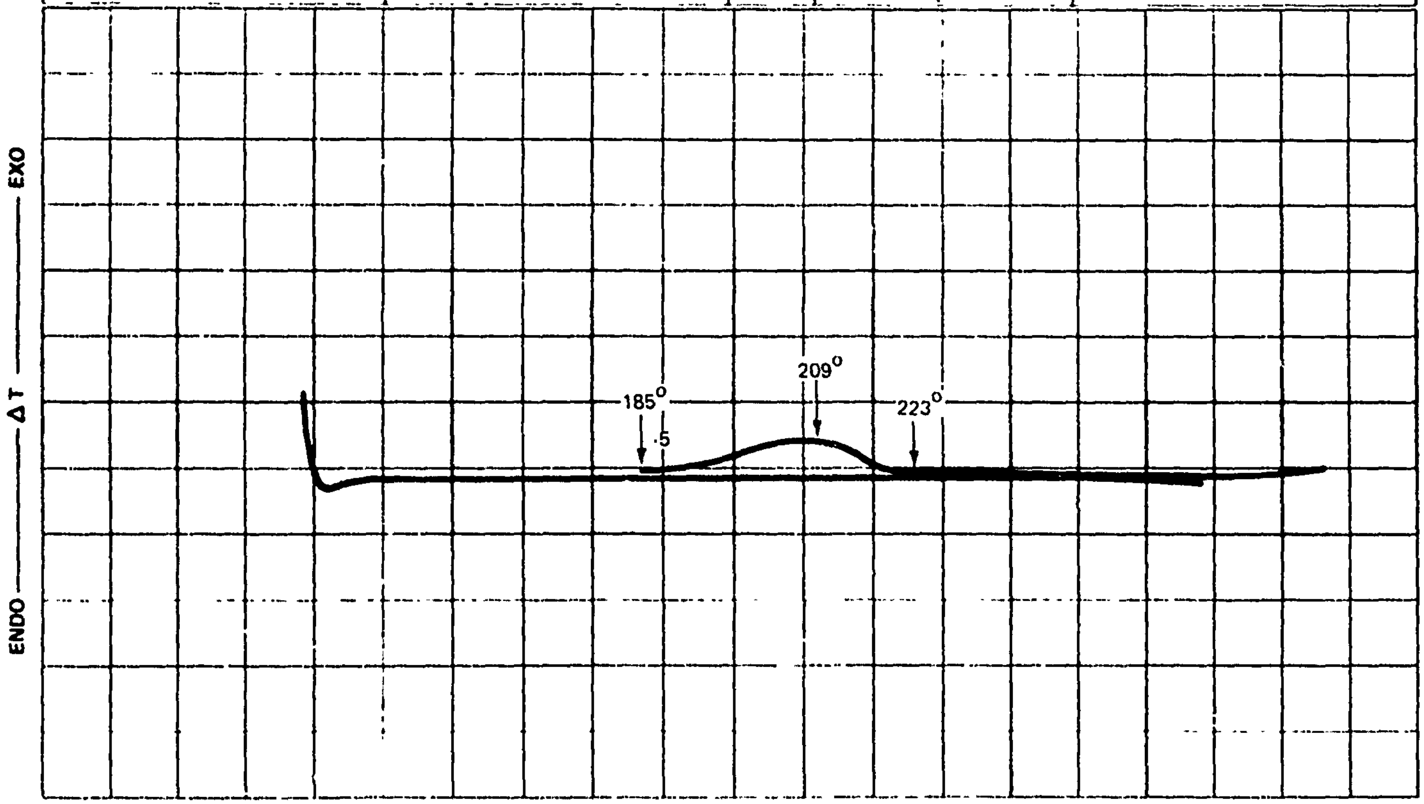
The 57.2% 42.8% mixture sealed in air showed a sharp exotherm starting at 81°C with a maximum at 109°C and a conclusion near 123°C. A second, much broader and thermally larger exotherm, started at 171°C with a maximum near 219°C and a broad exothermal shoulder up to 370°C, see Figure 6-14. The same mixture sealed in nitrogen (fresh sample) produced a sharp exotherm starting at 69°C with maximum at 107°C and a conclusion at 125°C, see Figure 6-15. This is substantially the same exotherm as noted in Figure 6-14. Although a program error interrupted heating for 3 seconds it is evident that the 219°C peak is not shown by the nitrogen blanketed sample. The broad exothermal shoulder is present. A second heating showed no additional curing. A small peak occurred near 82°C which is not explainable at present. The products from the air and nitrogen heatings were firm rubbers.



SAMPLE: Dow Corning R 6-3493 Resin A - Sealed in Air B - Sealed in N_2
ORIGIN:
SIZE A-6 426 mg, B-8 077 mg
REF. Pan
PROG. MODE Heat
RATE 20 °c/min START RT °C.
ATM. Air 760 MM
SCALE T 0 8 MV/IN ΔT 0.008 MV/IN
SHIFT T 0.-1? IN. ΔT 0 IN.
RUN NO. 5
DATE
OPERATOR
BASE LINE SLOPE 0

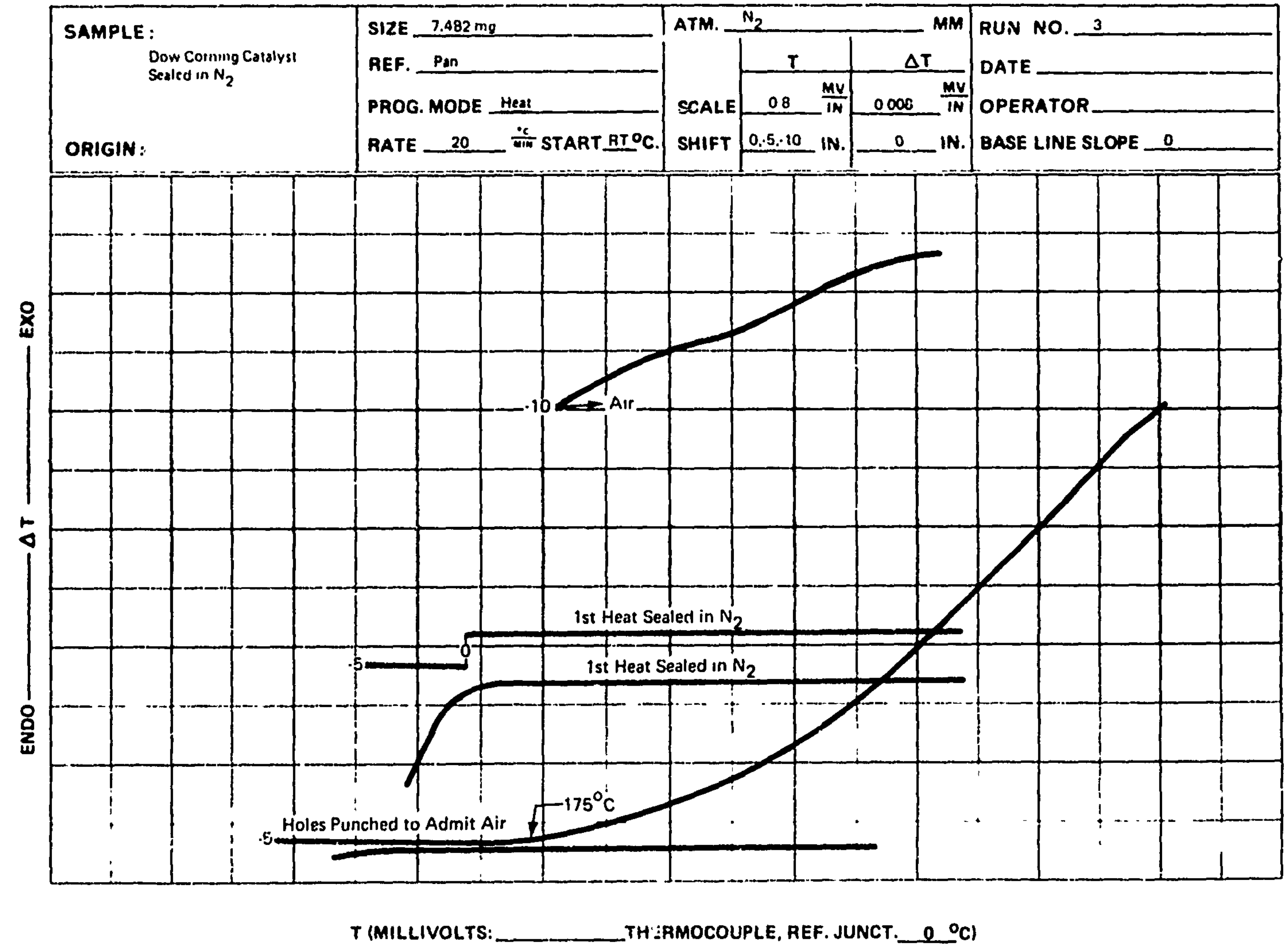
Figure 6-11. Thermograms for XR 63 493 Base Material Sealed in Air and Nitrogen

SAMPLE: Dow Corning Catalyst Sealed in Air	SIZE 3 0325 mg	ATM. N_2 760 MM	RUN NO. 1
	REF. Pan	T / ΔT	DATE
	PROG. MODE Heat	SCALE 0 8 MV/IN / 0 008 MV/IN	OPERATOR
ORIGIN:	RATE 10 °C/MIN START RT °C.	SHIFT IN. / 0 IN.	BASE LINE SLOPE 0



T (MILLIVOLTS:__________THERMOCOUPLE, REF. JUNCT. 0 °C)

Figure 6-12. Thermogram for XR 63 4°^ Cro. ''nk Material Sealed in Air



SAMPLE: Dow Corning Catalyst Sealed in N_2

ORIGIN:

SIZE 7.482 mg

REF. Pan

PROG. MODE Heat

RATE 20 °C/MIN START RT °C.

ATM. N_2 MM

	T	ΔT
SCALE	0.8 MV/IN	0.008 MV/IN
SHIFT	0,-5,-10 IN.	0 IN.

RUN NO. 3

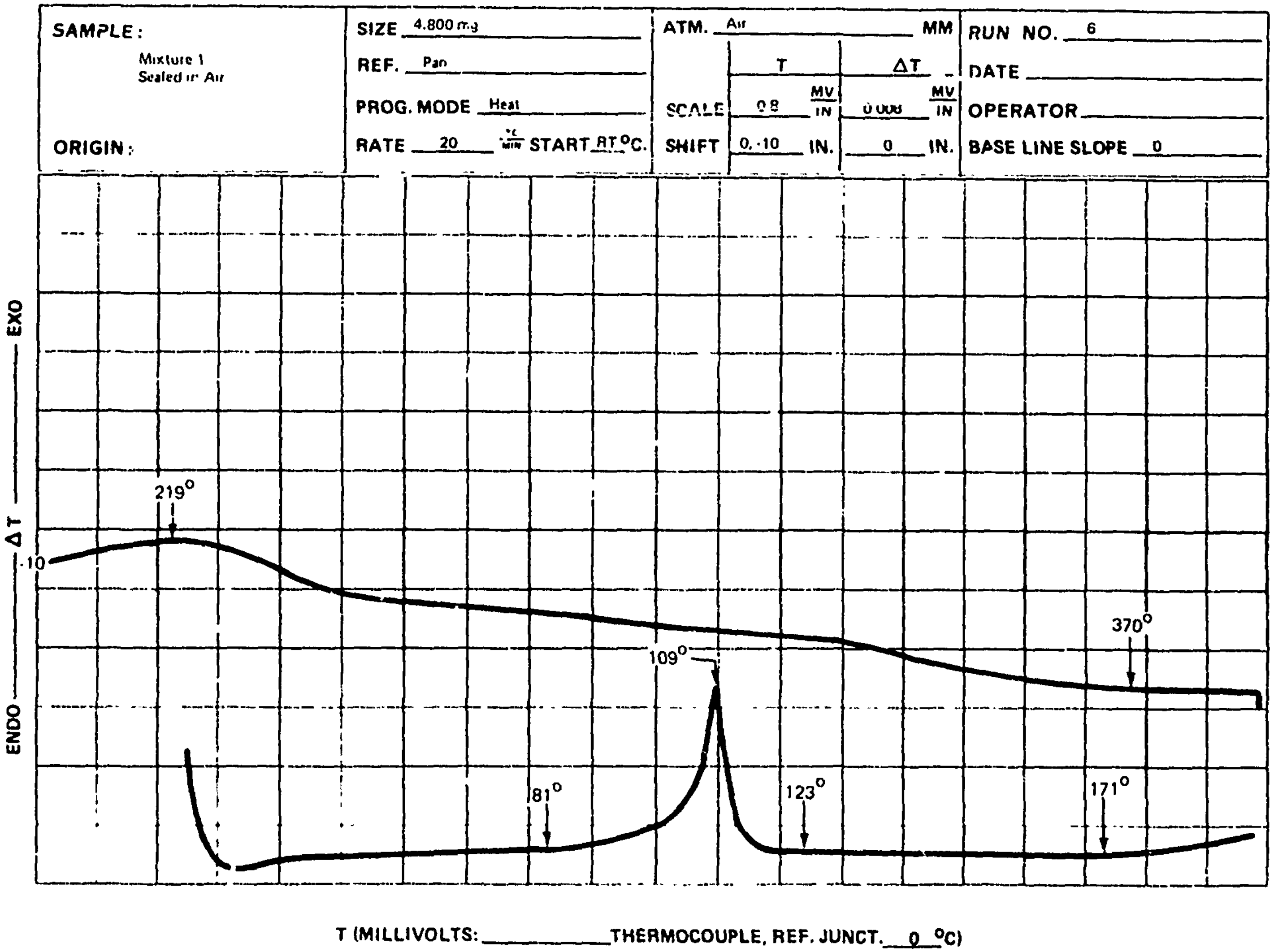
DATE

OPERATOR

BASE LINE SLOPE 0

T (MILLIVOLTS: THERMOCOUPLE, REF. JUNCT. 0 °C)

Figure 6-13. Thermogram for XR 63 493 C[illegible] Material Sealed in Nitrogen and in Air



SAMPLE: Mixture 1 Sealed in Air

ORIGIN:

SIZE 4.800 mg

REF. Pan

PROG. MODE Heat

RATE 20 °C/MIN START RT °C.

ATM. Air MM

	T	ΔT
SCALE	0.8 MV/IN	0.008 MV/IN
SHIFT	0, ·10 IN.	0 IN.

RUN NO. 6

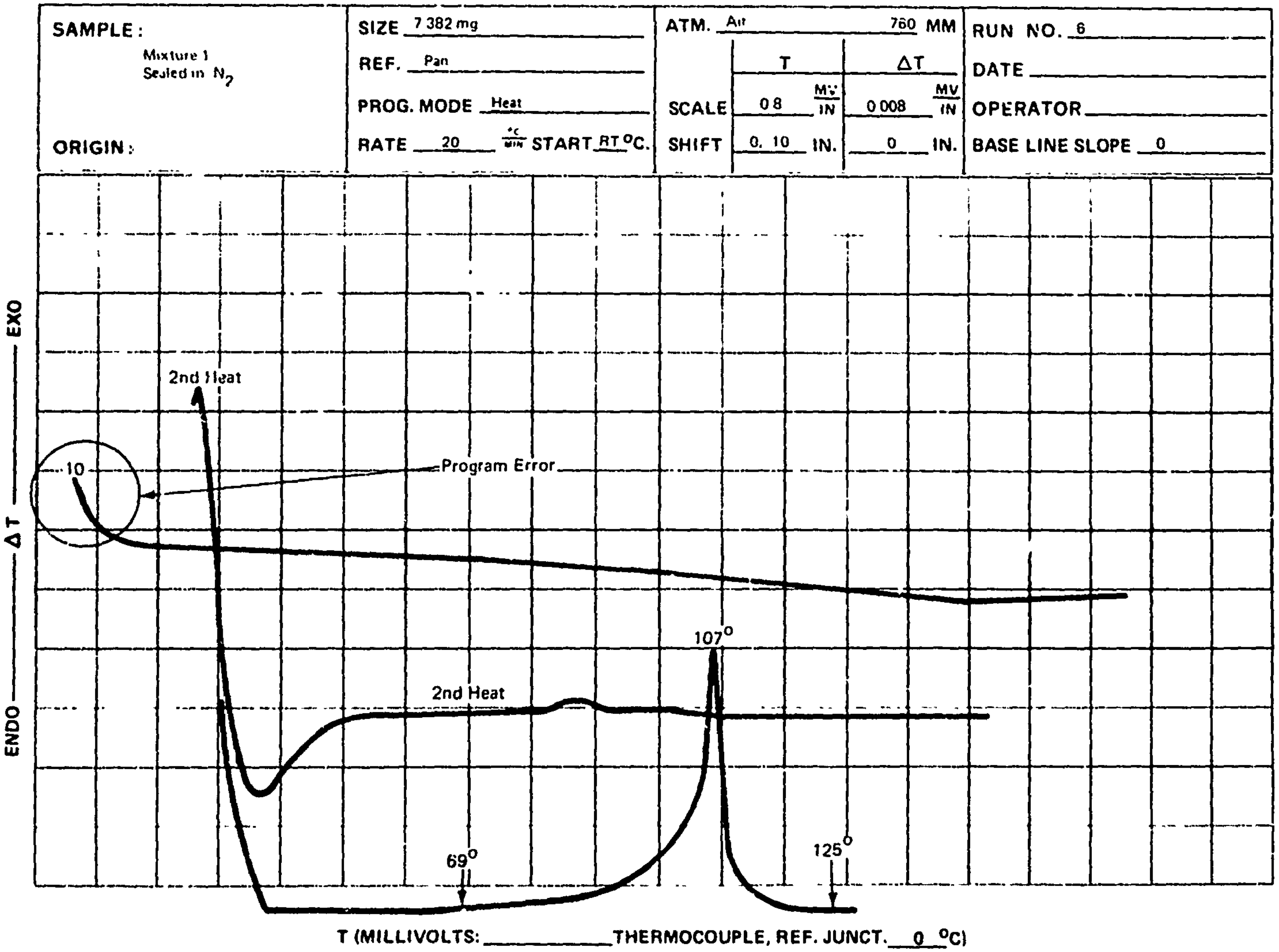
DATE

OPERATOR

BASE LINE SLOPE 0

T (MILLIVOLTS: ____ THERMOCOUPLE, REF. JUNCT. 0 °C)

Figure 6-14. Thermogram for XR 63 493 57.2% Crosslink to 42.8% Base Sealed in Air



SAMPLE: Mixture 1 Sealed in N_2

ORIGIN:

SIZE 7 382 mg

REF. Pan

PROG. MODE Heat

RATE 20 °C/MIN START RT °C.

ATM. Air 760 MM

SCALE T 0 8 MV/IN ΔT 0 008 MV/IN

SHIFT T 0. 10 IN. ΔT 0 IN.

RUN NO. 6

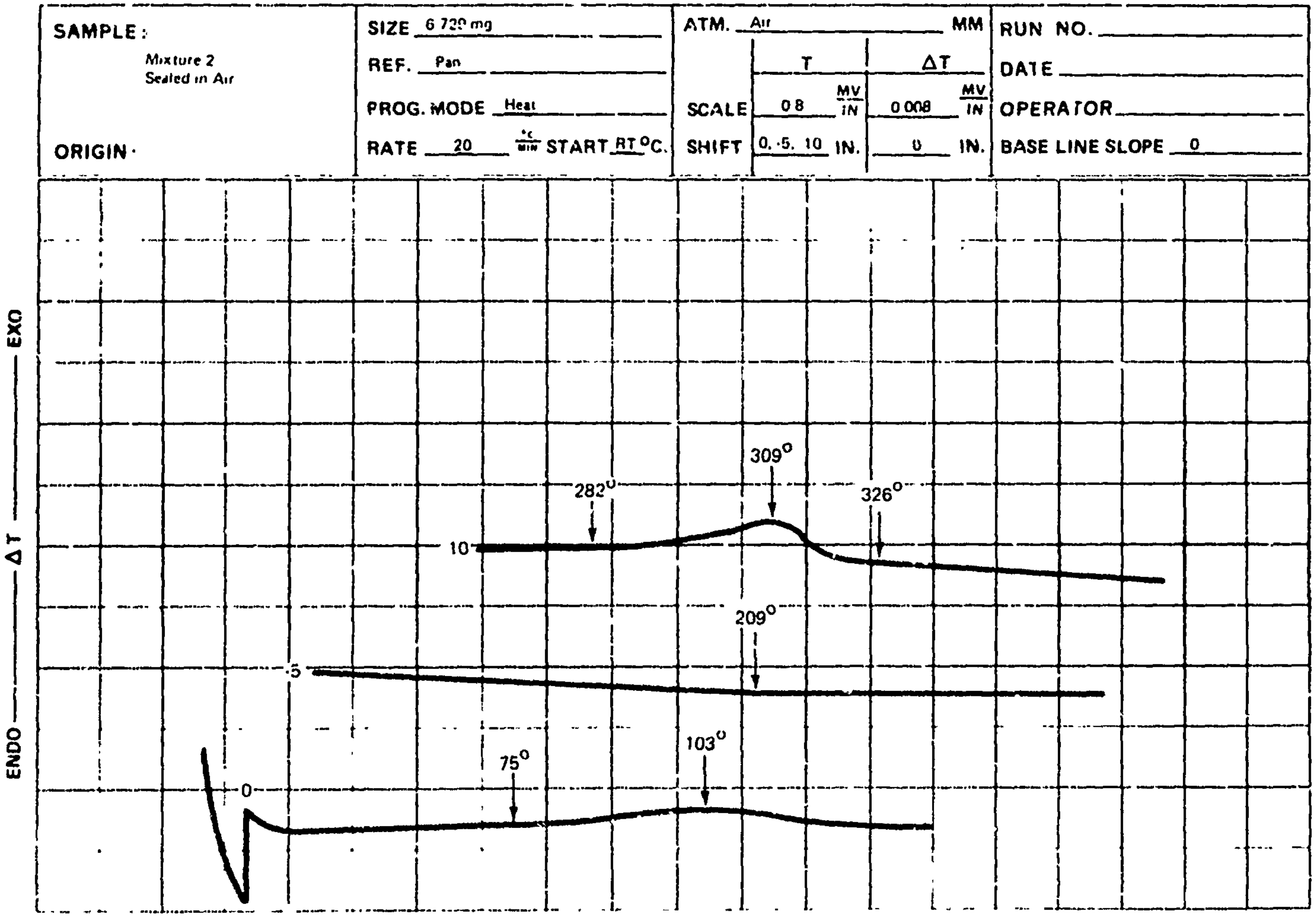
DATE

OPERATOR

BASE LINE SLOPE 0

T (MILLIVOLTS: THERMOCOUPLE, REF. JUNCT. 0 °C)

Figure 6-15. Thermogram for XR 63 493 57.2% Crosslink to 42.8% Base Sealed in Nitrogen



SAMPLE: Mixture 2 Sealed in Air	SIZE 6 720 mg	ATM. Air MM		RUN NO.
	REF. Pan	T	ΔT	DATE
	PROG. MODE Heat	SCALE 0 8 MV/IN	0 008 MV/IN	OPERATOR
ORIGIN·	RATE 20 °C/MIN START RT °C.	SHIFT 0, 5, 10 IN.	0 IN.	BASE LINE SLOPE 0

T (MILLIVOLTS: ____________THERMOCOUPLE, REF. JUNCT. 0 °C)

Figure 6-16. Thermogram for XR 63 493 3.4% Crosslink to 96.6% Base Sealed in Air

A mixture containing 96.6% base and 3.4% crosslinker catalyst was sealed in air and run, see Figure 6-10. This mixture exhibits a broad exotherm starting at 75°C, coming to a maximum at 103°C, and concluding near 209°C. This peak may be related to the sharp 107°C peak in the 50%/50% mixture. A second exotherm with a maximum at 309°C and a conclusion at 326°C occurs on further heating. This may be identified with the air reaction by the pure resin, Figure 6-11, with a vertex at 285°C. The shift to higher temperatures cannot be explained at this time. The new portion of the 96.6% resin mixture sealed in nitrogen exhibits a peak at 105°C but no higher temperature exotherm. This adds some evidence in support of the role of oxygen in the high temperature peak.

6.2.4 CONCLUSIONS

The following conclusions were made:

1) Oxygen from the atmosphere will react with both the base and the crosslinking agent
2) The principle thermosetting reaction occurs in the range 60°C to 125°C
3) Secondary reactions occur at higher temperatures, from 171° to 370°C
4) The excess base present in a mix ratio of 100 parts base to 3 parts crosslinking agent is available for reaction with the atmosphere.

6.3 THERMOMECHANICAL AND SOLVENT SWELLING STUDIES

The purpose of this experimentation was to determine the variation of crosslink density and elastic properties of the polymeric system as a function of crosslinker concentration at a fixed curing temperature. In addition, a suggested structure is proposed for the final polymer.

6.3.1 THEORETICAL ASPECTS

According to the statistical theory of rubber-like elasticity, the equilibrium (i.e., time-independent) modulus of a crosslinked elastomer is given by:

$$E_e = 3v_e RT \qquad (1)$$

where E_e is Young's modulus, v_e is the moles of effective network chains per unit volume of rubber, R is the gas constant, and T is the absolute temperature.

When such an elastomer is immersed in a suitable solvent, the elastomer swells until a constant final volume is attained. This final volume depends on the crosslink density (a common measure being v_e) and on an interaction parameter X_1, which depends on the nature of both the solvent and the rubber. The relation between crosslink density and the degree of swelling is ordinarily considered to be given by:

$$v_e = \frac{-\left[\ln(1-v_2) + v_2 + X_1 v_2^2\right]}{V_1 (v_2^{1/3} - \frac{v_2}{2})} \qquad (2)$$

where v_2 is the volume fraction of polymer in the swollen specimen and V_1 is the molar volume of the solvent.

One method for evaluating x_1 involves measuring both E_e and v_2 on elastomers having different crosslink densities. By eliminating v_e from Equations 1 and 2, the following results:

$$-\left[\frac{E_e V_1}{3\,RT} (v_2^{1/3} - \frac{v_2}{2}) + v_2 + \ln (1 - v_2)\right] = X_1 v_2^2 \qquad (3)$$

Hence, a plot of the left side of Equation 3 against v_2^2 should give a straight line whose slope equals X_1.

A simple method for determining Young's modulus, which requires only a small specimen, consists of measuring the depth of penetration of a rigid sphere under a normal force into a rubber specimen. The modulus E is given by:

$$F = \frac{16}{9} E r^{1/2} p^{3/2} \qquad (4)$$

where F is the force or load, r is the radius of the sphere, and p is the depth of penetration. The equation is based on the assumption that the specimen is large compared to the sphere and that the penetration is small compared to the radius of the sphere. (Equations 1 to 4 can be found in References 1 and 2.)

6.3.2 EXPERIMENTAL PROCEDURE

1) Sample Preparation: Samples containing 3%, 4%, 6%, 10%, 15%, 30%, 40%, 50% and 60% crosslinker by weight were prepared by weighing resin XR 63 493 (first batch) and catalyst into a beaker. The components were carefully mixed together with a glass rod and decanted into aluminum foil molds 2 cm high by 1.5 cm diameter. These samples were cured as a group at 80°C in air for 16 hours. At the conclusion of curing, the samples were removed

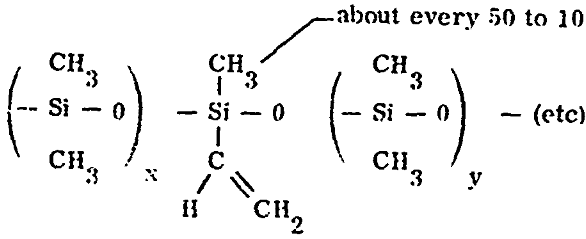
from the oven, cooled to room temperature, and stripped of aluminum foil. Cubes approximately 5 mm per edge were sliced from each sample for use in the duPont Thermo Mechanical Analyzer. To test the effect of thickness, several 3 mm cubes were also studied with no effect noted. Several samples were made in duplicate (batches 1 and 2). Above the 10% crosslinker range, the samples were identical; the 3% and 4% crosslinker samples showed some variation. This is probably due to the extreme sensitivity of the properties to crosslinker content in this composition range.

2) Thermomechanical Analyzer: A duPont Thermomechanical Analyzer equipped with a spherical indentation foot 0.1416 cm in radius was used. Samples were initialized by slowly lowering the foot/linear voltage transformer assembly onto the top of the sample. This assembly was then loaded with a 1 g weight. The deflection (Figures 6-17, 6-18, and 6-19, for example) was recorded as a function of time until a constant value was obtained. The load was removed and a similar record was made. The difference between the loaded and relaxed values were taken as the penetration (p). In most cases, essentially no permanent deformation was noted within experimental accuracy limits. The process was repeated with 5 and 10 g weights placed on the load tray. The penetration as a function of composition is shown for 1, 5, and 10 g loads in Figure 6-20. The 3% catalyst sample could not be studied by this method due to its extreme softness.

3) Solvent Swelling: Single cubes of the various samples were cut to approximately 0.5 g. These were accurately weighed on an analytical balance and then placed in 25 ml of spectral grade n-hexane. The process was repeated after 48 hours. The swelling data are shown in Table 6-2 for 24 and 48 hours. No measure of extractables was made.

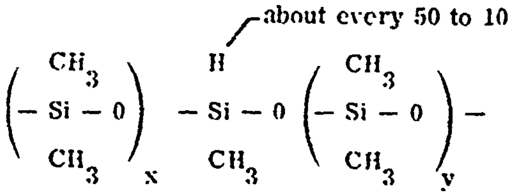
6.3.3 RESULTS

The structure of the silicone system is probably as follows:



$$\left(-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}\right)_x-\mathrm{Si}(\mathrm{CH_3})(\mathrm{CH{=}CH_2})-\mathrm{O}-\left(-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}\right)_y-\text{(etc)}$$

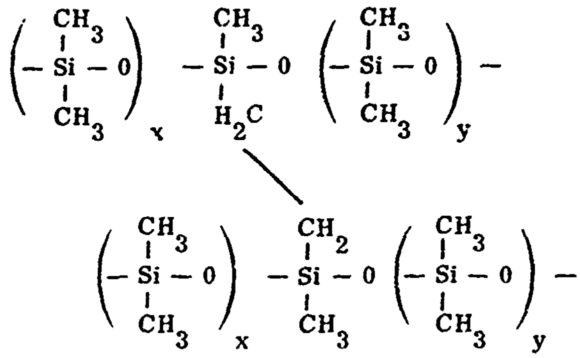
Base



$$\left(-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}\right)_x-\mathrm{Si}(\mathrm{H})(\mathrm{CH_3})-\mathrm{O}\left(-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}\right)_y-$$

Crosslinker

Combined in the presence of heat and a soluble platinum catalyst, the product is:



The crosslink is an ethylene bridge. The addition of progressively more crosslinker would produce increased crosslinking up to a point. In the presence of air, autocrosslinking through the pendant ethylene in the resin as shown previously is possible. However, this reaction becomes important only above 275°C and may be discontinued in this study.

To evaluate the modulus from the Thermo Mechanical Analyzer data, plots were made of F (the load expressed in grams) against $p^{3/2}$. In each instance, the data from tests under 1, 5 and 10 g gave a straight line passing through the origin. Values of the modulus, obtained from the slopes of the lines according to Equation 4, are included in Table 6-3 and shown in Figure 6-21 plotted against the catalyst concentration.

From the values of W (grams of hexane absorbed per gram of rubber) after 48 hours, the volume fraction of polymer in swollen specimens were calculated from

$$V_2 = \frac{\frac{1}{p_r}}{\frac{W}{p_h} + \frac{1}{p_r}}$$

where p_r (0.9926 g/cm^3) is the density of the rubber and p_h (0.660 g/cm^3) is the density of hexane. To evaluate X_1, the left side of Equation 3 was plotted against v_2^2. The resulting plot (Figure 6-22) gives $X \simeq 0.48$. In the literature[3] the value of $X_1 = 0.40$ is given for a conventional silicone rubber vulcanizate.

From Equation 2 and values of v_2 along with $x_1 = 0.48$, the crosslink density v_e was calculated; the results are given in Table 6-3 along with those obtained from Equation 1 and values of the modulus. The last column in Table 6-3 is v_e obtained from the swelling data divided by the value from modulus data. The close agreement indicates that the crosslink density can be evaluated from either swelling or modulus data.

Table 6-2

SWELLING OF SILICONE RUBBER SPECIMENS IN HEXANE

Crosslinker Concentration (%)	Grams of hexane absorbed per gram of rubber after	
	24 hr	48 hr
3	10.026	11.390
4 (1st prep)	7.053	7.949
4 (2nd prep)	7.220	8.108
10 (1st prep)	2.995	3.286
10 (2nd prep)	3.258	3.327
15	3.401	3.490
30	3.781	3.772
40	4.122	4.170
50 (1st prep)	4.144	4.358
50 (2nd prep)	4.746	5.047

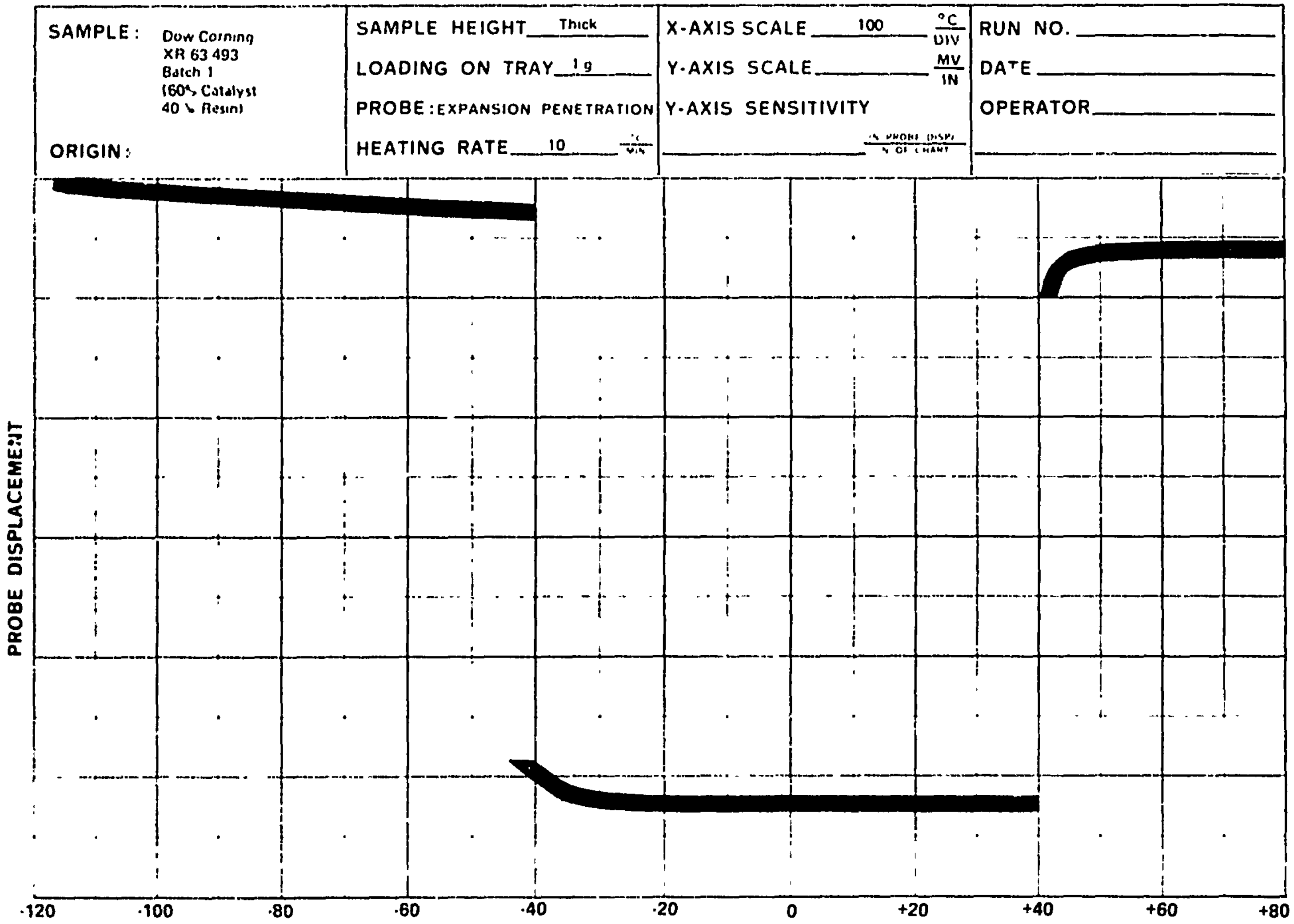
Density of 10% crosslinker rubber was 0.9926 ±1% g/cm^3 at 22°C on four determinations.

Density of spectral grade hexane = 0.6603 g/cm^3 at 20°C.

Table 6-3

RESULTS FROM MODULUS AND SWELLING DATA ON SILICONE RUBBERS

Crosslinker Concentration (%)	$E \times 10^6$ (dynes/cm^2)	V_2 after 48 hours	$v_e \times 15$ (moles/cm^3) From		Ratio
			Swelling	Modulus	
3	-	0.0552	0.258	-	-
4 (1st prep)	0.384	0.0772	0.558	0.517	1.08
4 (2nd prep)		0.0758	0.534	-	-
6	2.66	-	-	3.59	-
10 (1st prep)	2.88	0.1683	3.907	3.87	1.01
10 (2nd prep)	-	0.1666	3.802	-	-
15	2.28	0.1600	3.419	3.07	1.12
30	2.20	0.1499	2.878	2.96	0.98
40	2.12	0.1375	2.304	2.65	0.87
50 (1st prep)	1.58	0.1324	2.089	2.13	0.98
50 (2nd prep)	-	0.1164	1.509	-	-
60	1.70	-	-	2.30	



SAMPLE: Dow Corning XR 63 493 Batch 1 (60% Catalyst 40 % Resin)

ORIGIN:

SAMPLE HEIGHT Thick

LOADING ON TRAY 1 g

PROBE: EXPANSION PENETRATION

HEATING RATE 10 °C/MIN

X-AXIS SCALE 100 °C/DIV

Y-AXIS SCALE MV/IN

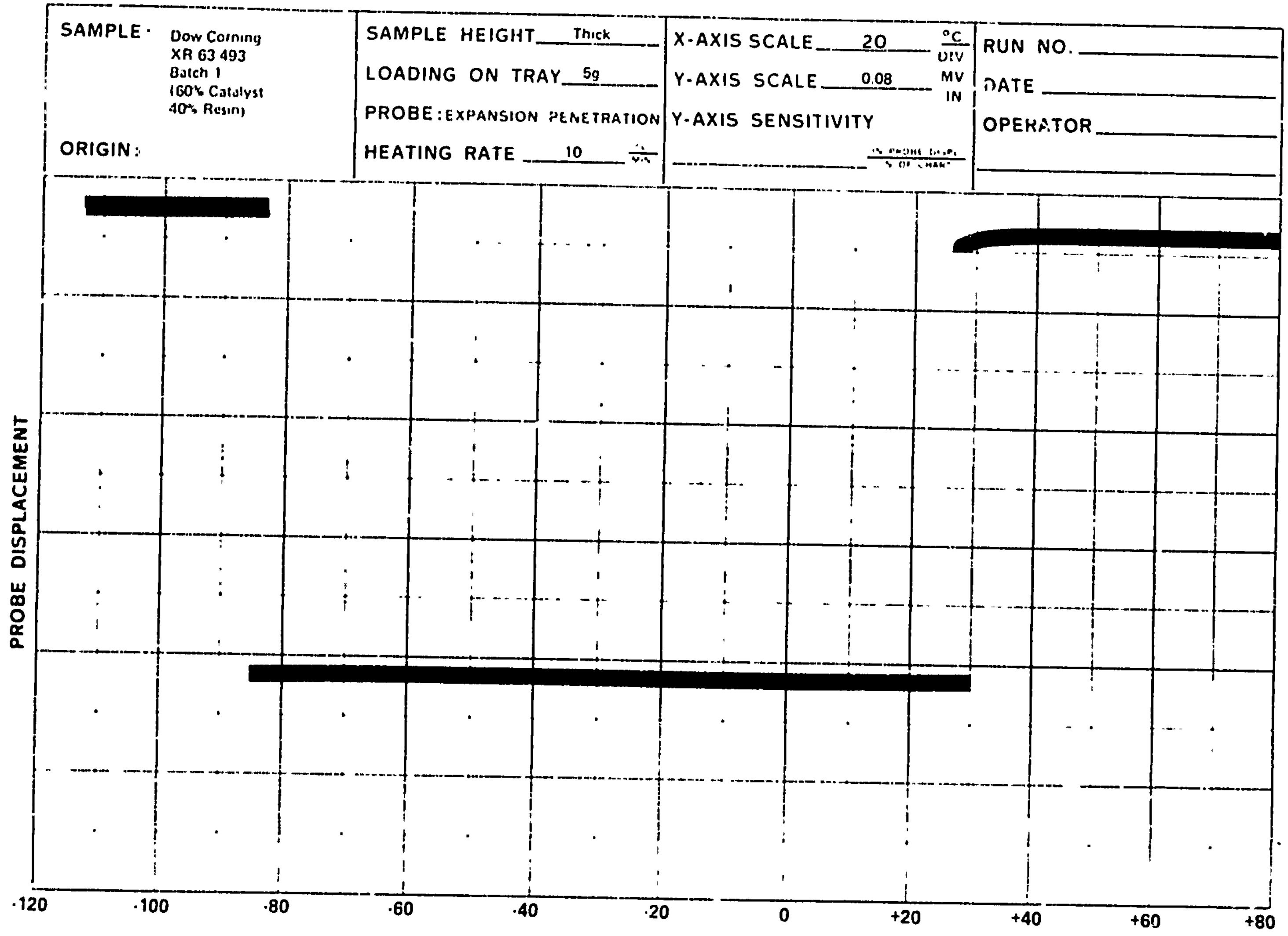
Y-AXIS SENSITIVITY % PROBE DISP/% OF CHART

RUN NO.

DATE

OPERATOR

Figure 6-17. Penetration Run of 60% Crosslinker, 40% Base Silicone Rubber, 1 g Load



SAMPLE · Dow Corning
XR 63 493
Batch 1
(60% Catalyst
40% Resin)

ORIGIN:

SAMPLE HEIGHT Thick

LOADING ON TRAY 5g

PROBE: EXPANSION PENETRATION

HEATING RATE 10 °/MIN

X-AXIS SCALE 20 °C/DIV

Y-AXIS SCALE 0.08 MV/IN

Y-AXIS SENSITIVITY

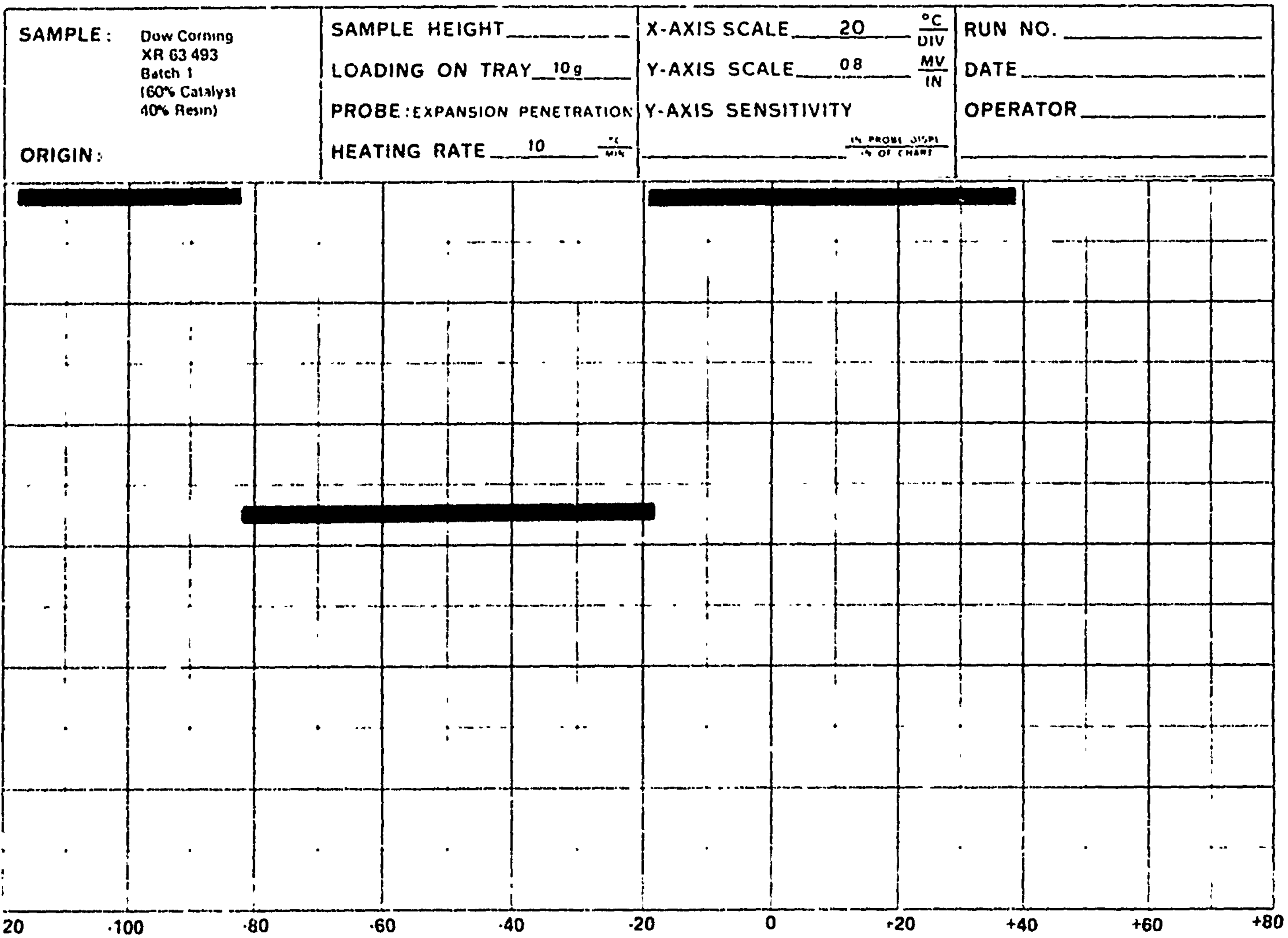
% PROBE DISPL. / % OF CHART

RUN NO.

DATE

OPERATOR

Figure 6-18. Penetration Run on 60% Crosslinker, 40% Base Silicone Rubber, 5 g Load



SAMPLE: Dow Corning XR 63 493 Batch 1 (60% Catalyst 40% Resin)

ORIGIN:

SAMPLE HEIGHT

LOADING ON TRAY 10 g

PROBE: EXPANSION PENETRATION

HEATING RATE 10 °C/MIN

X-AXIS SCALE 20 °C/DIV

Y-AXIS SCALE 08 MV/IN

Y-AXIS SENSITIVITY IN PROBE DISPL/IN OF CHART

RUN NO.

DATE

OPERATOR

Figure 6-19. Penetration Run on 60% Crosslinker, 40% Base Silicone Rubber, 10 g Load

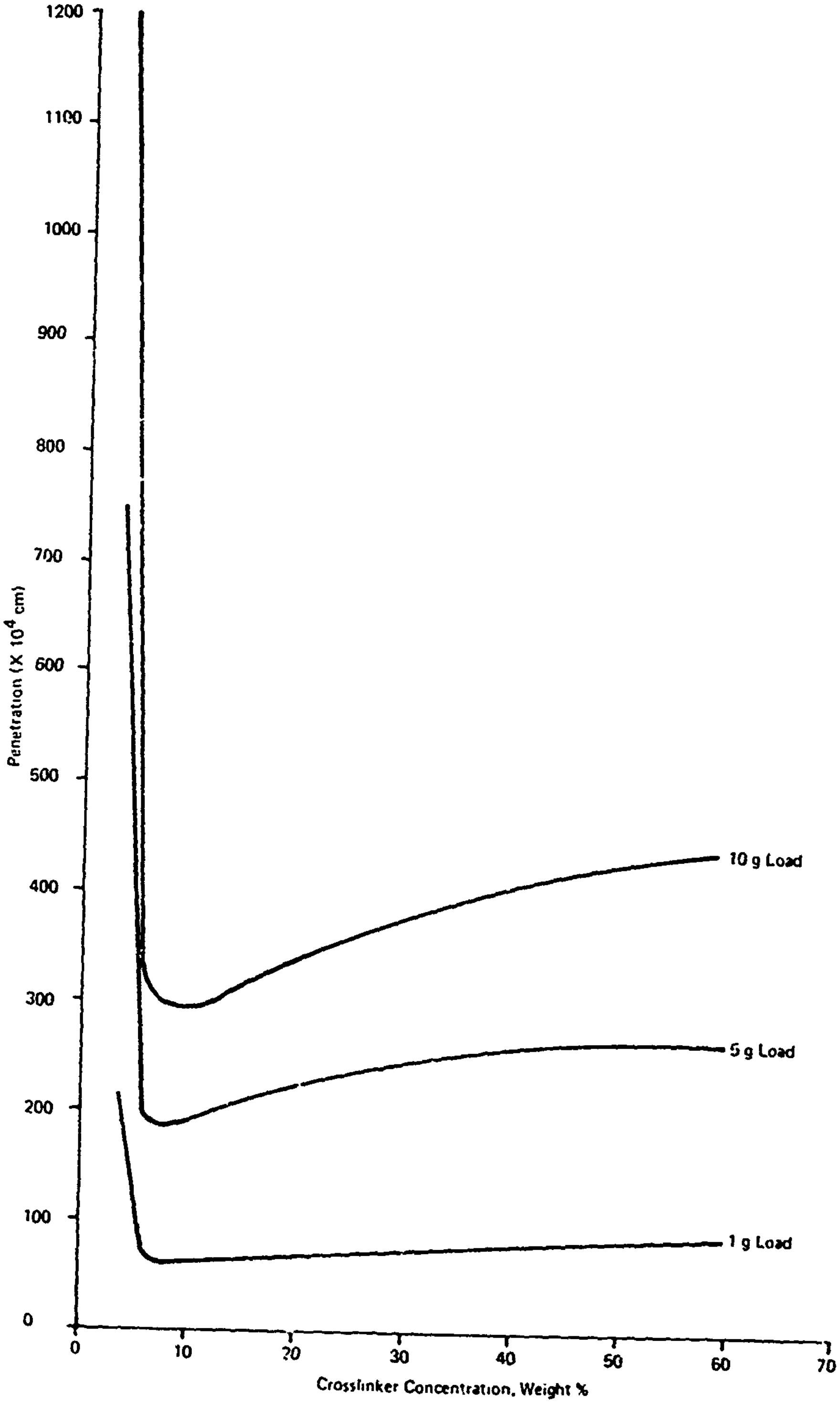


Figure 6-20. Penetration as a Function of Silicone Rubber Crosslinker Content

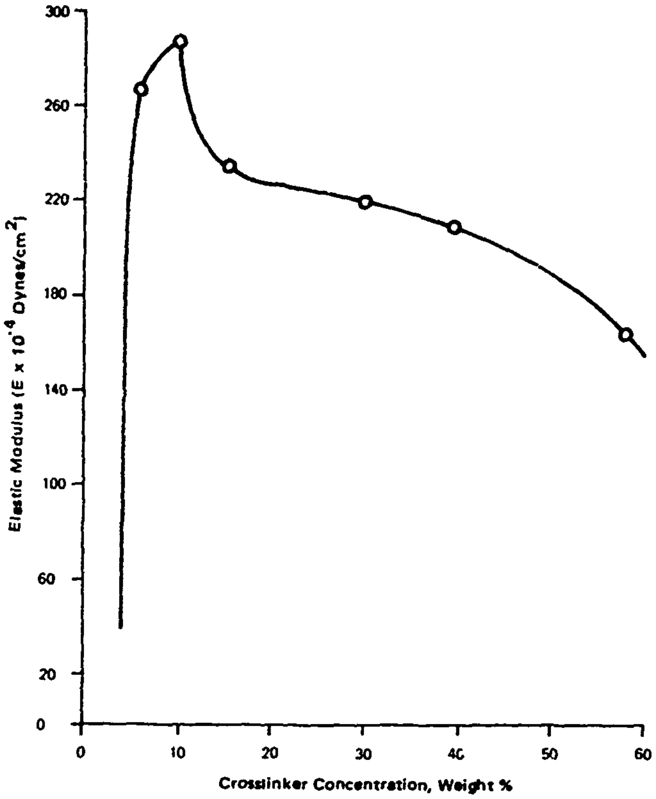


Figure 6-21. Effect of Crosslinker Concentration on Elastic Modulus

6.3.4 CONCLUSION

Because the modulus, and thus the crosslink density, is a maximum at about 10% crosslinker concentration, it may be concluded that the crosslinker and base components have been added in equivalent amounts. When the crosslinker concentration is greater than 10%, all of the pendant ethylene groups in the base have reacted but the excess crosslinker component effects a reduction in crosslink density owing to the introduction of long dangling chains attached to the three-dimensional network. At a sufficiently large crosslinker concentration (apparently greater than 60%), a true three-dimensional network would not form.

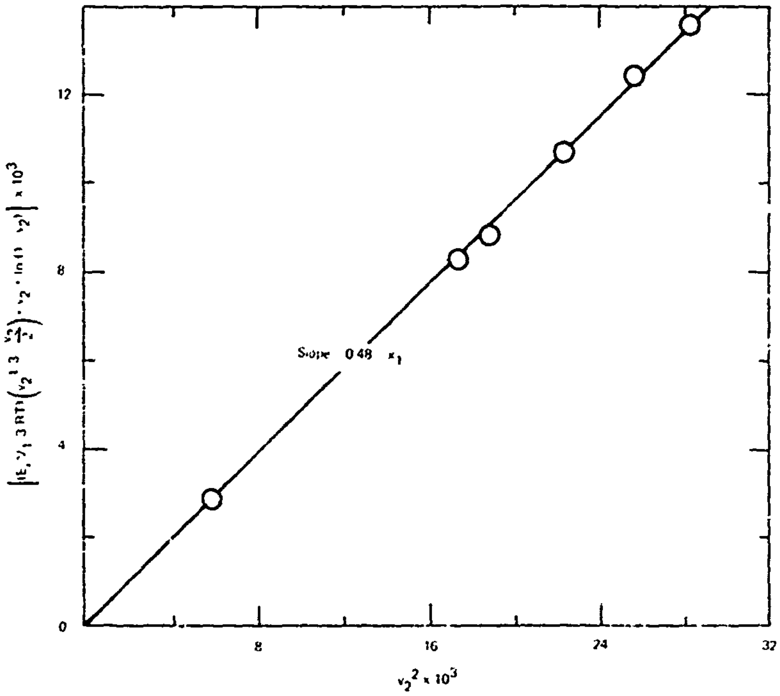


Figure 6-22. Determination of Interaction Parameter (X_1) from Swelling and Modulus Data

The crosslink density (v_e) can be converted into an effective molecular weight between crosslinks (M_c) by the relation $M_c = p_r/v_e$. Thus for the 10% crosslinker sample, $M_c = 25,400$. If the number of repeated units between pendant ethylene groups is 100 (i.e., if y in the structural formula given above is 100), then the minimum attainable value of M_c would be about 7400. From gel phase chromatography data on the base component, it has been estimated that $M_n = 8000$ and $M_w = 17,460$. Thus, the molecular weight distribution is quite broad and undoubtedly a number of monofunctional molecules (those having a single pendant ethylene group) are present. Hence, even if the base and crosslinker components are mixed in equivalent amounts and the curing reaction goes to completion, the resulting network will contain a number of long dangling chains and probably some soluble (extractable) polymer material. Such a structure will have an effective M_c considerably greater than the molecular weight between the pendant ethylene groups in the high molecular weight base component.

6.4 YOUNG'S MODULUS

The purpose of independently determining Young's modulus (see Section 6.3) was to obtain a relationship between the deformographic polymers. In addition, it would, with other data, aid in selecting other materials for use as a deforming member (see Table 6-4).

Table 6-4

EXPERIMENTAL DETERMINATION OF YOUNG'S MODULUS

Sample	Young's Modulus (dynes/cm^2)	Molecular Weight** (Number Average)
78 060, Lot 10182	2.7×10^6	136,000
*78 060, Lot 10182	3.1×10^6	103,000
*78 060, Lot 09092	4.6×10^6	29,200
*XR 63 493, Lot 09091	5.3×10^6	23,200

*Average of two samples
**From gel permeation chromatography data

Each of the monodispersed samples submitted and the last sample of XR 63 493 was mixed with 10% of the associated crosslinking agent and polymerized in sheet form. Samples were cut from these sheets according to ASTM D412 and, using Instron tensile testing equipment, stress and strain calculations were made.

As the molecular weight increases in this family of resins, they become softer and more easily deformed. Also, from target testing data, the resolution becomes worse with increasing molecular weight. With a sufficient amount of such data, the prediction of an optimum molecular weight for the deformographic material could be made.

6.5 YERSLEY OSCILLOGRAPH

In an effort to obtain a relationship between the target characteristics and the mechanical properties of the deformographic material, it was anticipated that the Yersley oscillograph could be employed. This instrument is normally capable of generating data relating to rubber.

The use of this oscillograph and the measurement of the usual rubber properties are critically dependent upon casting cylinders of the material to be evaluated within dimensions set forth in ASTM D945-59. With our materials, particularly at crosslink-to-base ratios which deform at $6\text{-}10^{-8}$ coulombs/cm^2 for a 30:1 light output, the casting of such test cylinders could not be made. However, at higher crosslink-to-base ratios, i.e., those close to equivalent [illegible] were prepared and data was obtained (see Table 6-5). At greater than the equivalent [illegible] base-to-crosslinker, many samples fractured during evaluation.

Table 6-5

SOME MECHANICAL PROPERTIES OF THE DEFORMOGRAPHIC POLYMER (ASTM D945-59)

Resin	X-link Base (%)	Static Modulus at 20% Def. (lb/in^2)	Load @ 20% Def. (lb/in^2)	Yersley Resilience	Frequency
78 060 Lot 707-1	5	99	13.2	73.3	1.94
	10	128	17.1	85.3	2.17
	15	145	17.8	84.9	2.14
	20	141	18.4	84.4	2.18
78 060 Lot 707-2	5	151	18.4	95.5	1.87
	10	Fractured Samples			
	15	Fractured Samples			
	20	Fractured Samples			
XR 63 493 Lot 8	5	14	2.2	80	.7
	10	130	20	87	2.2
	15	Fractured Samples			
	20	Fractured Samples			
SR 63 493 Lot 09091	5	22.1	4.4	74	1.06
	10	152.	31.3	96	2.51
	15	Fractured Samples			
	20	Fractured Samples			

The data obtained by this method does not yield information on the mechanical properties of the polymer at crosslink ratios found most desirable for the DSDT. It does allow a comparison between some properties of the fully crosslinked polymer which are found useful where high sensitivity performance is not required in the target. In general, however, this test was found to be of much less value than was anticipated at the beginning of the program.

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