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A STUDY OF THE POSSIBLE EFFECT OF A THERMAL POST CURE ON THE MECHANICAL PROPERTIES OF THE 404 CARBON-PHENOLIC RING OF THE SPACE SHUTTLE SOLID ROCKET MOTOR NOZZLE

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by

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ABSTRACT

Erratic pockets of erosion have occurred on the inner perimeter of the 404 rocket nozzle ring during liftoff firing. In some cases the erosion has been serious. It is thought that it may be caused by pockets of volatile matter entrapped during manufacture. A thermal post cure has been suggested as a possible means of outgassing such pockets, if they in fact do exist.

To confirm an outgassing during a post cure and to establish a working upper temperature limit, thermal gravimetric and differential calorimetric analyses were made on a number of samples from two 404 rings (#42 and #45) supplied by the manufacturer. Continuous weight loss was observed over the temperature range explored (750° F) indicating outgassing, and a strong exothermic reaction occurs beginning about 390° F. Thus, an upper post cure temperature of 350° F is recommended. Preparations are underway to carry out a series of post cure cycles to 330° F and to 350° F, with and without hold periods at 275° F.

To determine the possible effect of a post cure on physical properties, the following tests will be made on matched sets of cured and post cured material: x-radiography (internal structure), linear dimensions, weight, porosity, cross ply thermal expansion, drop and double notch shear strengths, and tensional strength in the ply direction.

X-radiographs of ring cross sections have shown significant irregularities in internal structure within each of the rings and between the two rings. The ply of the carbon cloth shows a strong concave curvature on the top (inlet) side, diminishing to almost straight on the bottom side. Alternating bands of greater and lesser density parallel to the ply exist in both rings, but are more pronounced in ring 45. Also, random irregular lenses of minimum density are present parallel to the ply. They are more pronounced in ring 42. The lenses may be gas-filled voids. If so, post curing may degass them, but may not remove them. To establish the actual cause of the observed x-radiograph density differences, a microstructural study via optical microscopy techniques is recommended.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Messrs. E. McKannan, R. L. Nichols and R. G. Clinton for having been selected to participate in the Summer Faculty Fellowship Program. I wish to also express thanks to Bill Hall, Ben Goldberg and Jeff Brewer for their guidance and help in pursuing the research discussed in this report.

The knowledge and experience gained in the area of space-age materials through discussion with associates and participation in meetings and seminars will, I feel, contribute significantly to my career as a professor and researcher.

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INTRODUCTION

Erratic pockets of erosion have been found on the inner surface of a number of the space shuttle solid rocket motor nozzles upon recovery after flight. In a number of cases the damage was sufficiently severe that at the end of the burn time of the motor not many seconds of operational life remained.

It is thought that the pockets of erosion may be caused by spallation induced by the thermal expansion of entrapped volatile matter. The entrapment of pockets of volatiles is postulated to occur during the curing of the carbon cloth-phenolic resin composite material. During the manufacture of the nozzle material, thermal curing of the resin is carried out under a vacuum in a compressing apparatus called an hydroclave. The vacuum system is supposed to draw off volatiles both entrapped during the rolling out of the cloth-resin components on the construction mandrel and released as reaction products of resin polymerization during the thermally driven cure. If there are indeed pockets of volatile matter entrapped in the finished material, it would appear that the vacuum system of the curing operation is not functioning according to expectations.

Operating under the assumption that pockets of volatile matter do exist within the nozzle material, a second thermal cure cycle was considered a possible means of alleviating the condition. Work would be carried out on production units of the 404 ring of the rocket motor nozzle. The 404 ring is located immediately below the nozzle inlet cap and above the throat ring. The erosion pockets have been concentrated on the inside surface of the 404 ring. The study would consist of two major parts: to establish optimum conditions for a second thermal cure of the nozzle material that might yield an outgassing of entrapped volatiles, and to assess changes in the physical properties of the nozzle material that the post cure treatment might induce. The latter would have to be considered by the design engineers of the rocket nozzle.

It was not possible to complete the full scope of the project during the course of the summer fellowship. That part which was concluded is described in the following sections.

OBJECTIVES

The objectives of this work were to:

1) Determine optimum time-temperature conditions for a post cure thermal treatment of the rocket nozzle composite material that would maximize an outgassing of entrapped volatiles with minimum deleterious effects on its ablative and physical properties.

2) Characterize the macrostructure and selected physical properties important to design parameters both before and after post cure thermal treatment.

RESULTS

The Wasatch Division of Morton Thiokol, Inc., manufacturer of the space shuttle solid rocket motor, provided four approximately 45^{o} segments from each of two 404 production rings for this study. Their respective identification numbers are 42 and 45. Five vertical cross sections, each about 1.1 inches thick, have been cut from the ends of three of the segments from ring 42, and five from one end of the fourth. With respect to ring 45, five sections were cut from each end of two segments, five from one end of the third, and the full fourth segment is being held in reserve. Alternate sections are being retained as control pieces with the other cut sections being committed to post cure tests. A schematic of our sampling method and labelling is illustrated by Figure 1. The layout used for dimensional measurements and the extraction of test specimens is illustrated by Figure 2. Cross section dimensions of the samples committed to post cure are given in Table 1.

To explore the feasibility of outgassing entrapped volatiles by a thermal post cure treatment, thermogravimetric analyses were done over the temperature range 75^{o} to 750^{o} F. A continuous and smooth loss in weight occurred over the range. Typical data for material from the two rings are illustrated by Figures 3 and 4. Average weight loss and rate data for the samples analyzed are given in Table 2. The data show that the material of ring 42 lost about 75% less weight than did the material from ring 45.

To determine a reasonable temperature range over which to conduct a post cure thermal treatment, differential scanning calorimetric analyses were carried out on samples from the two rings. Material from ring 42 showed a strong exothermic reaction beginning at about 410^{o} F, whereas that from ring 45 showed the reaction beginning from about 285^{o} to 375^{o} F. These data suggest a greater degree of cure for ring 42 relative to ring 45. Typical heat flow behavior of ring 42 material is illustrated by Figure 5. The range of behavior observed for ring 45 material is illustrated by Figures 6 and 7. Based on gravimetric and calorimetric data, plus recommendations provided by HITCO, post cure cycles to 330^{o} F and to 350^{o} F, with and without hold periods at 275^{o} F, have been selected.

To monitor changes that a post cure might produce, the following analyses will be made: x-radiography to define internal structure, linear dimensions of cross section pieces to define expansion or contraction, dry and water-saturated weights to define density and porosity changes, and drop shear, double notch shear, and tensile tests to define strength changes. For control, parallel tests will be made on matched sets of cured and post cured materials.

The dry weights and water saturated weights of 16 cross section pieces are given in Table 3. The dry weights were measured after heating the pieces under 32-inches-mercury vacuum to 120° F for four hours, followed by 20 hours at 75° F. Water saturated weights were measured after keeping the pieces in an humidity chamber maintained at 100°F and a relative humidity of 85%. The chamber would not produce a 100% RH. Also included in Table 3 is the apparent pore volume determined on the basis of internally adsorbed water. The average pore space thus determined is about 45% less in ring 42 relative to ring 45.

X-radiographs of the cross sectional pieces also show significant differences between rings 42 and 45. Photos from three ring-42 segments are shown in Figure 8, and from three ring-45 segments in Figure 10. Respective interpretive schematics of texture and density features are given by Figures 9 and 11. The ply of the carbon cloth in ring 42 has a modest concave curvature. An estimate of the radius of curvature is about 20 inches. The concave curvature of the ply in ring 45 is more severe, with an estimated radius of curvature of about 15 inches. The curvature in ring 42 is fairly uniform from top to bottom of the cross section, but in ring 45 it appears to be most severe at the top and only slight at the bottom. This curvature violates the ply orientation specifications of the ring design. Bands of density difference parallel to the lay of the ply also exist. The differences are much greater in ring 45 than in 42. The overall density of 42 is greater than that of ring 45. In addition, irregular lenses of minimum density are observed to be distributed randomly along the lay of the carbon cloth ply. They occur in both rings, but appear to be more pronounced in ring 42. The minimum density lenses may represent gas filled voids. If so, post curing will probably devolatilize them but may not remove them.

This is as far as the work has progressed at the writing of this report.

CONCLUSIONS AND RECOMMENDATIONS

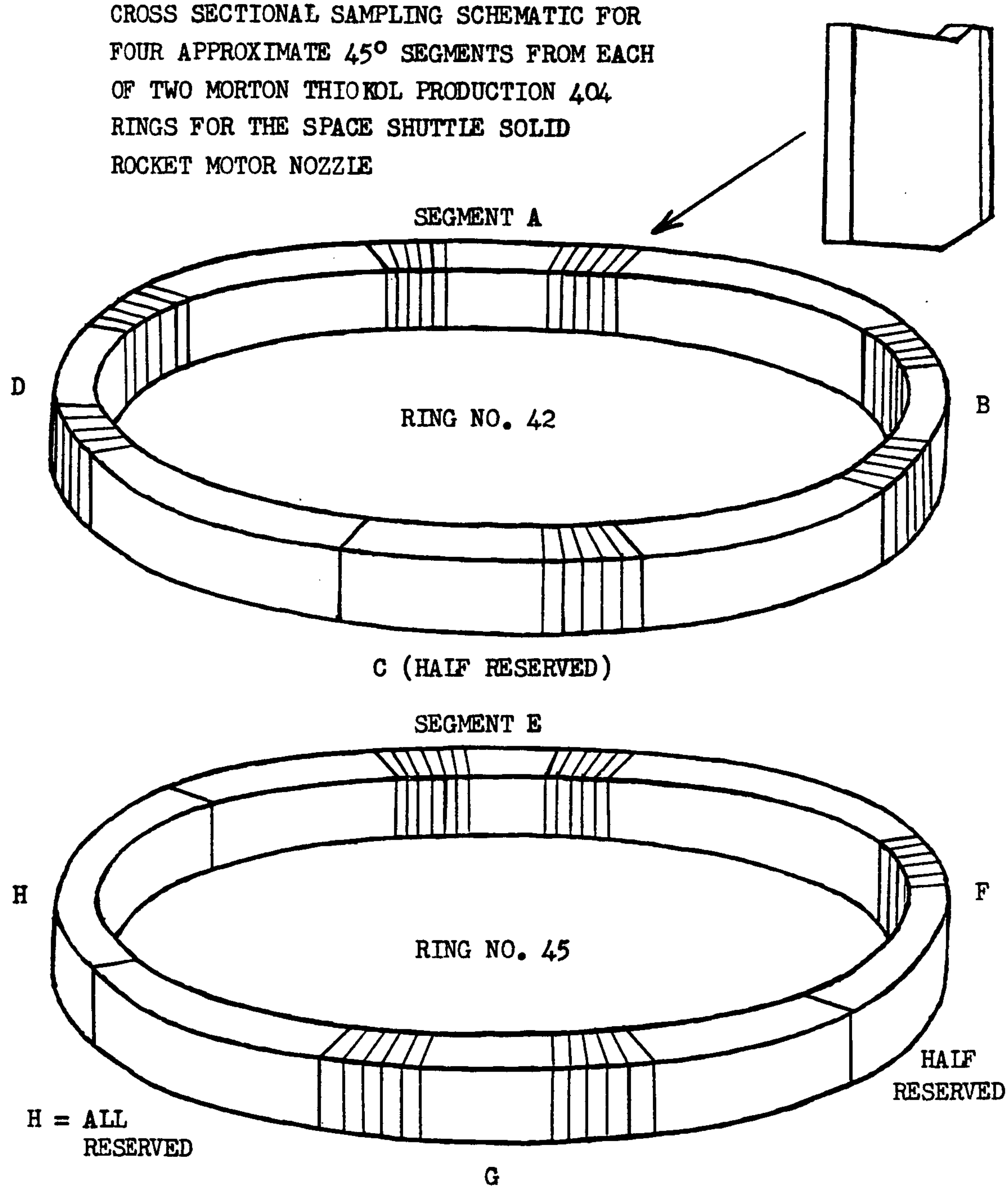
Work performed in the course of this study has shown that 404 rings are not homogeneous internally, and that their internal structure varies from ring to ring, at least to the degree exhibited by rings 42 and 45.

Thermal data suggest that ring 42 is more cured than ring 45. Weight data suggest that ring 42 is less porous than 45, and combined with evidence given by the x-radiographs suggests that 42 contains more phenolic than 45 and that it is more uniformly distributed.

The lenses of minimum density shown by the x-radiographs may be gas-filled voids. If so, they may be the primary cause of pockets of erosion. Post curing, in view of the weight loss observed from thermogravimetric tests, should tend to devolatilize such lenses. However, it must be stressed that the interpretation given here of the observed radiographic density differences reflects speculation. An experimental effort is recommended to determine the actual cause of the differences. This most likely can be readily achieved by a microscopic study of optical thin sections of the ring material.

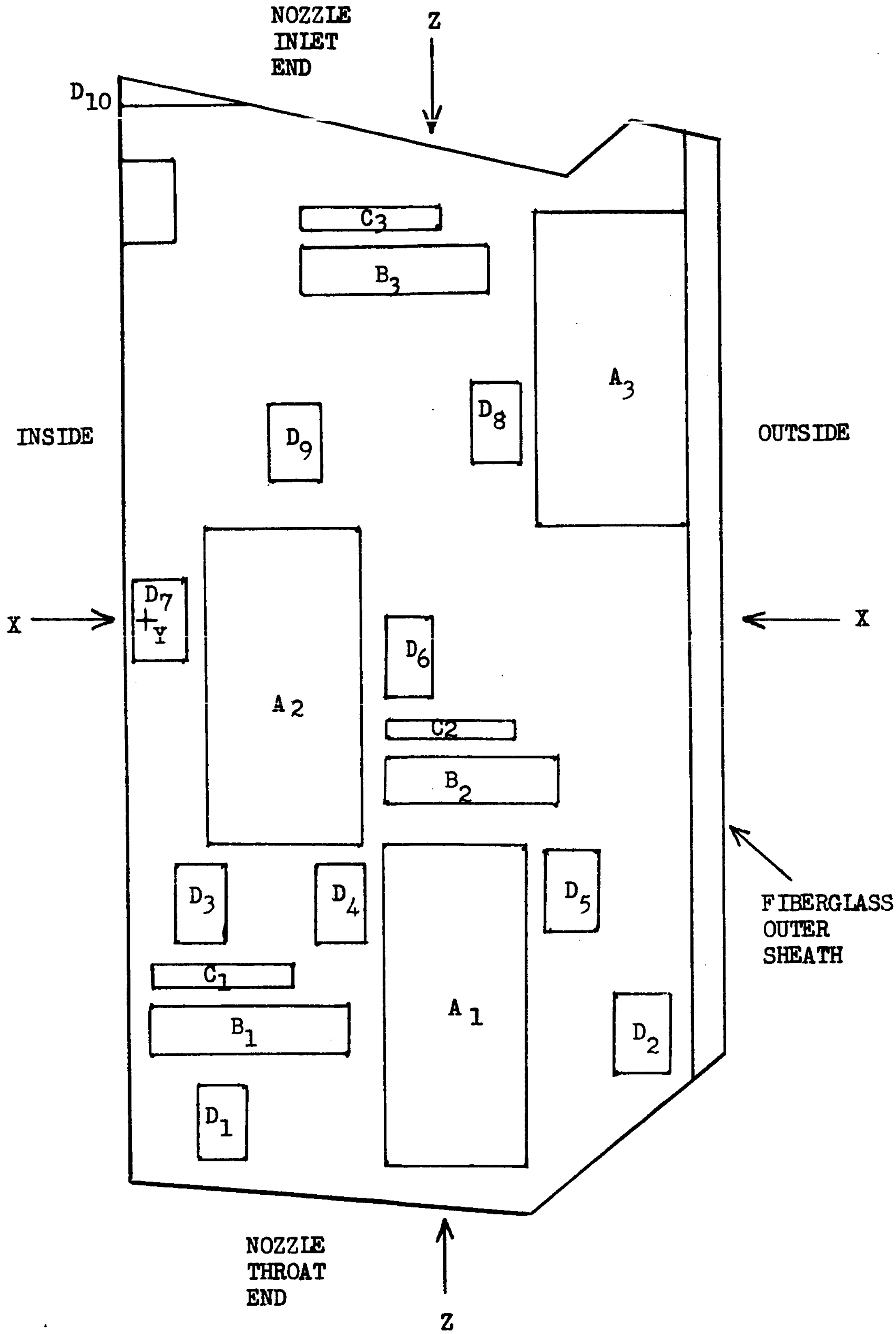
The observed bands of density variation parallel to the carbon cloth ply and the curvature of the ply indicate that the present production method of the 404 ring requires correction.

FIGURE 1.
CROSS SECTIONAL SAMPLING SCHEMATIC FOR FOUR APPROXIMATE 45° SEGMENTS FROM EACH OF TWO MORTON THIOKOL PRODUCTION 404 RINGS FOR THE SPACE SHUTTLE SOLID ROCKET MOTOR NOZZLE



FIVE CROSS SECTIONAL PIECES ABOUT 1.1 INCHES THICK (SEE UPPER RIGHT CORNER) WERE CUT FROM EACH END OF SEGMENTS A,B,D,E & G, AND FROM ONE END OF SEGMENTS C & F. ALTERNATE CROSS SECTIONS WILL BE RETAINED AS CONTROL SPECIMENS.

FIGURE 2.
LAYOUT FOR TEST PIECE EXTRACTIONS FROM 404 RING CROSS SECTIONS



A = CROSS PLY TENSILE TESTS
B = DOUBLE NOTCH SHEAR TESTS
C = SHORT BEAM SHEAR TESTS
D = TGA, DSC, CPTE & MISC. TESTS

X,Y,Z CROSS SECTION PIECE DIMENSIONS

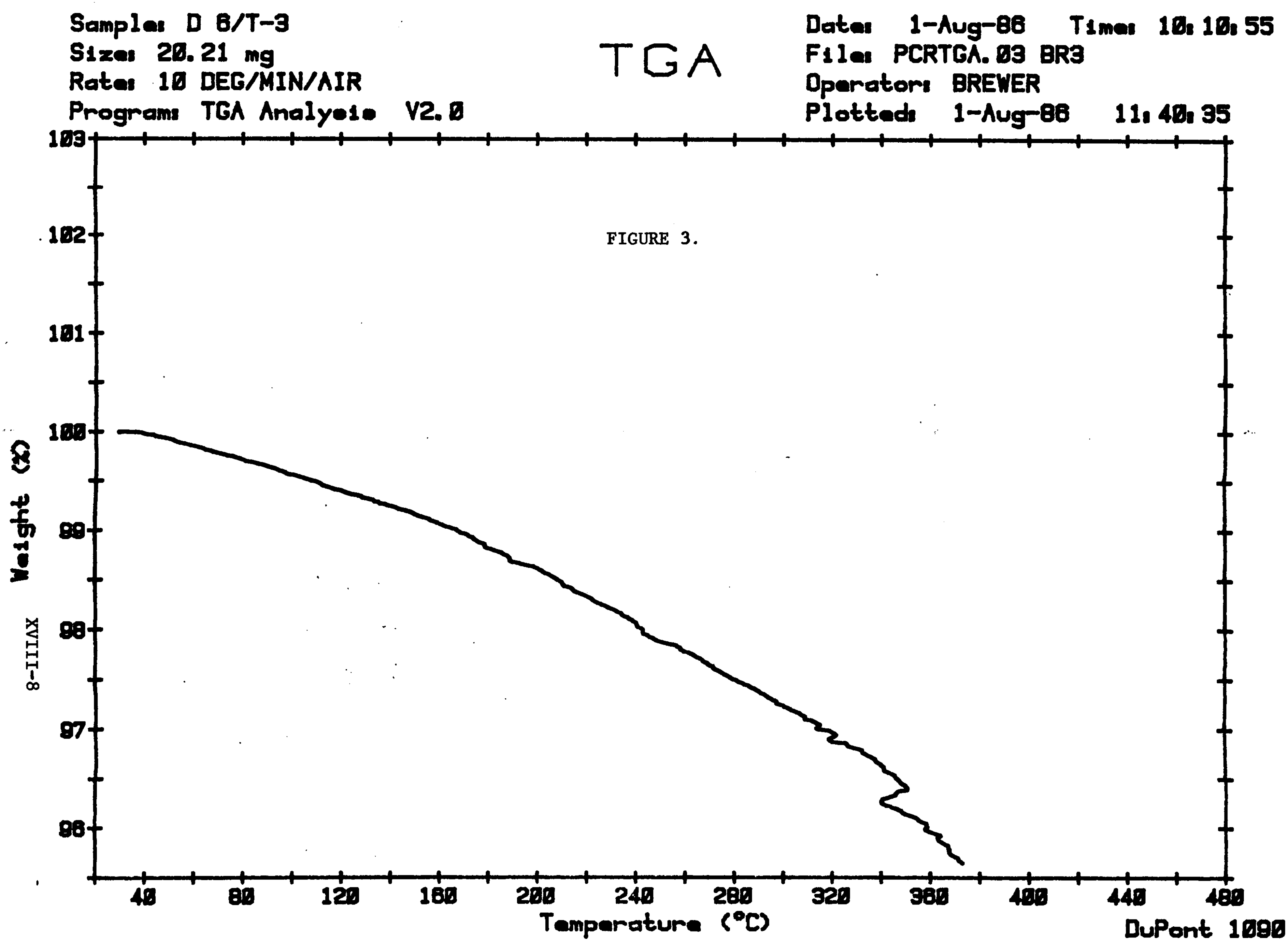

Sample: D 6/T-3
Size: 20.21 mg
Rate: 10 DEG/MIN/AIR
Program: TGA Analysis V2.0
TGA
Date: 1-Aug-86 Time: 10:10:55
File: PCRTGA.03 BR3
Operator: BREWER
Plotted: 1-Aug-86 11:40:35
Weight (%)
103
102
101
100
99
98
97
96
40
80
120
160
200
240
280
320
360
400
440
480
Temperature (°C)
DuPont 1090

FIGURE 3.

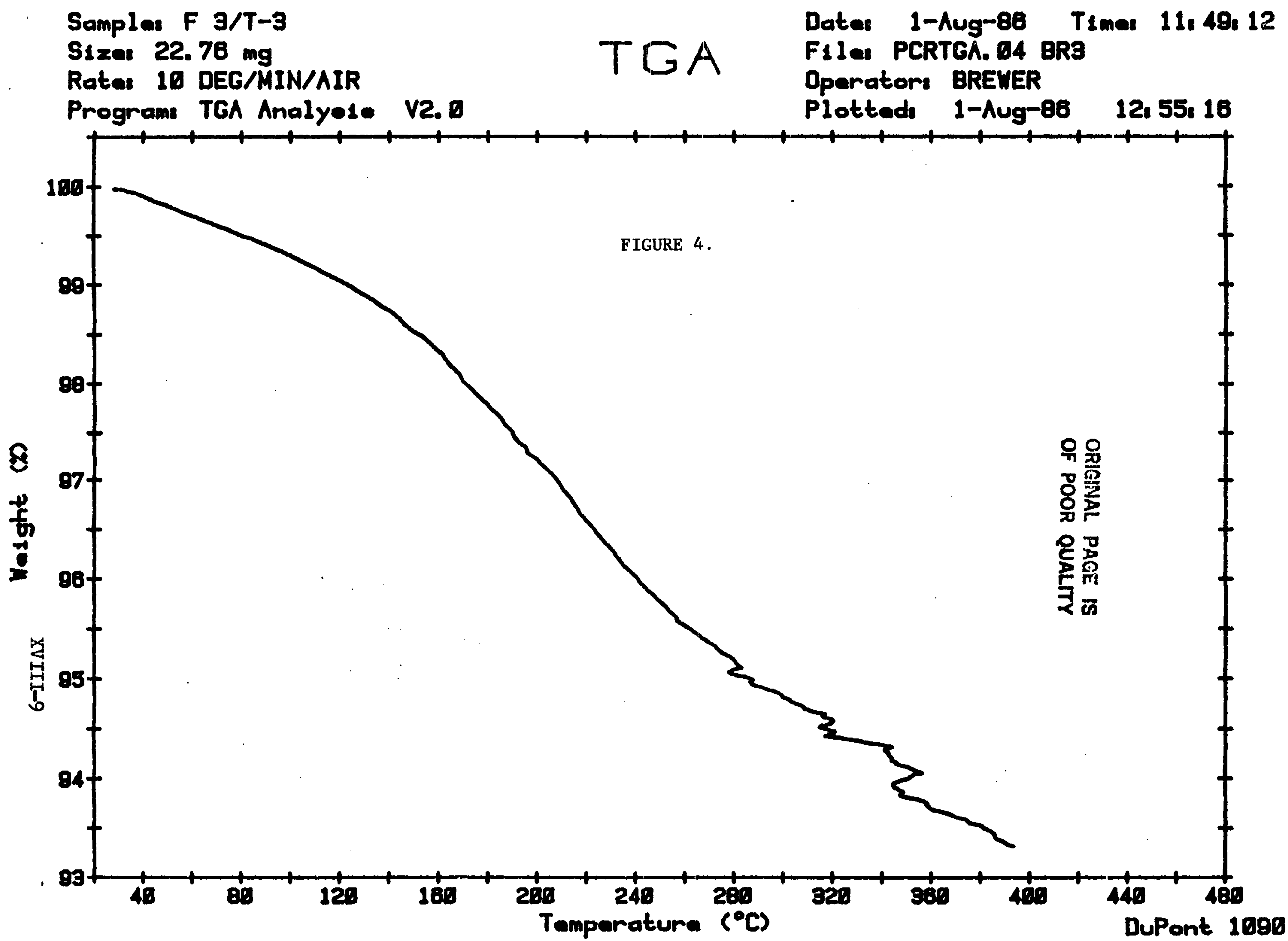

Sample: F 3/T-3
Size: 22.76 mg
Rate: 10 DEG/MIN/AIR
Program: TGA Analysis V2.0
TGA
Date: 1-Aug-86 Time: 11:49:12
File: PCRTGA.04 BR3
Operator: BREWER
Plotted: 1-Aug-86 12:55:16
Weight (%)
100
99
98
97
96
95
94
93
40
80
120
160
200
240
280
320
360
400
440
480
Temperature (°C)
DuPont 1090
ORIGINAL PAGE IS
OF POOR QUALITY

FIGURE 4.

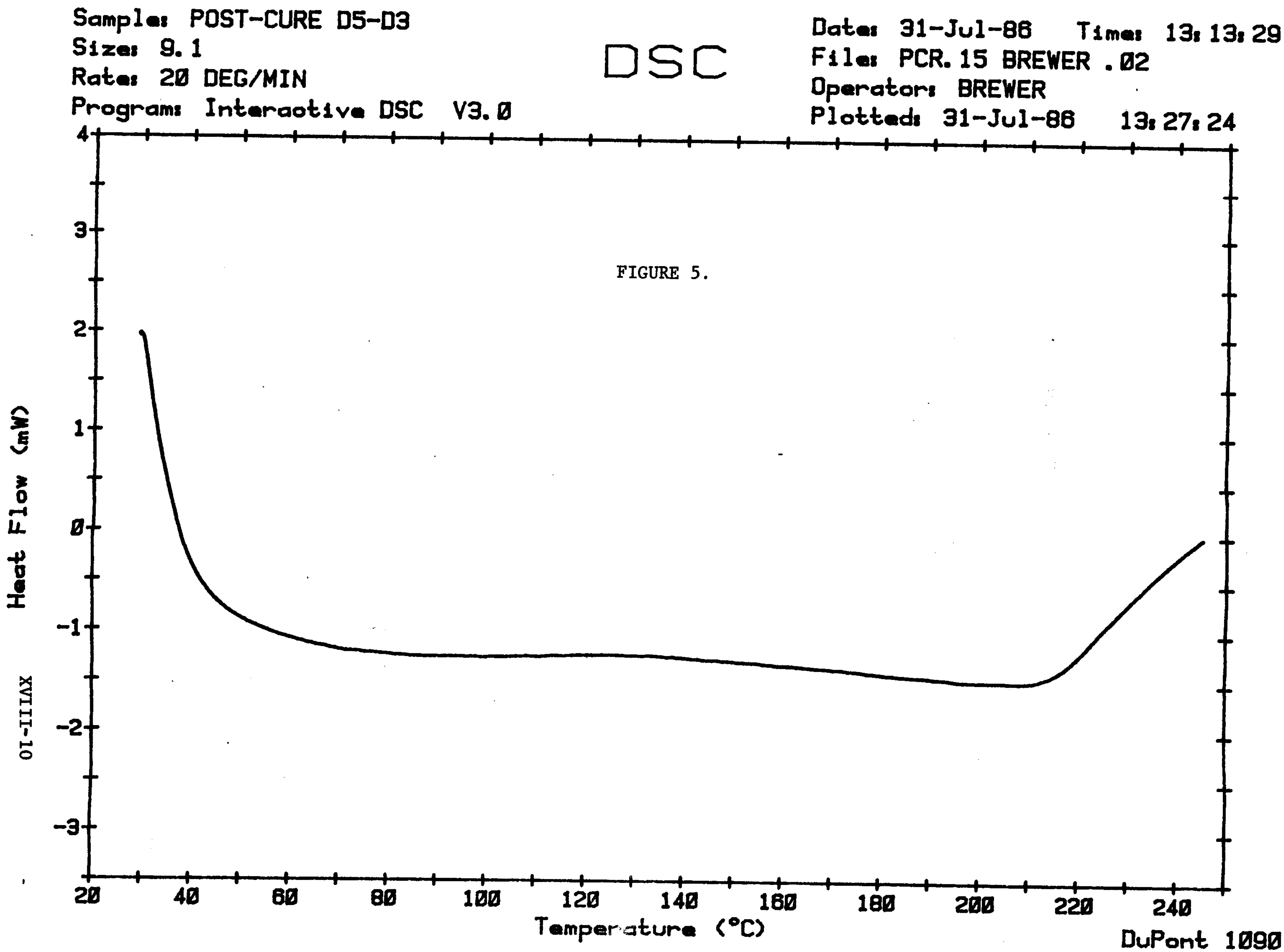

Sample: POST-CURE D5-D3
Size: 9.1
Rate: 20 DEG/MIN
Program: Interactive DSC V3.0
DSC
Date: 31-Jul-86 Time: 13:13:29
File: PCR.15 BREWER .02
Operator: BREWER
Plotted: 31-Jul-86 13:27:24
Heat Flow (mW)
4
3
2
1
0
-1
-2
-3
20
40
60
80
100
120
140
160
180
200
220
240
Temperature (°C)
DuPont 1090

FIGURE 5.

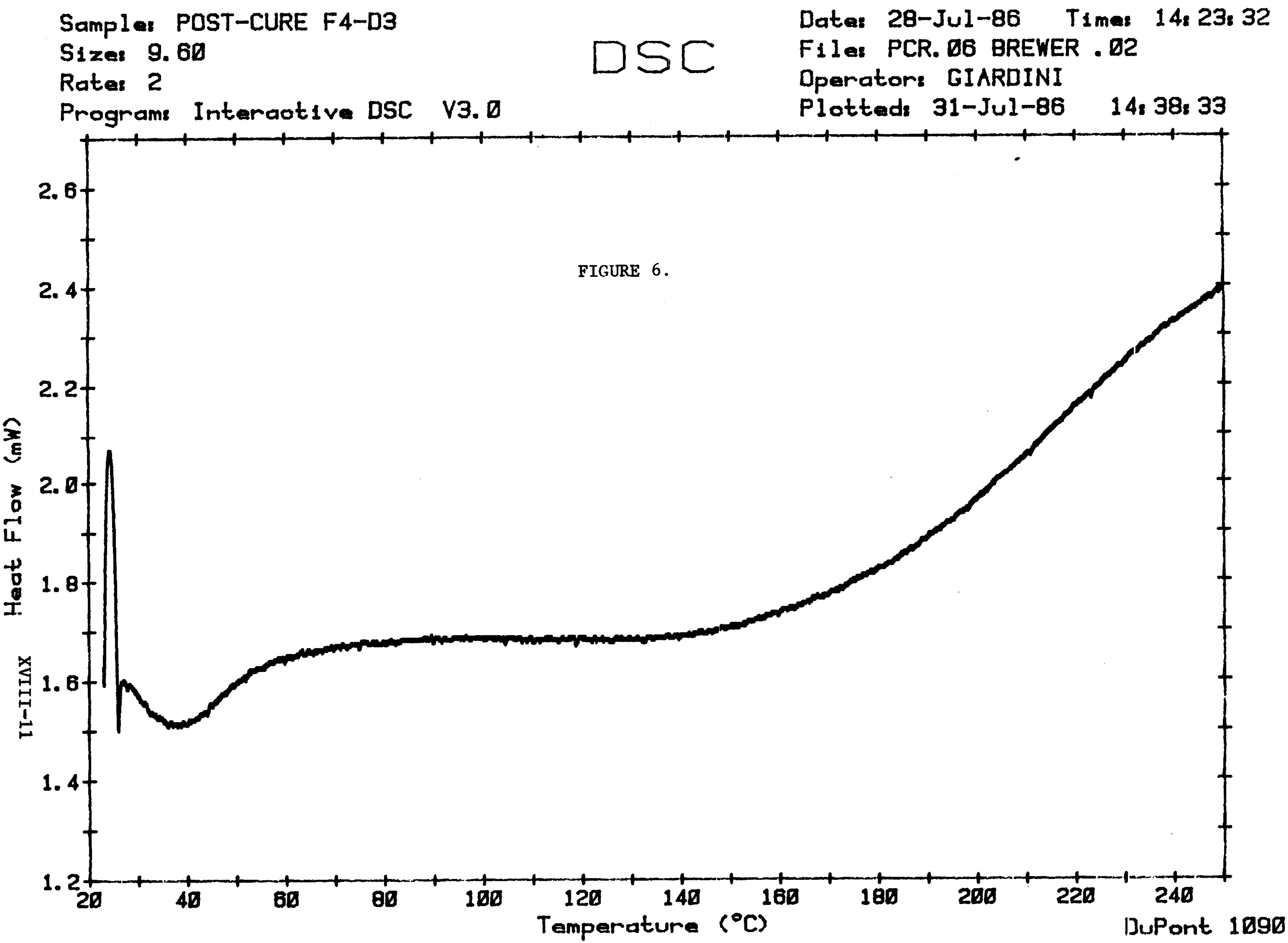
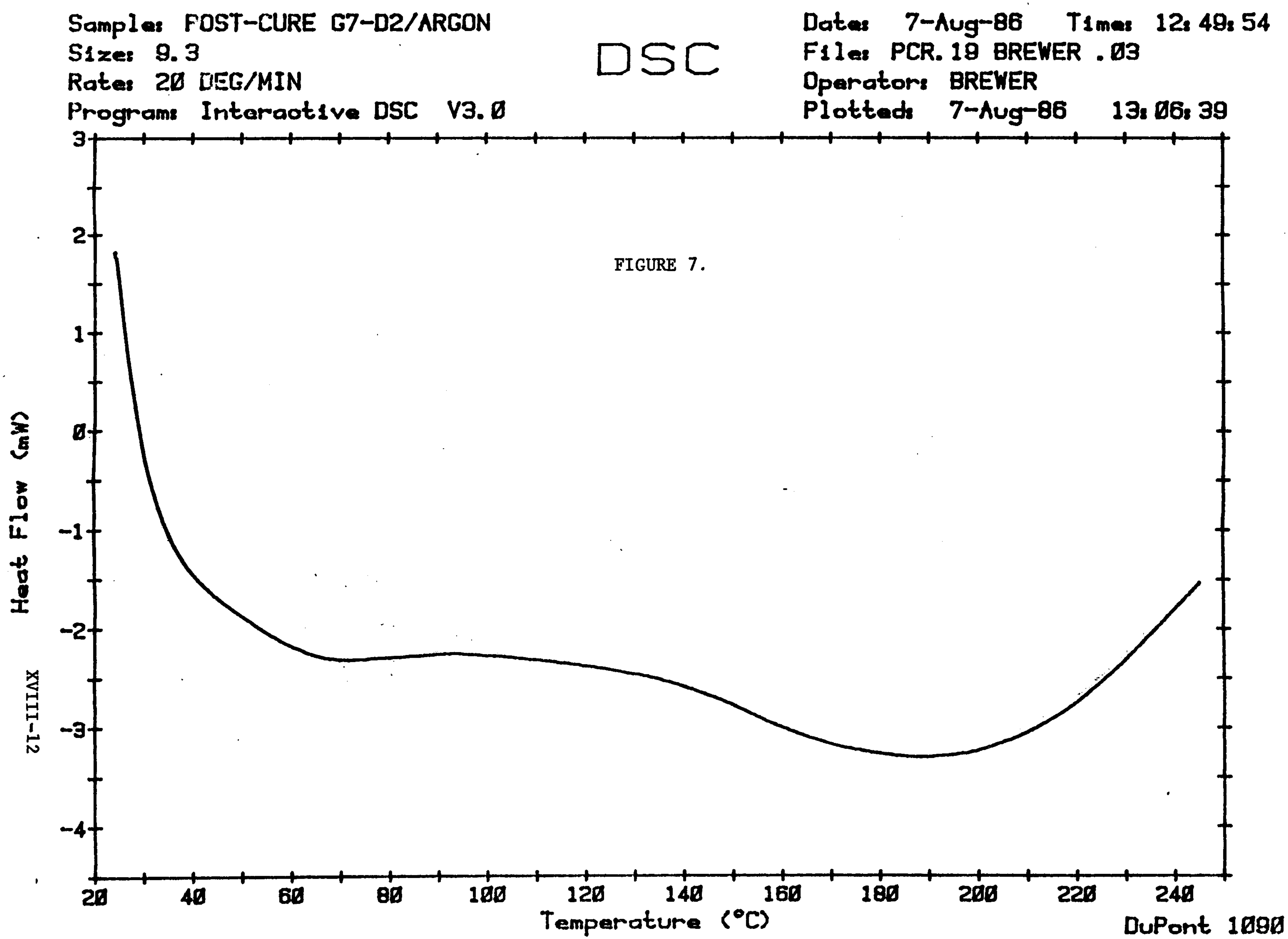

Sample: POST-CURE F4-D3
Size: 9.60
Rate: 2
Program: Interactive DSC V3.0
DSC
Date: 28-Jul-86 Time: 14:23:32
File: PCR.06 BREWER .02
Operator: GIARDINI
Plotted: 31-Jul-86 14:38:33
Heat Flow (mW)
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
20
40
60
80
100
120
140
160
180
200
220
240
Temperature (°C)
DuPont 1090

FIGURE 6.



Sample: FOST-CURE G7-D2/ARGON
Size: 9.3
Rate: 20 DEG/MIN
Program: Interactive DSC V3.0
DSC
Date: 7-Aug-86 Time: 12:49:54
File: PCR.19 BREWER .03
Operator: BREWER
Plotted: 7-Aug-86 13:06:39
Heat Flow (mW)
3
2
1
0
-1
-2
-3
-4
20
40
60
80
100
120
140
160
180
200
220
240
Temperature (°C)
DuPont 1090

FIGURE 7.

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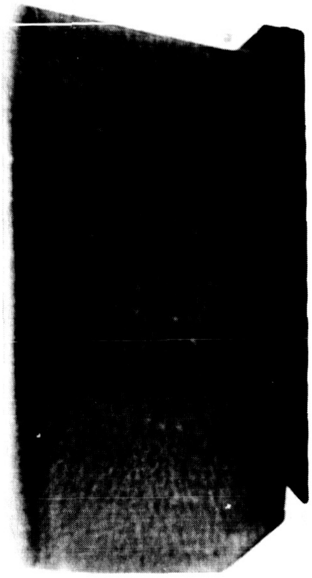
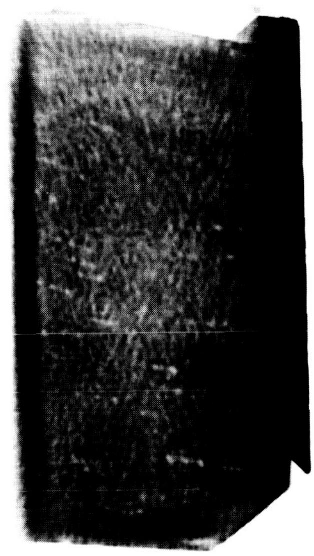
SEGMENT A



SEGMENT B



SEGMENT D

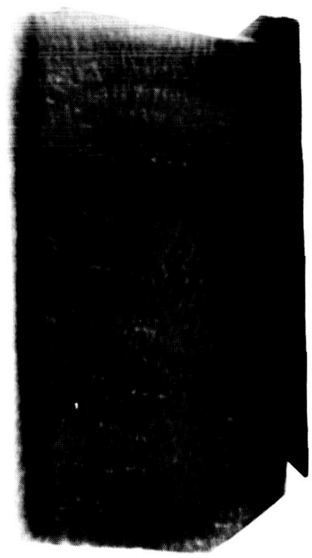


Figure 8. CROSS SECTIONAL CAT-SCAN X-RADIOGRAPH OF RING SEGMENTS A, B AND D FROM 404 RING NUMBER 42.

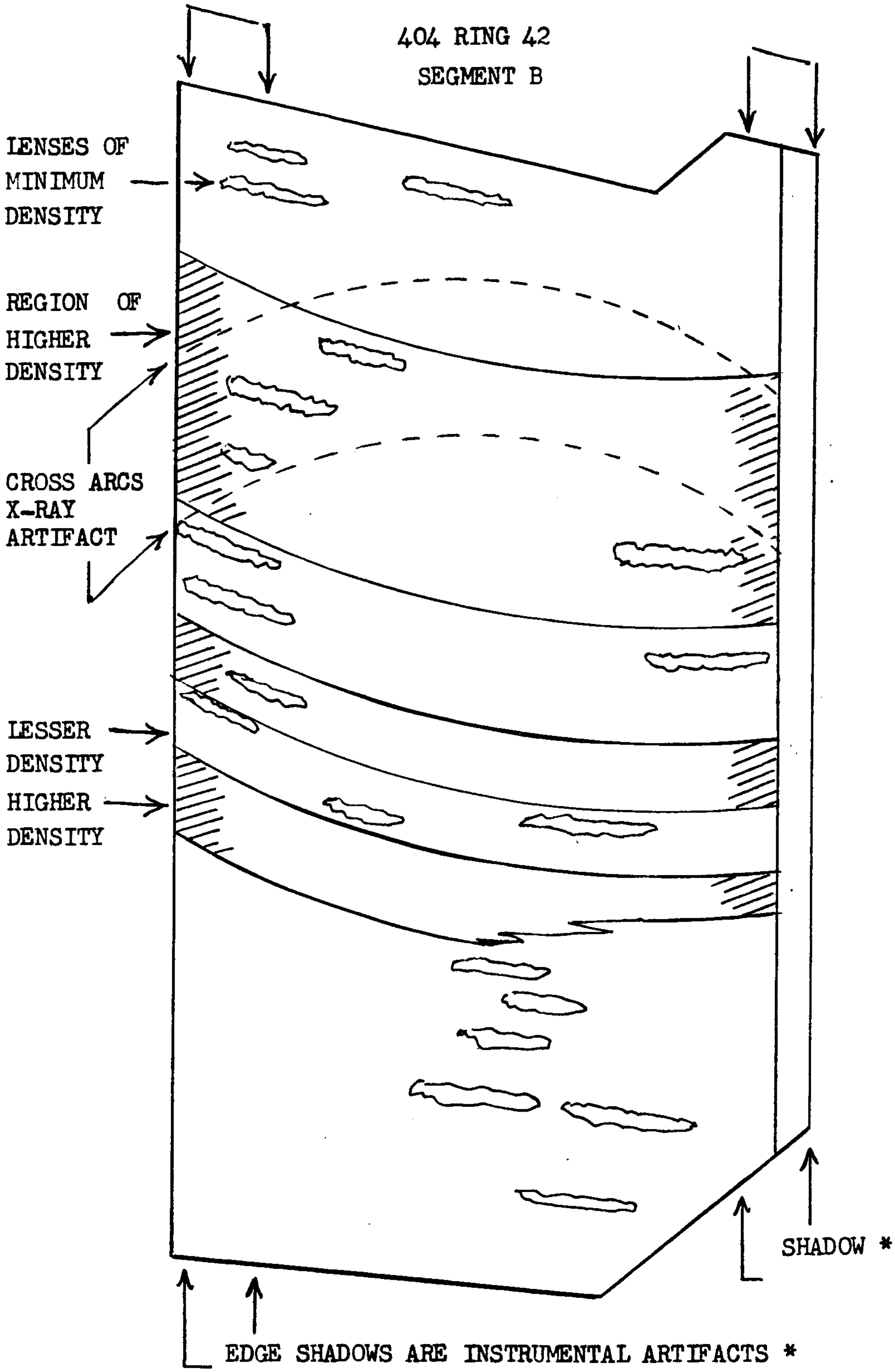
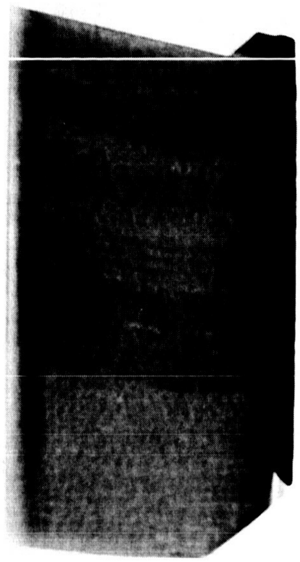
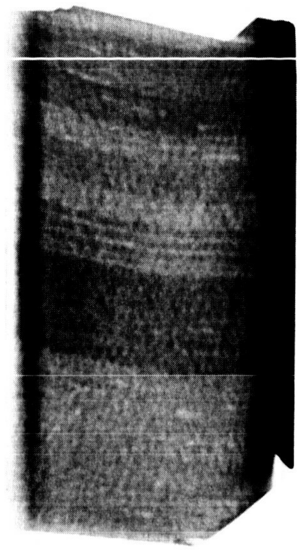


Fig.9 DENSITY VARIATIONS AND CARBON FABRIC RADIUS OF CURVATURE ARE LESS SEVERE IN 404 RING NUMBER 42 SHOWN HERE THAN IN RING NUMBER 45 (SEE FIG. 10).

SEGMENT E



SEGMENT F



SEGMENT
G

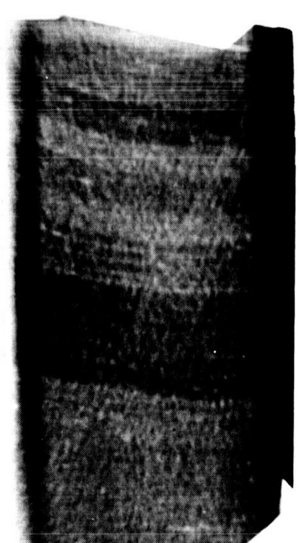


Figure 10. CROSS SECTIONAL CAT-SCAN X-RADIOGRAPHS OF RING SEGMENTS E, F AND G FROM 404 RING NUMBER 45.

C-6

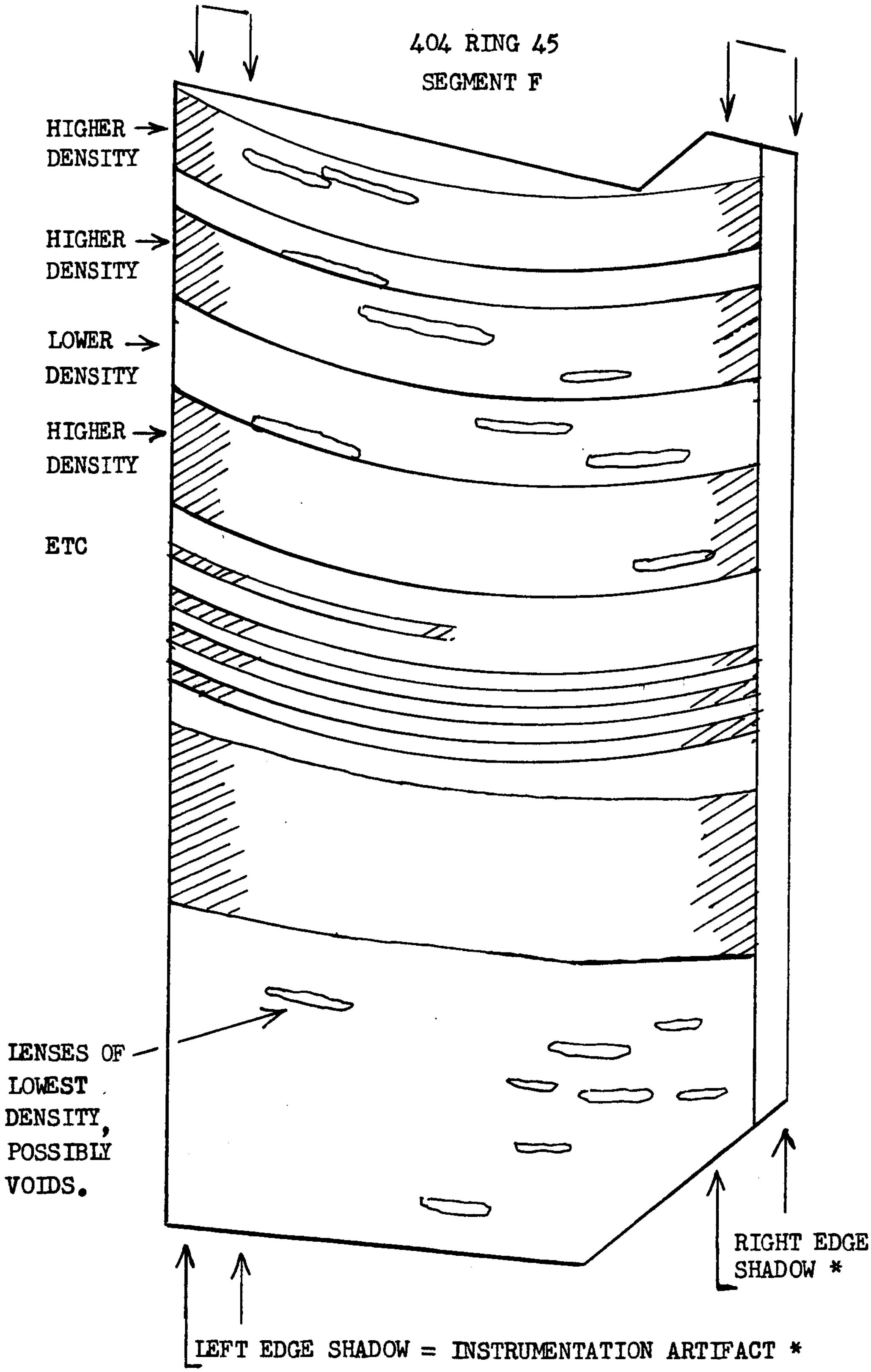


Fig. 11 THE RADIUS OF CURVATURE OF THE CARBON FIBER FABRIC IN THE UPPER HALF IS ABOUT 15 INCHES. IT LIES ALMOST FLAT IN THE LOWER THIRD.

TABLE 1. Measurements in inches of the height, cross sectional width, and cut thickness of test sections cut from 45° segments of 404 rings #42 and #45.

Ring #42 segments	Height*	Cross section*	Thickness*
A-1	6.769	3.806	1.130
A-2	6.770	3.802	1.105
A-3	6.765	3.806	1.139
A-4	6.767	3.807	1.098
B-5	6.758	3.807	1.175
B-6	6.771	3.806	1.130
B-7	6.764	3.809	1.103
B-8	6.761	3.805	1.123
C-1	6.770	3.791	1.155
C-2	6.761	3.790	1.129
D-3	6.770	3.799	1.148
D-4	6.766	3.797	1.136
D-5	6.772	3.801	1.090
D-6	6.774	3.804	1.117

Ring #45 segments	Height*	Cross section*	Thickness*
E-7	6.775	3.771	1.163
E-8	6.779	3.772	1.155
E-9	6.770	3.775	1.120
E-10	6.769	3.774	1.150
F-3	6.765	3.777	1.090
F-4	6.755	3.775	1.102
G-5	6.769	3.776	1.194
G-6	6.764	3.774	1.133
G-7	6.764	3.777	1.125
G-8	6.765	3.776	1.139

* The above values are the average of three measurements each. Limits of variation were ± .001. Measurements have been made with a vernier caliper against fiduciary marks enscribed upon the specimen. They were made for the purpose of monitoring dimensional changes that might be caused by post cure thermal treatment. See Figure 2.

TABLE 2. Percent weight loss and average rate of weight loss data for 404 ring material obtained from approximate 20 milligram samples using a Dupont thermogravimetric analyzer.*

Ring #42 segments	Average weight % loss from 75° to 350° F	Average weight loss rate over 75° to 350°F
A-3	1.38	0.0042 wt.%/°F
C-2	1.48	0.0046
D-5	1.20	0.0037
D-6	1.10	0.0034
Ring #42 av.	1.29	0.004
E-9	1.90	0.0058
E-10	1.90	0.0059
F-3	2.20	0.0068
F-4	2.60	0.0080
G-8	2.70	0.0083
Ring #45 av.	2.26	0.007

* See Figures 3 and 4 for representative weight loss versus temperature curves.

TABLE 3. Dry weights, water saturated weights, and a relative volume of permeable pore space of cross sectional test sections of 404 rings #42 and #45.

Ring #42 segments	Dry weight (gr)	Wet weight (gr)	Pore space (cc)
A-1	737.22	738.74	1.52
A-2	720.37	721.78	1.41
A-3	740.15	741.70	1.55
A-4	711.28	- *	-
B-5	750.35	751.83	1.48
B-6	733.41	734.83	1.42
B-7	716.45	717.91	1.46
B-8	726.30	-	-
C-1	751.12	-	-
C-2	713.78	715.27	1.49
D-3	747.34	748.86	1.52
D-4	734.41	735.95	1.54
D-5	715.28	-	-
D-6	724.99	726.47	1.48
		av.	1.49
Ring #45 segments			
E-7	736.81	-	-
E-8	731.86	734.20	2.33
E-9	724.40	726.50	2.09
E-10	727.52	-	-
F-3	702.87	-	-
F-4	699.02	701.03	1.82
G-5	759.02	761.19	2.16
G-6	719.60	-	-
G-7	720.62	722.78	2.15
G-8	706.75	709.06	2.30
		av.	2.14

* One third of the specimens were not humidified (48 hrs at 100° F and 85 % relative humidity) in case such exposure proved to be deleterious to the material properties.