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DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U. S. GOVERNMENT CONTRACT DA-44-109-QM-64

PROGRESS REPORT

FOR THE PERIOD

DECEMBER 5, 1951 to JUNE 4, 1952

REPORT No. 11

CONNECTICUT HARD RUBBER COMPANY

NEW HAVEN, CONNECTICUT

THE ARMED SERVICES TECHNICAL INFORMATION AGENCY
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JUN 11 1954

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Leroy R. Barnes
for ALBERT E. HINDMARSH
Captain, USN
Deputy Director, Security

THE CONNECTICUT HARD RUBBER COMPANY NEW HAVEN, CONNECTICUT

AD494888

①

DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

⑮

U. S. GOVERNMENT CONTRACT DA-44-109-QM-64 AD 494886

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Progress Rep[redacted]t, no. 11, [redacted]

5 Dec[redacted] [redacted]51-4 Jun[redacted] [redacted]52,

[redacted] ⑩ F. L. Kilbourne, Jr.,
W. Stubblebine
C. A. Walker

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SUMMARY OF RESULTS

Note: This report covers the contract period from December 5, 1951, to June 4, ~~1952, but~~ refers exclusively to that portion of the research which is concerned with a study of the mechanism of swelling of silicone rubber. Report No, 12 will cover the same period of time and all other work done under this contract during this period. Results previously reported in Report No. 10 which had to do with the early swelling experiments are repeated below for the convenience of the reader.

From Report No. 10:

1. Silicone rubber swells rapidly in benzene and other good solvents during the first 10 hours at 25°C. After this time, swelling continues at a gradual rate up to at least 1000 hours and shows no indications of reaching a stationary state. This continued incremental swelling is attributed to the breaking of the molecular structure by thermal agitation of the swollen molecular structure.
2. Extrapolation of this portion of the swelling curve to zero time gives values of v_2, the volume fraction of polymer in the swollen network. This thermodynamic quantity can be used to calculate M_c, the molecular weight between cross-links of the vulcanized polymer.
3. The swelling measurements were found to be affected by the simultaneous extraction of polymer by the swelling liquid. The swelling measurements were corrected for this

extraction, this being the first time as far as we can learn from the literature, that swelling measurements have been thus corrected. In the case of a very lightly vulcanized sample this correction is absolutely essential since the sample starts to de-swell after about 30 hours in the solvent. The percentage of polymer that is extractable decreases with increasing concentration of curing agent as does also the degree of swelling. These changes are proportional to the concentration of benzoyl peroxide below 2 per cent but there is very little difference in the polymers which are cured with 2 and 8 per cent benzoyl peroxide.

4. A completely novel method of measuring swelling continuously was devised and the equipment was designed, constructed and used in this work.

5. Data have been accumulated for calculation of M_c after the determination of μ, the interaction coefficient between solvent and polymer.

6. Experimental work on swelling has been correlated with the theoretical equations developed by Flory, Huggins, Gee and others who have studied swelling by following thermodynamic principles.

<u>From the present report</u>:

7. Incremental swelling was observed with all of the solvents used except with perfluoro(methylcyclohexane) which did not swell the silicone polymer at all and

methyl ethyl ketone which was the poorest swelling agent of the nine remaining solvents. The statement in result No. 1 above, that swelling "shows no sign of reaching the stationary state," must be qualified by saying that it probably does not apply to poor swelling agents.

8. In Test 3, the effect of varying the benzoyl peroxide curative from 0.5 to 2.0 and 8.0, was explored by means of the swelling measurements. Exact values for M_c, the molecular weight between cross-links, cannot be calculated from the data since the value of μ, the polymer-solvent interaction coefficient, for each pair of rubber and solvent, has never been determined. It was possible, however, to place maximum and minimum limits on M_c and then to average these values arriving at reasonable average values of M_c. These are given in the table on the following page.

The values of M_c show clearly that the first 2 per cent of benzoyl peroxide added to a silicone recipe is far more efficient in its cross-linking action then the next 6 per cent. The average M_c with 2 per cent of benzoyl peroxide was 11,000 and with 8 per cent was 9,000.

9. In Test 4 wide variations in the degree of vulcanization of silicone rubber were made and swelling tests again carried out. The resulting maximum and minimum M_c values were again averaged and the results are given in the table.

Variation of M_c with the Method of Preparation of Silicone Rubber*

Test	Per cent Benzoyl Peroxide	Press Cure Time Min	Press Cure Temp, °F.	Oven Cure Time Hr.	Oven Cure Temp. °F.	M_c
3a	0.5	15	250	24	300	>24,000
3c	2.0	15	250	24	300	11,000
3i	8.0	15	250	24	300	9,000
4a	2.0	10	250	24	300	17,000
4b	2.0	[illegible]	[illegible]	24	300	14,000
4c	2.0	45	230	24	300	18.000
4d	2.0	15	[illegible]	24	300	11,000
4e	2.0	15	250	1	300	24,000
4f	2.0	15	250	48-hr. cycle to 480°F.		13,000

*Important variables underlined.

10. The average values of M_c indicate that a 1-hour oven cure at 300°F. produces enough cross-links to bring the molecular weight down to 24,000, while a 24-hour cure at 300°F. reduces it to from 11,000 to 18,000. A gradually rising temperature cycle extending over 48 hours at a maximum temperature of 480°F. had the effect of reducing M_c to 13,000 in a single test.

11. It is known that the primary vulcanization reaction with benzoyl peroxide is completed in the initial press cure or in the very early stages of the oven cure. Since further cross-linking is evident during prolonged oven curing, it is suggested that loss of chain ends during the oven cure results in further cross-linking.

12. Perfluoro(methylcyclohexane) does not swell silicone rubber within experimental error.

13. In increasing order of degree of swelling at

equilibrium, the solvents used are listed below, together with the equilibrium v_2 values:

Test	Solvent	v_2 equil.
6j	Perfluoro(methylcyclohexane)	1.0
6h	Methyl ethyl ketone	.285
6i	Benzene	.206
6g	d-Limonene	.183
6c	Xylene	.182
6a	Toluene	.170
6d	Cyclohexane	.148
6e	n-Octane	.141
6b	n-Hexane	.138
6f	Methylcyclohexane	.137

14. Since the solvents in the above list were compared for swelling activity with a single sample of cured rubber in which M_c was, therefore, constant, it was possible to arrive at relative values of μ, the solvent-polymer interaction coefficient, in each case. By assuming certain maximum and minimum values for M_c, corresponding maximum and minimum values for μ were calculated. From these values a relationship between μ and $V_1 \delta_1$ was plotted. Thermodynamic considerations by Gee and Flory and others predict the existence of this relationship between μ, which is related to the heat of mixing, and δ_1, which is the cohesive energy density. This relationship is plotted on page 41.

15. An improvement in Gee's method of calculating the value of δ_c, cohesive energy density of the rubber, has been worked out. By this method, the cohesive energy density of vulcanized silicone rubber (General Electric SE-76) has been found to be 7.50 ± .05.

16. No correlation between the rate of swelling of silicone rubber and the liquid diffusivity, or between the rate of swelling and the ultimate value of v_2 was found.

17. The polymer-solvent interaction coefficient μ (Flory) does not correspond to the similar function found in osmotic pressure equations (Huggins), at least for polydimethylsiloxane and methyl ethyl ketone.

18. It is suggested in the Discussion how it will be possible to arrive exactly at values of M_c and μ. It is also suggested that swelling measurements will serve as a tool to investigate the mechanism of reinforcement. It is obvious, also, that this tool will be useful in investigating the curing action of certain surface-active pigments.

19. It is felt that this work is an important contribution to the theory of structure of vulcanized elastomers.

I. MOLECULAR WEIGHT AND SWELLING STUDIES ON SILICONE RUBBER

A. Introduction

The program of this swelling study was outlined in a series of eight experiments which was presented in Table IV-A-1, page 75 of Progress Report 10. This same outline is presented in Table A-1, page 3 of this report.

Tests 1, 2, 3 and 8 were reported in the previous Progress Report; and a review of Test 3 along with Tests 4 and 6 is reported in the following sections. These tests bear considerable practical as well as theoretical importance and will provide a sound basis for further investigations on the nature of pigment reinforcement.

Future work will be directed toward Test 7, Determination of the Effect of Pigment Reinforcement on the Rate and Magnitude of Swell of Silicone Rubber, in an effort to learn more about the practical as well as the theoretical mechanism of pigment reinforcement.

The apparatus for volume measurement was described in Section IV-B, pp. 76-82, of Progress Report 10, and the procedure was varied only slightly for the subsequent tests during the period this report covers. This variation involved the weighing of swollen rubber samples within a tare bottle containing the proper solvent; frequent gravimetric measurements and volume calculations therefrom thus served as a check on the accuracy of the volumetric measurements and provided accuracy to ±1 per cent.

A compendium of all test conditions and results is presented in Table A-2, page 4.

TABLE A-1

Program of Swelling Study

Test	Object	Conditions
1	a. Determination of the precision of swelling measurement. b. Investigation of size of sample in relation to the rate of swell and the precision of measurement.	Silicone polymer. No pigment. 2% benzoyl peroxide. Benzene solvent. Varied sample size.
2	a. Investigation of a secondary swell. b. Determination of the existence of an equilibrium swell.	Repeat swell of samples of Test 1 in benzene.
3	Determination of the effect of benzoyl peroxide concentration on the swell of silicone rubber.	Silicone polymer. No pigment. Varied benzoyl peroxide. Constant cure. Benzene solvent.
4.	Determination of the effect of curing conditions on the swell of silicone rubber.	Silicone polymer. No pigment. 2% benzoyl peroxide. Varied cure. Benzene solvent.
5.	Determination of the effect of heat treatment of silicone polymer prior to compounding.	Silicone polymer heat treated. No pigment. 2% benzoyl peroxide. Benzene solvent.
6.	a. Determination of the effect of various solvents and calculation of heat and entropy of mixing. b. Attempt to correlate thermodynamic properties with swelling results.	Silicone polymer. No pigment. 2% benzoyl peroxide. Constant cure. Varied solvents.
7.	Determination of the effect of pigment reinforcement on the rate and magnitude of swell of silicone rubber.	Silicone polymer. Varied pigments, pigment loadings. 2% benzoyl peroxide. Constant cure. Benzene solvent.
8	Determination of the rate of extraction of silicone polymer from vulcanized network by solvent action.	Silicone polymer. No pigment. Varied benzoyl peroxide. Varied cure. Benzene solvent.

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Test	Variable Studied	Sample Preparation						Solve
		Formula parts b.perox.	Curing Conditions				Size in. x.070"	
			Time min.	Temp °F.	Time hr.	Temp °F.		
1	Sample Size	2.0	15	250	24	300		Benze
a							3/8 x 1/4	
b							"	
c							9/16 x 1/4	
d							"	
e							3/4 x 1/4	
f							"	
2	Secondary Swell							Benze
a		sample 1c after 238-hour swell and de-swell						
b		1d						
c		1e						
d		1f						
3	Compounding formula		15	250	24	300		Benze
a_1a_2		0.5					1/2 x 3/16	
c_1c_2		2.0					3/4 x 1/4	
i_1i_2		8.0					3/4 x 1/4	
4	Curing Conditions						3/4 x 1/4	Benze
a_1a_2		2.0	10	250	24	300		
b_1b_2			10	230	24	300		
c_1c_2			15	230	24	300		
d_1d_2			15	250	24	300		
e_1e_2			15	250	1	300		
f_1f_2			15	250	48 to 480°F. gradual rise			
6	Solvent	2.0	15	250	24	300	3/4 x 1/4	
a_1a_2								Tolue
b_1b_2								n-Hex
c_1c_2								Xylen
d_1d_2								Cyclohe
e_1e_2								n-Oct
f_1f_2								Methylcyclohe
g_1g_2								d-Limo
h_1h_2								Methyl ethyl ket
i_1i_2								Benze
j_1j_2								Perfluoro(methylcyclohex

TABLE A-2

COMPENDIUM OF TEST CONDITIONS AND RESULTS

olvent	Molal Vol. c.c.	Solubility Parameter	Duration of Swell hr.	v_2 equil.	M_c max.	M_c min.	μ max.	μ min.
enzene	89.40	9.16	238					
enzene	89.40	9.16	1012					
nzene	89.40	9.16						
			174	.084	1,000,000	24,200	.521	.436
			144	.206	14,900	6560		
			218	.229	12,000	5400		
nzene	89.40	9.16					.521	.436
			146	.187	24,200	8970		
			145	.205	20,500	7600		
			146	.193	25,900	8840		
			144	.206	14,900	6560		
			145	.180	38,000	10,900		
			145	.195	19,300	7830		
					14,900	6560		
luene	106.85	8.91	174	.170			.439	.295
Hexane	131.60	7.27	144	.138			.323	.068
lene	123.46	8.82	144	.182			.458	.311
hexane	108.74	8.20	144	.148			.400	.211
Octane	163.52	7.55	175	.141			.308	.000
hexane	128.33	7.83	144	.137			.333	.071
monene	162.2	8.5	144	.183			.416	.224
etone	90.16	9.22	144	.285			.577	.531
nzene	89.40	9.16	144	.206			.521	.436
exane)	173.3	6.5	145	1.00				

2

B. Experimental

Test 3 - Effect of Benzoyl Peroxide Loading on Swelling Characteristics

Object: This test was for the purpose of determining the effect of vulcanization with varied benzoyl peroxide concentration on the swelling characteristics of silicone polymer, and thus by calculation of M_c to substantiate authentically the decreasing effectiveness of benzoyl peroxide as a cross-linking agent when used in concentrations above the optimum of about 2.0 parts per 100 parts of polymer.

Procedure: Test samples 3a, 3c and 3i were prepared from slabs compounded with 0.5, 2.0 and 8.0 parts of benzoyl peroxide per 100 parts of silicone polymer. Milling conditions were similar, and slabs were press cured 15 minutes at 250°F. and oven cured 24 hours at 300°F.

Samples were immersed in pure benzene at 25.0°C. and volumes were measured at frequent intervals. After completion of the test, samples were de-swelled and weighed.

Calculations of v_2 were made by the same procedure as discussed on page 85 of Progress Report 10.

Results: The results of Tests 3a and 3i were presented in Figures IV-C-4 and IV-C-5 following page 92 of Progress Report 10. The swelling of sample 3c was similar to that of Test 1 (samples were prepared similarly) but the present results are more accurate.

Distinctly linear log-log relationships of v_2 (the volume fraction of polymer in the swollen network) with time were obtained as in previous tests with a gradual transition between the initial and incremental periods. The rate as well as the magnitude of swell varied considerably with the benzoyl peroxide content, as is shown by the following equations of the linear curves:

	Initial Period	Incremental Period
Test 3a	.083 to 4.0 hours	25 to 175 hours
	$\ln v_2 = -.496 \ln(t) -1.368$	$\ln v_2 = -.0254 \ln(t) -2.407$
Test 3c	.083 to 1.5 hours	6 to 145 hours
	$\ln v_2 = -.310 \ln(t) -1.194$	$\ln v_2 = -.0186 \ln(t) -1.537$
Test 3i	.083 to 2.0 hours	10 to 230 hours
	$\ln v_2 = -.257 \ln(t) -1.036$	$\ln v_2 = -.0521 \ln(t) -1.286$

Equilibrium swell as defined by J. R. Scott was determined in Figure B-1, page 11, (replacing Figure IV-C-6 of Report 10); from these values and from the molal volume of benzene and the density of polymer, equations for M_c in terms of μ were calculated by means of Flory's equation on page 44:

Test	Per cent Benzoyl Peroxide	V_2 Equil.	M_c
3a	0.5	.084	$\frac{4890}{.525-\mu}$
3c	2.0	.206	$\frac{1000}{.588-\mu}$
3i	8.0	.229	$\frac{838}{.591-\mu}$

D. W. Scott(1) of the General Electric Company investigated the molecular weight distribution of a polydimethylsiloxane elastomer which he described as follows:

Fraction	Description	Per cent of Polymer	Average Molecular Weight
A	Elastic	17	2,800,000
B	Soft & Plastic	14	1,500,000
C	Soft & Plastic	18	610,000
D	Very Plastic	27	290,000
E	Viscous Liquid	15	Much less than 290,000

The elastomer used in this study, General Electric SE 76, is chemically identical with that used by Scott but the molecular weight distribution may be slightly different.

For calculation purposes, it was assumed that the average molecular weight of the polymer used in this

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(1) Scott, D.W., J. Amer. Chem. Soc. 68, 1877-1879 (1946)

study did not exceed 1,000,000. Since it was impossible that M_c, the molecular weight between cross-links, could exceed the linear molecular weight previous to cross-linking, the limiting value of $M_c \leq 1,000,000$ was applied to the above equation of Test 3a where M_c is given in terms of μ . This provided a limiting maximum value of $\mu \leq 0.521$, and from this the limiting values of M_c were calculated for Tests 3c and 3i.

From Test 6 it was found possible to define a minimum possible value of M_c for sample 3c and hence for the other samples. Therefore, the correct value of M_c for the various samples of this test lies within the following range:

Test	Per cent Benzoyl Peroxide	M_c max.	M_c min.
3a	0.5	1,000,000	24,200
3c	2.0	14,900	6,600
3i	8.0	12,000	5,400

Assuming that benzoyl peroxide causes cross-linking of silicone rubber by the formation of methylene groups, the decomposition of one molecule of benzoyl peroxide causes the formation of one cross-link between adjacent polymer molecules and hence two molecular chains between cross-links. Assuming such quantitative reaction, the minimum values of M_c for the various samples of this test would be:

3a $$M_c = \frac{(100)}{(0.5)}\frac{(242.22)}{(2)} = 24{,}200$$

3c $$M_c = \frac{(100)}{(2.0)}\frac{(242.22)}{(2)} = 6050$$

3i $$M_c = \frac{(100)}{(8.0)}\frac{(242.22)}{(2)} = 1520$$

The effectiveness of benzoyl peroxide, expressed as the ratio of the number of cross-links formed to the number that would be formed by quantitative reaction, is hence given by ratios of the above values of M_c; values are tabulated below:

Test	Per cent Benzoyl Peroxide	Effectiveness
3a	0.5	2.4 - 100 %
3c	2.0	40.6 - 92 %
3i	8.0	12.7 - 28 %

Conclusions: The swelling characteristics and the molecular weight between cross-links of silicone rubber are definitely functions of the amount of benzoyl peroxide used for vulcanization. The number of cross-links increases with the amount of benzoyl peroxide used, but the effectiveness of the latter reagent decreases when used at higher concentrations.

Use of Flory's equation for M_c of a polymer sample which is only slightly cross-linked (such as 3a) is theoretically inaccurate due to the large number of loose-ends and polymer molecules which are not a stable portion of the cross-linked network. Furthermore, where v_2 is extremely small, the denominator of the Flory equation becomes a minute difference between two relatively large numbers. Variation of v_2 by as little as 1 per cent can cause as much as 25 per cent variation of the calculated M_c.

Volume measurements in this test are considered accurate to ±1 per cent; graphical calculations of v_2 at equilibrium are probably accurate to ±2 per cent.

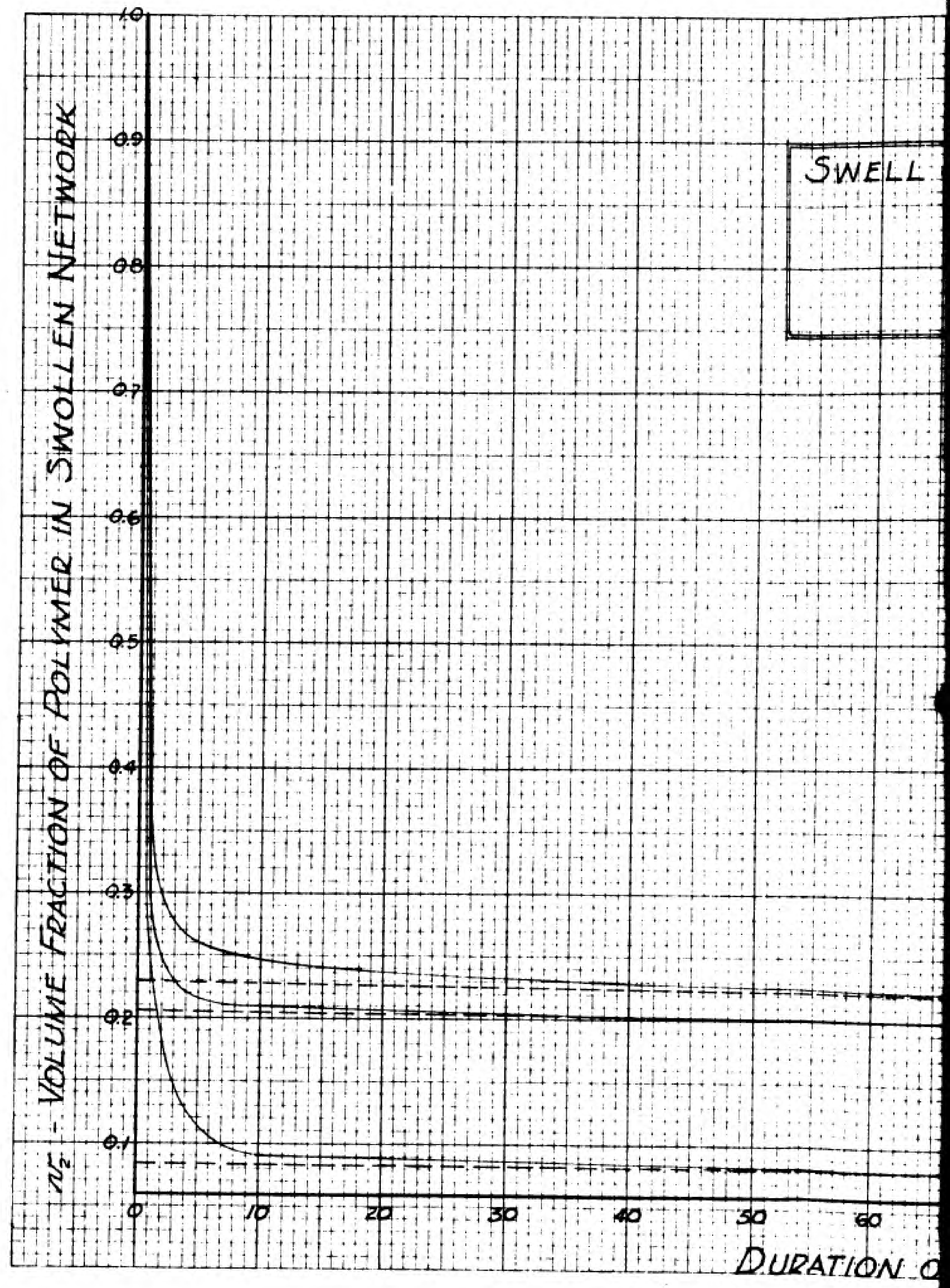
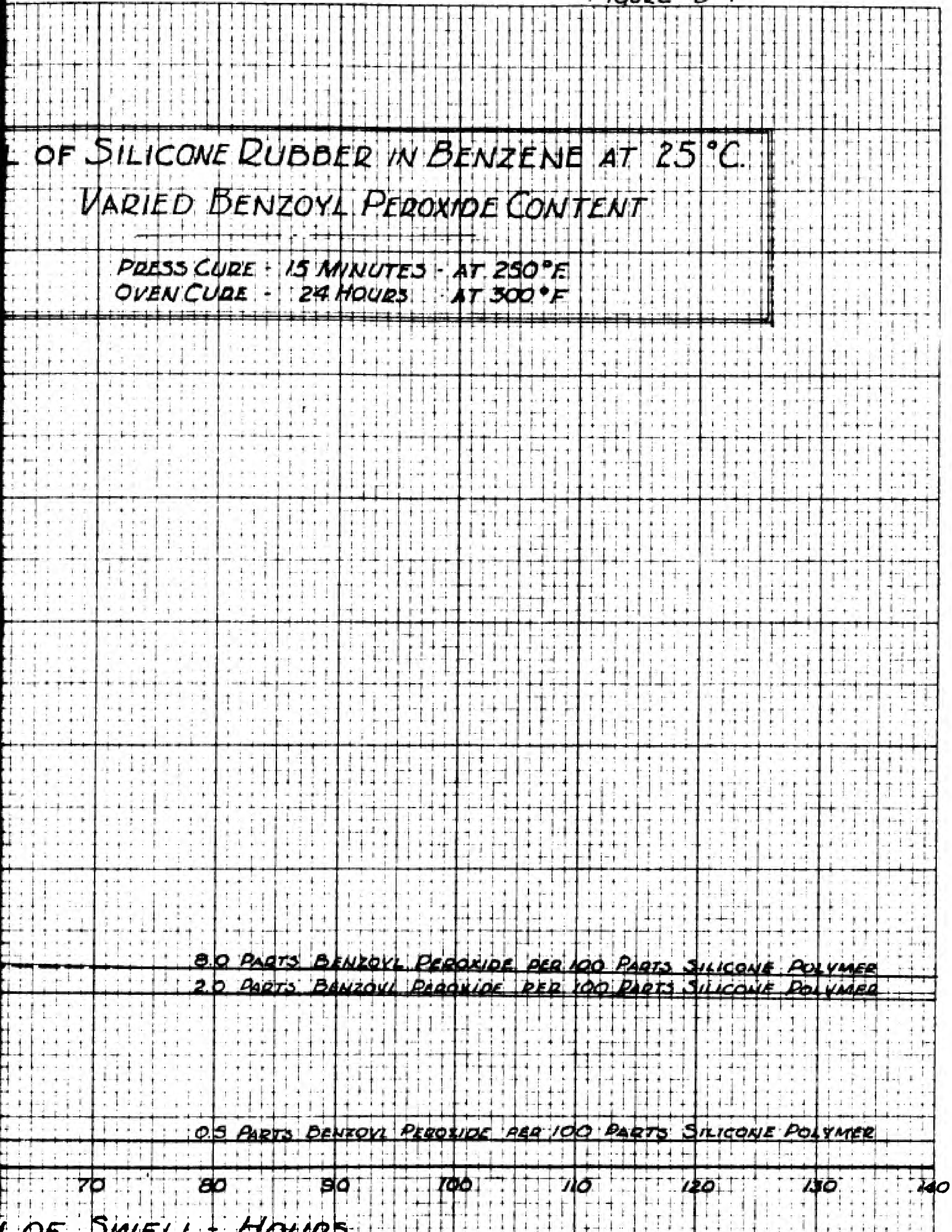

v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
SWELL
DURATION O

FIGURE B-1


L OF SILICONE RUBBER IN BENZENE AT 25°C.
VARIED BENZOYL PEROXIDE CONTENT
PRESS CURE - 15 MINUTES - AT 250°F
OVEN CURE - 24 HOURS AT 300°F
8.0 PARTS BENZOYL PEROXIDE PER 100 PARTS SILICONE POLYMER
2.0 PARTS BENZOYL PEROXIDE PER 100 PARTS SILICONE POLYMER
0.5 PARTS BENZOYL PEROXIDE PER 100 PARTS SILICONE POLYMER
70
80
90
100
110
120
130
140
OF SWELL - HOURS

Test 4, Effect of Curing Conditions on Swelling Characteristics

Object: The object of this test was to study various press and oven cure conditions of time and temperature and to determine the effect of these conditions on the swelling characteristics of silicone elastomer.

Procedure: A large master-batch of polymer was prepared by milling together 2.0 grams of benzoyl peroxide with 100 grams of SE 76. This batch was separated into four portions and given four different press cures. Uniform oven cures were given to three of the samples, and two different oven cures were given to the other. These curing conditions are listed below and are graphed in Figures B-2 and B-3, pages 19 and 20.

Slab	Test	Press Cure Time, Min.	Press Cure Temp, °F.	Oven Cure Time, Hr.	Oven Cure Temp, °F.
a	4a	10	250	24	300
b	4b	10	230	24	300
c	4c	15	230	24	300
d	4d = 3c	15	250	24	300
d	4e			1	300
d	4f			48-hour cycle at 480°F.	

The particular time-temperature cycle given to sample 4f was a standard factory-recommended oven cure.

The range of press and oven cure conditions in this test was designed to cover that normally encountered in industrial and laboratory vulcanizations of silicone rubber.

Loss of weight of the slabs during each curing operation was determined.

Samples were swelled in benzene at 25.0°F. and the rates of swell were determined during 5-minute to 145-hour periods. Loss of weight due to extraction during swelling was also determined.

The results of Test 3c were accepted for Test 4d since samples for that test were prepared according to conditions comparable to those desired for Test 4d; there may have been slight differences.

Results: Loss of weight of the slabs during press cure was independent of the curing conditions; loss of weight during the oven cure decreased slightly with increasing time and temperature of the previous press cure as shown by Table B-1, page 18.

As shown in Figure B-4, page 21, the rate of swell of silicone elastomer was only slightly affected by the press cure conditions. A considerable difference in the swelling of duplicate samples $4a_1$ and $4a_2$ was noted during the initial period of swelling, but the two samples exhibited the same rate of swell during the incremental period. For the graphical calculation of v_2, sample $4a_2$ was selected.

Likewise, in Tests 4d, e, and f (Figure B-5, page 22) the rates of swell were only slightly different during the initial period (except for the anomalous behavior of sample $4f_2$), but there was a distinct difference in rate and magnitude of swell during the incremental period.

Equations for the rates of swell were as follows:

Variation of press cure

Test	Initial Period	Incremental Period
4a	.083 to 1.0 hours $\ln v_2 = -.309 \ln(t) -1.309$	7.0 to 145 hours $\ln v_2 = -.0473 \ln(t) -1.507$
4b	.083 to 1.5 hours $\ln v_2 = -.306 \ln(t) -1.204$	5.0 to 175 hours $\ln v_2 = -.037 \ln(t) -1.466$
4c	.083 to 1.5 hours $\ln v_2 = -.296 \ln(t) -1.242$	5.0 to 145 hours $\ln v_2 = -.0611 \ln(t) -1.439$
4d	.083 to 1.5 hours $\ln v_2 = -.310 \ln(t) -1.194$	6.0 to 144 hours $\ln v_2 = -.0186 \ln(t) -1.537$

Variation of oven cure

4d	.083 to 1.5 hours $\ln v_2 = -.310 \ln(t) -1.194$	6.0 to 144 hours $\ln v_2 = -.0186 \ln(t) -1.537$
4e	.083 to 2.0 hours $\ln v_2 = -.303 \ln(t) -1.213$	5.0 to 145 hours $\ln v_2 = -.0512 \ln(t) -1.516$
4f	.083 to 1.0 hours $\ln v_2 = -.296 \ln(t) -1.22$	5.0 to 145 hours $\ln v_2 = -.056 \ln(t) -1.429$

In Figures B-6 and B-7, pages 23 and 24, are calculated the equilibrium values of v_2 according to R.L. Scott's definition which involves extrapolation of the incremental values to zero time. These values and the amount of extraction of polymer during the swelling period are listed below:

Test	Press Cure	Oven Cure	v_2 Equil.	Per cent Extracted
4a	10/250	24/300	.187	5.2
4b	10/230	"	.205	6.0-6.5
4c	15/230	"	.193	4.8
4d	15/250	"	.206	4.3
4e	"	1/300	.180	6.5-6.8
4f	"	cycle 480°F.	.195	5.5-7.2

The close comparison of the extreme tests, 4b and 4d, is contradictory to the trend of Tests 4b, c and a, which indicate a tendency toward decreasing v_2 with decreasing severity of press cure. It has been proven that benzoic acid, which is a product of the vulcanization reaction, causes depolymerization of silicone polymer. Since freedom of escape was restricted in the mold, the increased presence of benzoic acid may have counter-acted the increased cross-linking reaction during the longer duration and higher temperature of the press cure of 4d.

The amount of polymer extracted during the immersion in benzene (as well as the weight loss during oven cure) was inversely related to severity of the press cure, which indicated that longer time and higher temperature in this operation provided a more stable cross-linked network with fewer non-vulcanized and hence volatile or extractable polymer molecules.

The high-temperature oven cure of Test 4f probably caused some depolymerization of the network which resulted in a greater amount of swelling and of polymer extraction than was obtained with the more moderate cure of sample 4d. The slight oven cure of sample 4e led to a relatively high degree of swelling.

According to the previous and subsequent assumptions regarding possible maximum and minimum values of M_c and μ , values calculated from the Flory equation (page 44) are listed below:

Test	M_c max.	M_c min.
4a	24,200	6970
4b	20,500	7600
4c	25,900	8840
4d	14,900	6560
4e	38,000	10,900
4f	19,300	7830

Comparison of Tests 4d and 4e shows that the cross-linking reaction definitely continues during the 1- to 24-hour period of the oven cure at 300°F.

Conclusions: The effects of moderate variation of press cure conditions (when followed by a good oven cure) on the swelling characteristics and on M_c of the silicone elastomer are slight. Longer press cures at higher temperatures lead to less volatilization during oven cure and less extraction during swelling of silicone rubber which has been vulcanized with 2 per cent of benzoyl peroxide.

The volatilization of polymer increases with time of oven cure at 300°F. and the molecular weight between cross-links decreases considerably during the same period. Since benzoyl peroxide is completely decomposed prior to this time, it is reasonable to speculate that volatilization of end fragments of the polymer chains may cause further condensation polymerization which would result in a more tightly cross-linked network.

TABLE B-1

Sample Preparation for Test 4

Master batch: Silicone polymer #81176, 100.0 grams

Benzoyl peroxide, 2.0 grams

Batch milled 15 minutes, separated into four portions for their respective cures.

	Press Cure		Weight, gm.			Oven Cure		Weight, gm.			
Sample	Time, Min.	Temp. °F.	Before	After	Loss	Time, Hr.	Temp. °F.	Before	After	Loss	%Loss
a	10	250	25.45	24.82	0.63	24	300	6.6492	6.1046	.5446	8.19
b	10	230	25.44	24.95	0.49	24	300	6.4836	5.9418	.5418	8.37
c	15	230	25.42	24.69	0.73	24	300	6.6027	6.0825	.5202	7.88
d	15	250	25.45	25.11	0.34	24	300	[a] 12.784	12.061	.723	5.66
e	15	250				1	300	3.6056	3.3314	.2742	6.65
f	15	250				48-hour gradual rise to 480°F.		3.9790	3.6106	.3684	9.25

Note a - This data from Sample 3c

FIGURE B-2

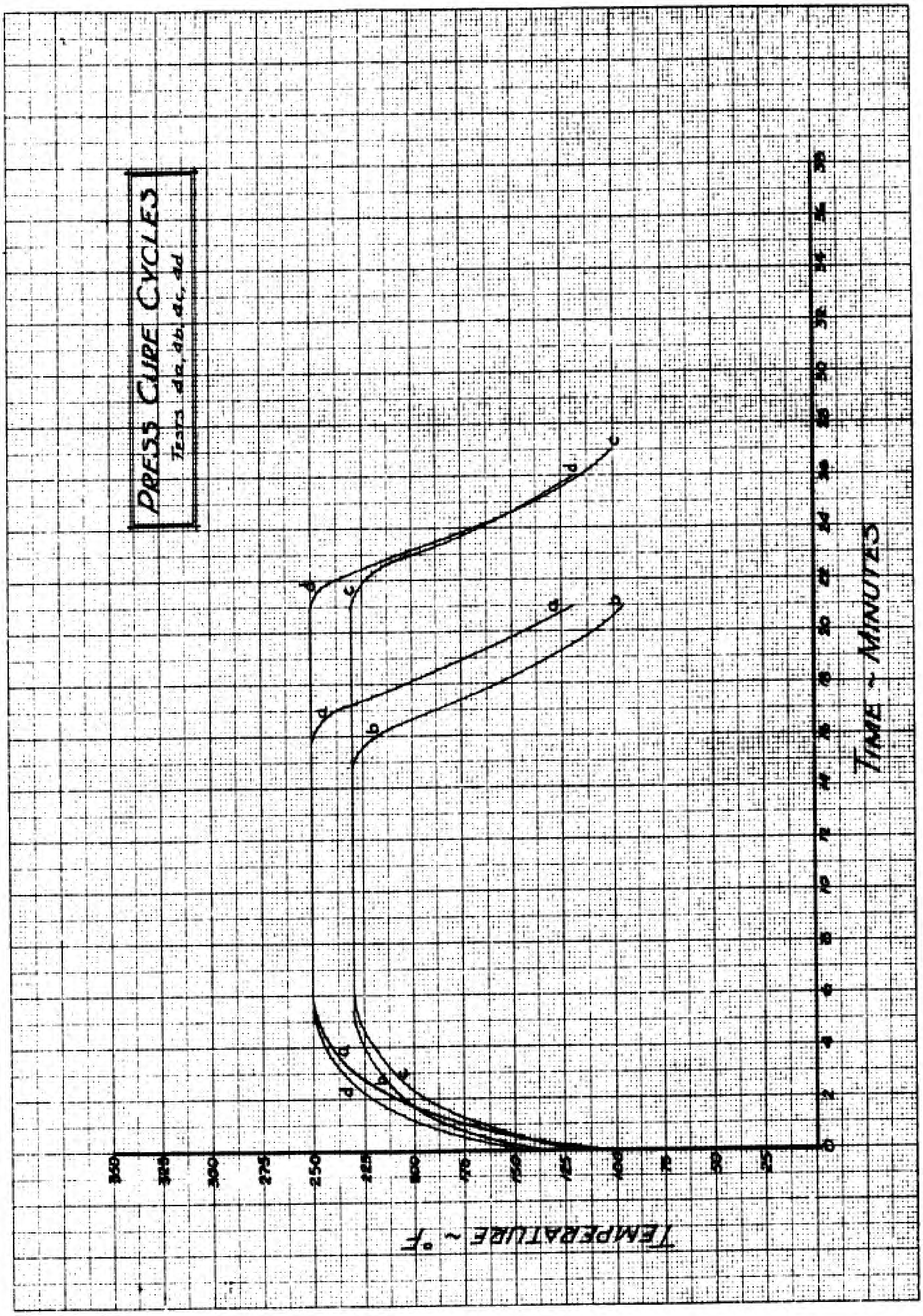
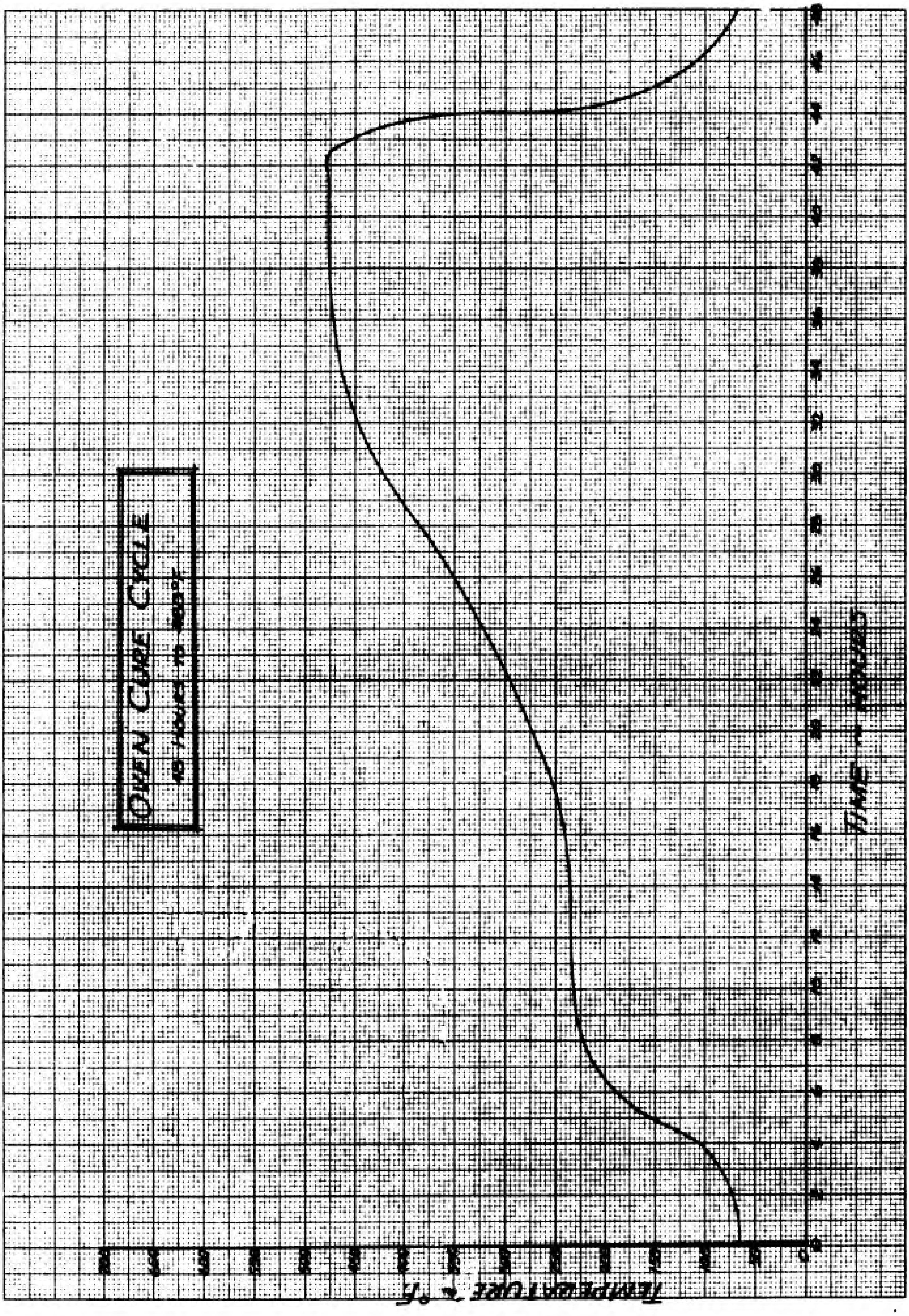
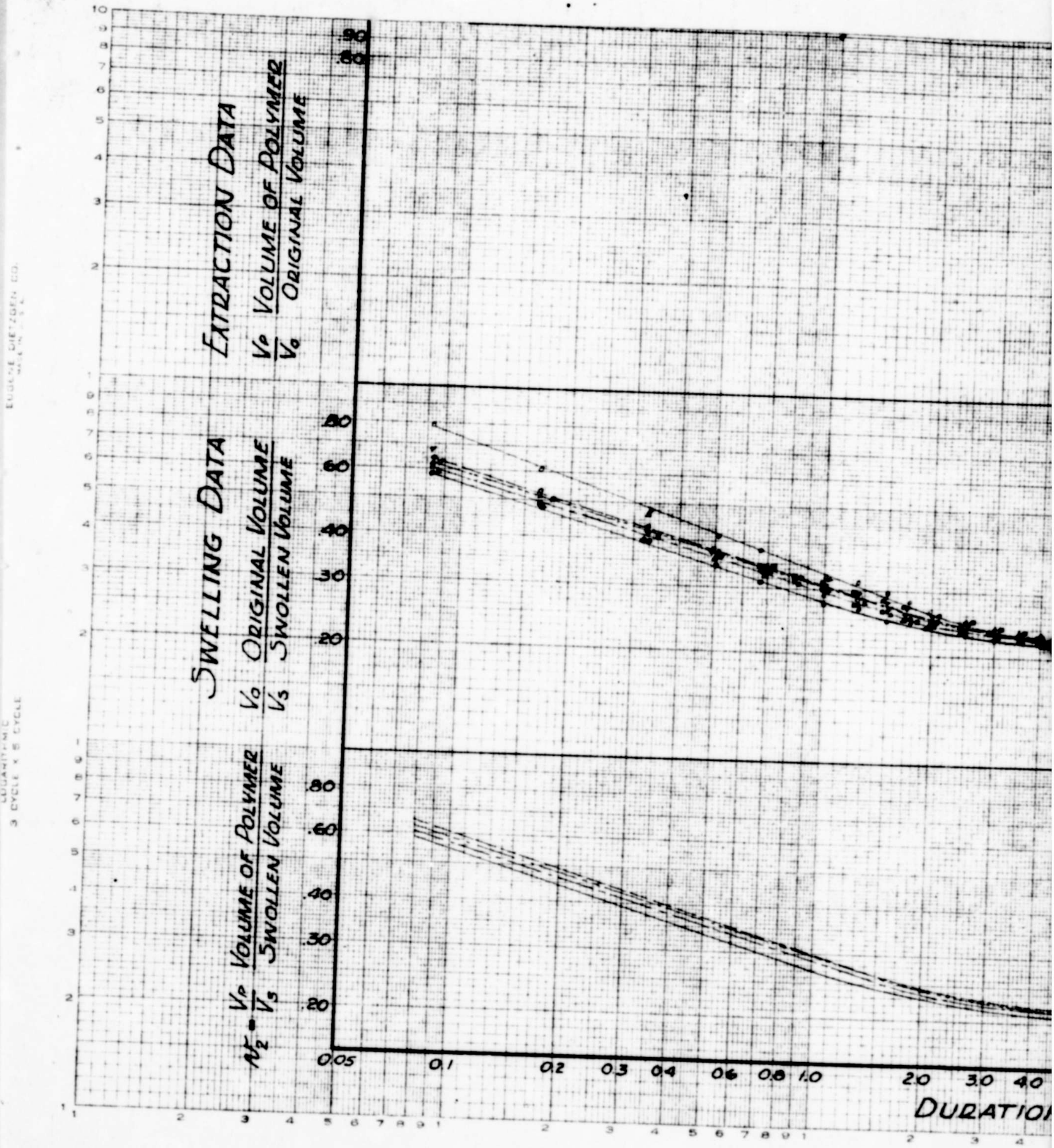

PRESS CURE CYCLES
Tests da, db, dc, dd
TEMPERATURE ~ °F
TIME ~ MINUTES
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
a
b
c
d

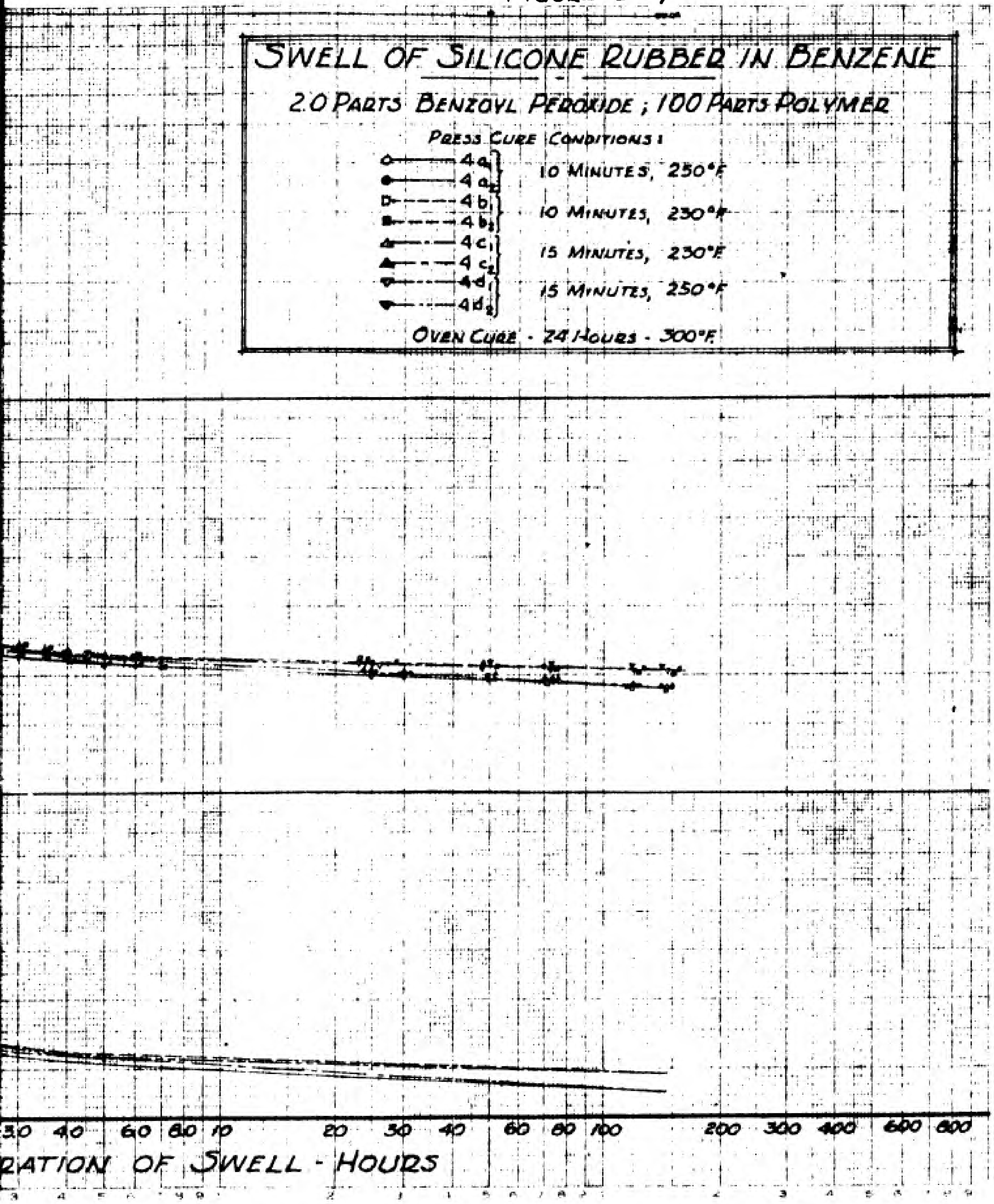
FIGURE B-3




EXTRACTION DATA
$\frac{V_P}{V_O}$ = VOLUME OF POLYMER / ORIGINAL VOLUME
.90
.80
SWELLING DATA
$\frac{V_O}{V_S}$ = ORIGINAL VOLUME / SWOLLEN VOLUME
.80
.60
.40
.30
.20
$\mathcal{N}_2 = \frac{V_P}{V_S}$ = VOLUME OF POLYMER / SWOLLEN VOLUME
.80
.60
.40
.30
.20
0.05
0.1
0.2
0.3
0.4
0.6
0.8
1.0
2.0
3.0
4.0
DURATIO
EUGENE DIETZGEN CO.
LOGARITHMIC
3 CYCLE X 5 CYCLE

1

FIGURE B-4


SWELL OF SILICONE RUBBER IN BENZENE

2.0 PARTS BENZOYL PEROXIDE ; 100 PARTS POLYMER

2

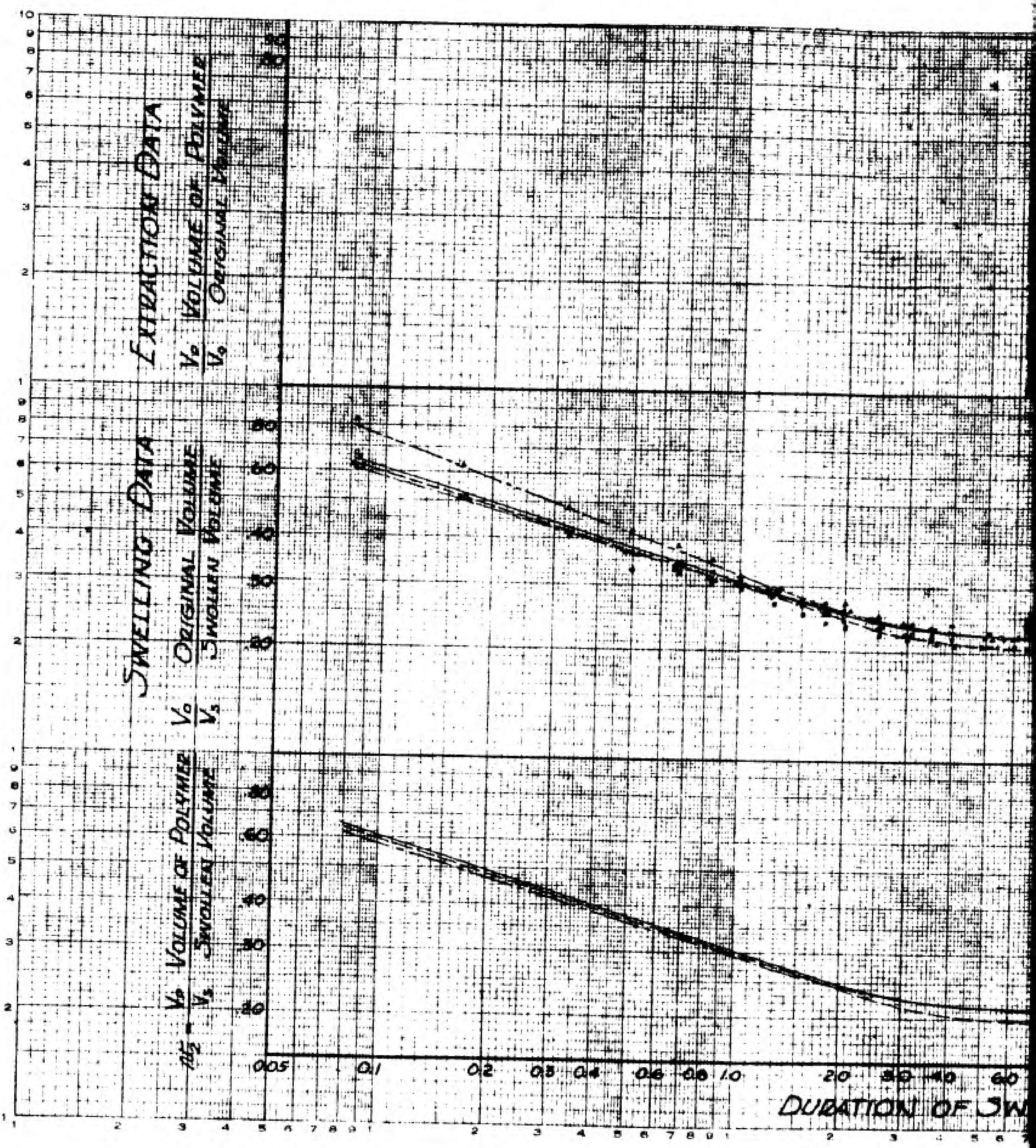
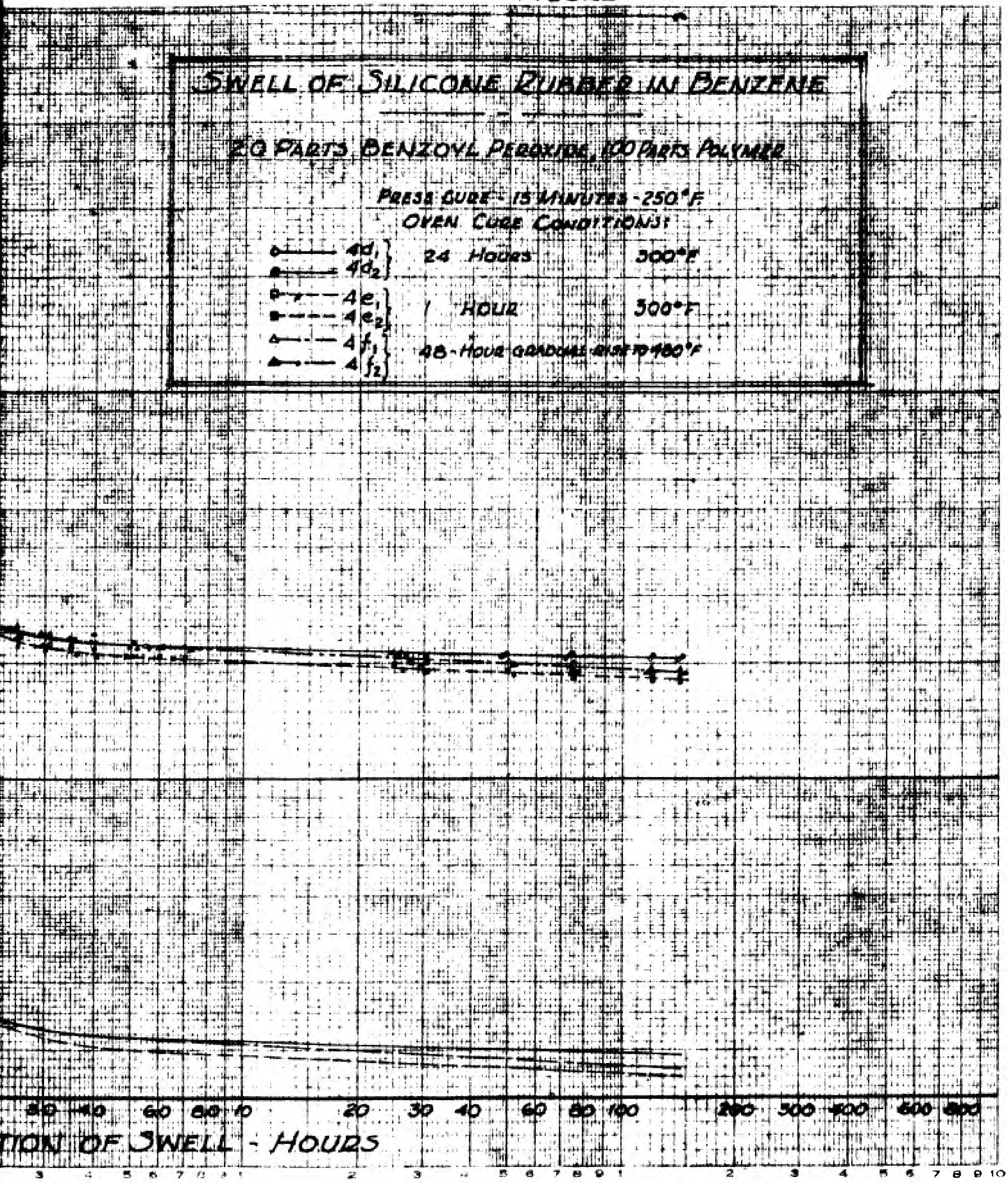

EXTRACTION DATA
$\frac{V_0}{V_0}$ VOLUME OF POLYMER / ORIGINAL VOLUME
SWELLING DATA
$\frac{V_0}{V_s}$ ORIGINAL VOLUME / SWOLLEN VOLUME
$\frac{1}{Q_2} = \frac{V_0}{V_s}$ VOLUME OF POLYMER / SWOLLEN VOLUME
.90
.80
.80
.60
.40
.30
.20
.80
.60
.40
.30
.20
0.05
0.1
0.2
0.3
0.4
0.6
0.8
1.0
2.0
3.0
4.0
6.0
DURATION OF SW
3 CYCLE X 5 CYCLE
MADE IN U.S.A.

FIGURE B-5


SWELL OF SILICONE RUBBER IN BENZENE
2.0 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER
PRESS CURE - 15 MINUTES - 250°F
OVEN CURE CONDITIONS:
4d₁ } 24 HOURS 300°F
4d₂
4e₁ } 1 HOUR 300°F
4e₂
4f₁ } 48-HOUR GRADUAL RISE TO 480°F
4f₂
20 40 60 80 10 20 30 40 60 80 100 200 300 400 600 800
TION OF SWELL - HOURS
3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 10

2

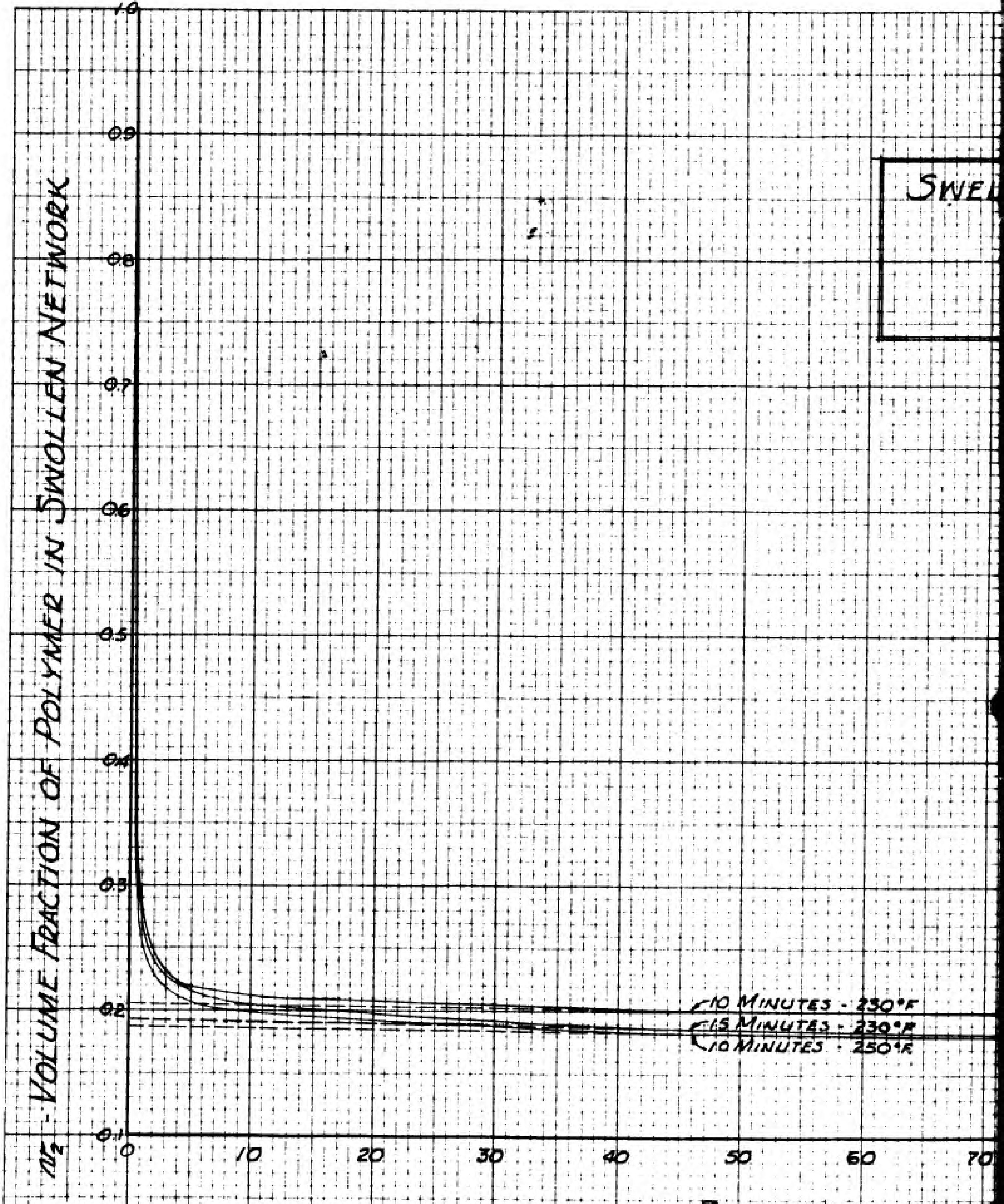
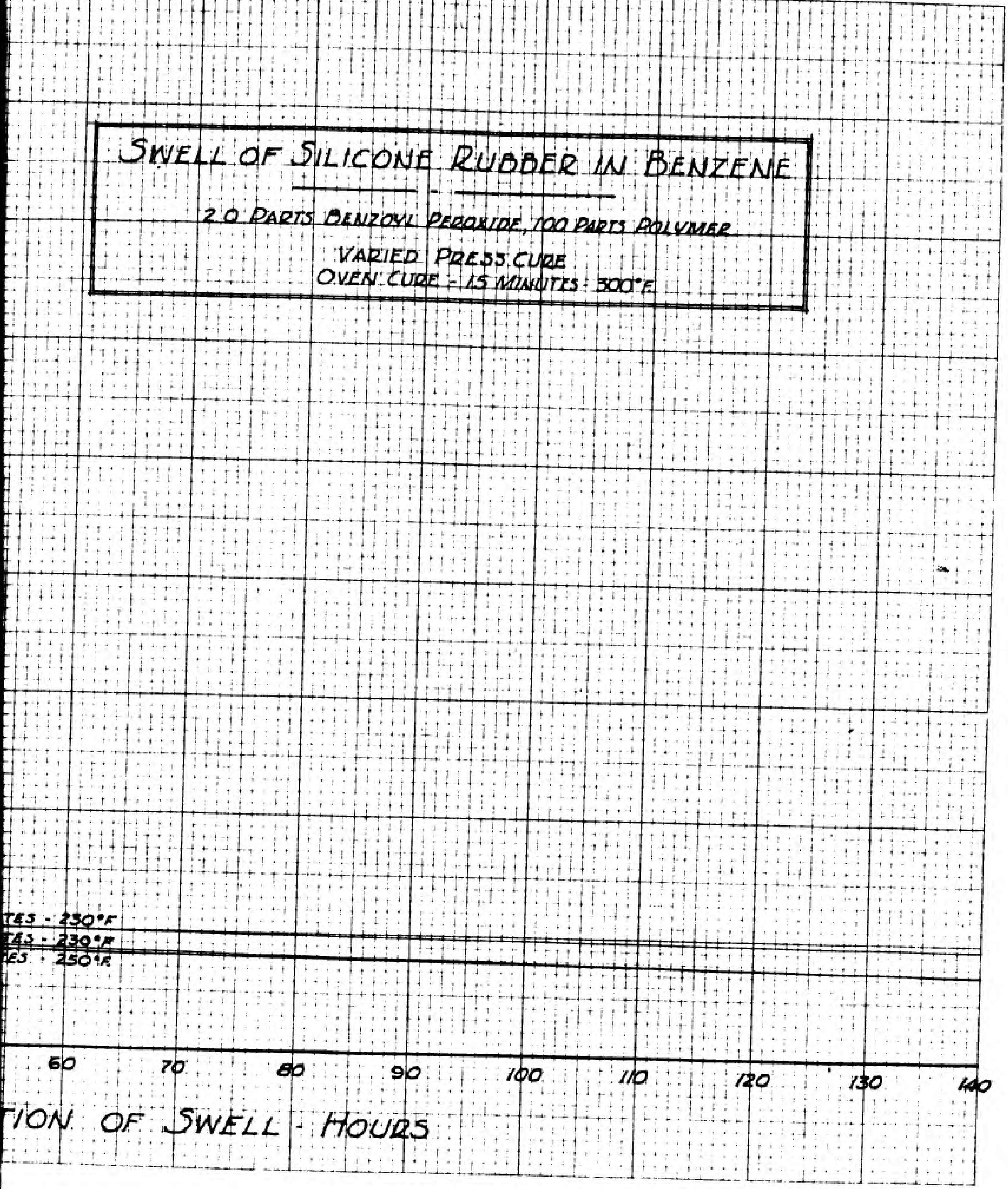

SWEL
v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
10 MINUTES - 230°F
15 MINUTES - 230°F
10 MINUTES - 250°F
DURATION OF S

FIGURE B-6


SWELL OF SILICONE RUBBER IN BENZENE
2.0 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER
VARIED PRESS CURE
OVEN CURE - 15 MINUTES : 300°F.
TES - 250°F
TES - 230°F
ES - 250°F
60
70
80
90
100
110
120
130
140
TION OF SWELL - HOURS

2

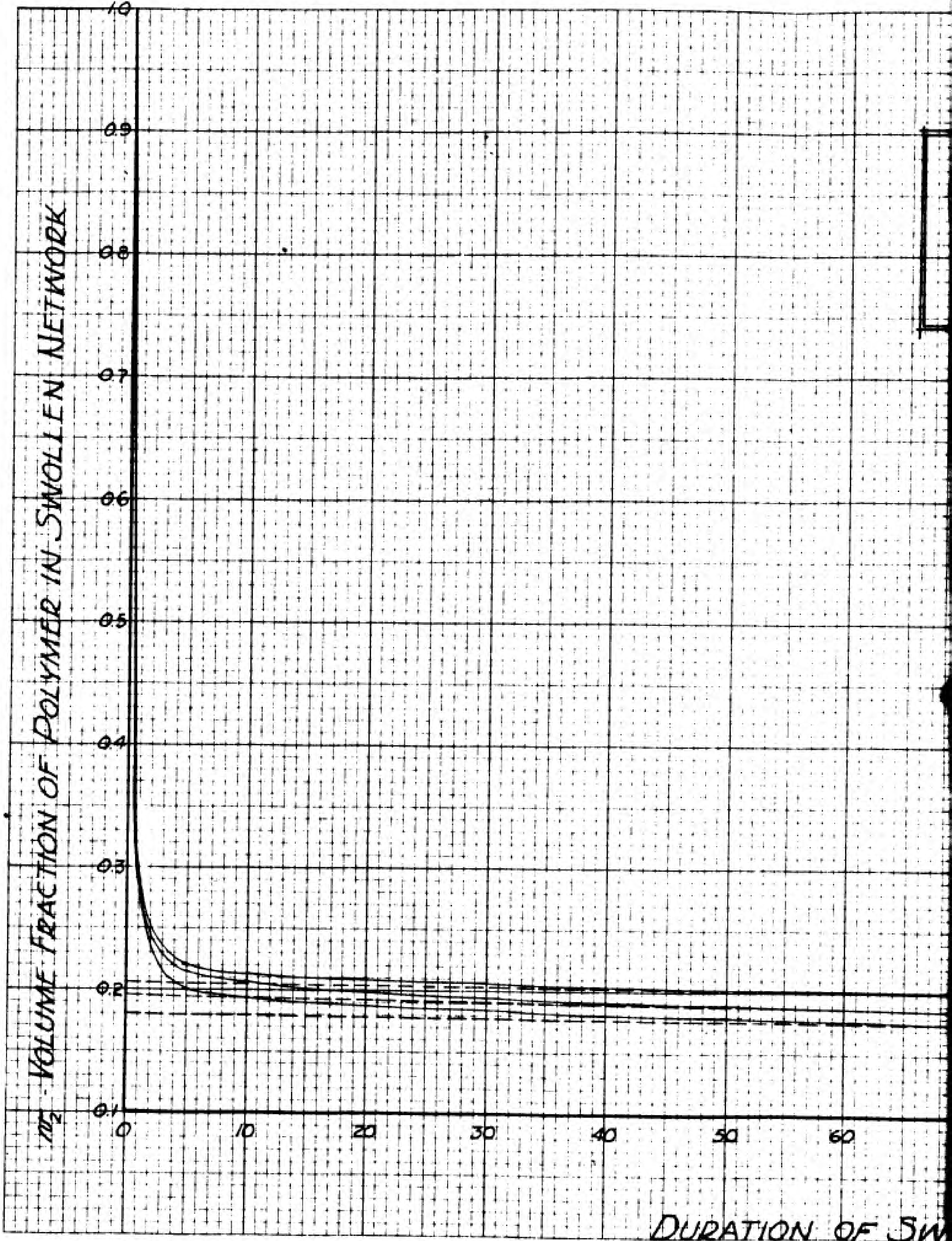
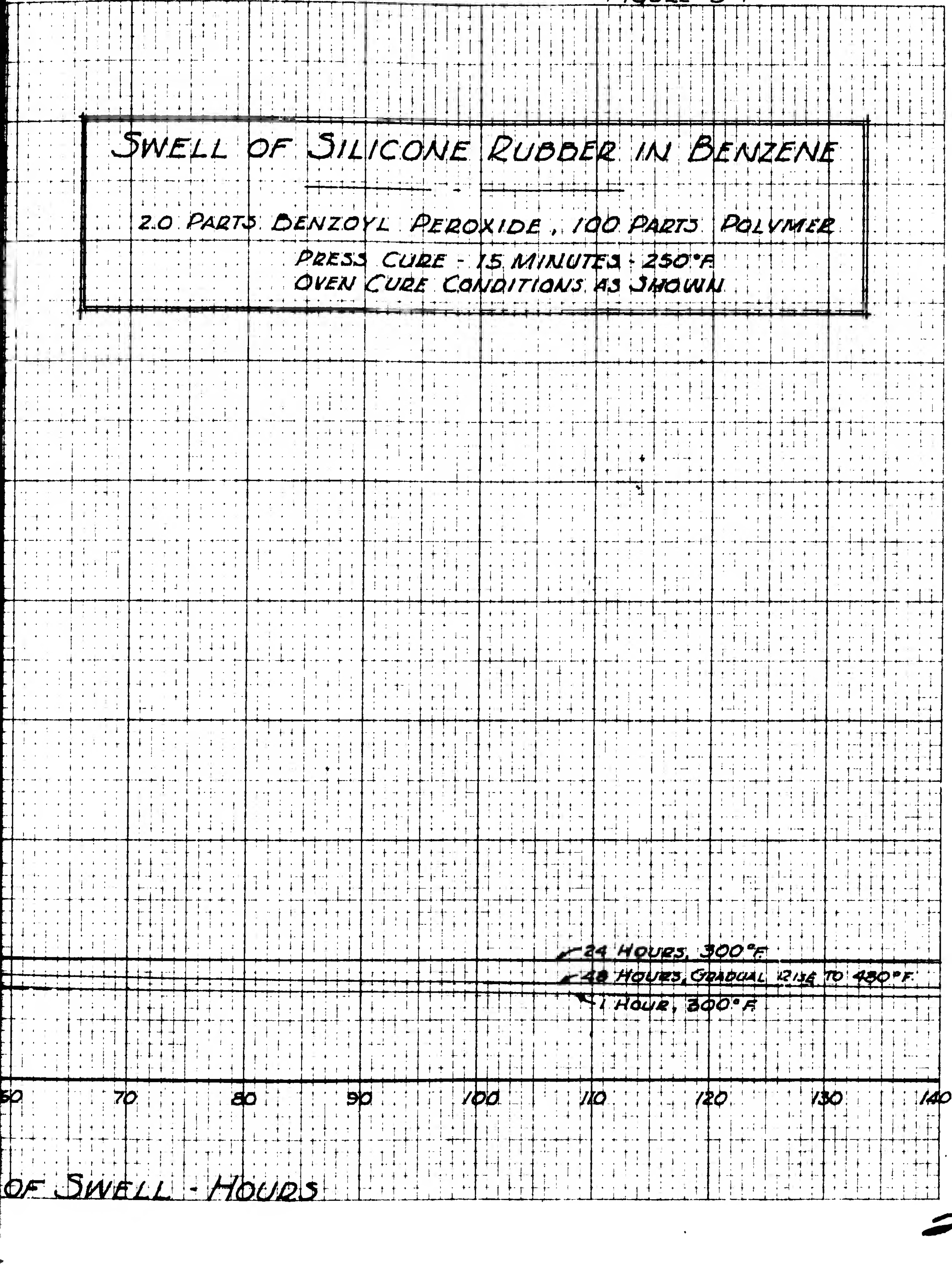

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
v_2 VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
0
10
20
30
40
50
60
DURATION OF SW

FIGURE B-7



SWELL OF SILICONE RUBBER IN BENZENE

2.0 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER
PRESS CURE - 15 MINUTES - 250°F.
OVEN CURE CONDITIONS AS SHOWN

2

Test 6, Swell of Silicone Elastomer in Various Solvents

Object: The purpose of this test was to investigate the degree and rate of swell of silicone elastomer in various solvents and to relate the results to current theories on the nature of the swelling of elastomers.

Procedure: Samples of silicone elastomer were cut from slab 3c of Test 3, which had been compounded with 2 per cent of benzoyl peroxide, press cured for 15 minutes at 250°F. and oven cured for 24 hours at 300°F.

Wherever possible the ten solvents used in this test were distilled for high purity. Swelling tests at 25.0°C. were, in general, carried out over periods of 5 minutes to 145 hours, and the amount of polymer extraction was determined in each case.

Results: The data of all tests except 6j are presented in Figures B-8 and B-9, pages 33 and 34. In Test 6j, swell in perfluoro(methylcyclohexane), the degree of swelling was less than 2 per cent and, considering the possibility of experimental error, the swell was considered approximately zero.

Rates of extraction were not determined for the various solvents; hence it was assumed that log($^{V}p/V_o$) was linear with log (t) as was found approximately accurate in earlier tests where ultimate extraction was less than 6 per cent. The ultimate extraction of polymer at 145 hours varied slightly according to solvent in the range of 3 to 6 per cent. No correlation of the amount of extraction with solvent properties or with the degree of swelling was observed.

The rates of swell of the silicone elastomer in the various solvents differed considerably as expected. In every case the duplicate tests provided comparable results. Equations for the rates of swell were calculated and are listed in Table B-2, page 35.

In Figures B-10 and B-11, pages 36 and 37, the rate of swell curves were extrapolated to zero time for determination of v_2 equilibrium. These values are listed below in order of decreasing v_2 and hence increasing swell:

Test	Solvent	v_2 equil.
6j	Perfluoro(methylcyclohexane)	1.0
6h	Methyl ethyl ketone	.285
6i	Benzene	.206
6g	d-Limonene	.183
6c	Xylene	.182
6a	Toluene	.170
6d	Cyclohexane	.148
6e	n-Octane	.141
6b	n-Hexane	.138
6f	Methylcyclohexane	.137

These values of v_2 were used in Flory's equation for M_c in terms of μ and calculations are presented on page 44.

As all of the samples used in this test were from the same slab, the molecular weight between cross-links was constant throughout the test and μ was the variable. In Test 3, M_c of sample 3c was calculated to be not greater than 14,900. This limit for M_c max. was applied to the equations of Test 6 and provided values of μ max. which are listed below on page 28.

By assuming that μ_1 from Huggins' osmotic pressure equation (page 71, Progress Report 10) was equivalent to μ from Flory's equation, and by accepting D. W. Scott's value of $\mu_1 = 0.498$ for dimethylsiloxane polymer with methyl ethyl ketone, it was possible to calculate values of M_c and μ for each solvent of this test. However, this defined impossible negative values of μ and values of M_c which would require greater than 100 per cent reaction of the benzoyl peroxide. Hence, in order to define a lower limit for the range of M_c, it was assumed that μ min. = 0 for each of the solvents. This assumption defined the lower limit of M_c as 6560, which would be coexistent with μ min. = 0 for polydimethylsiloxane and n-octane. By this definition, the following values of μ min. were calculated for the other solvents:

Test	Solvent	$\mu_{max.}$	$\mu_{min.}$
6h	Methyl ethyl ketone	.577	.531
6i	Benzene	.521	.436
6c	Xylene	.458	.311
6a	Toluene	.439	.295
6g	d-Limonene	.416	.224
6d	Cyclohexane	.400	.211
6f	Methylcyclohexane	.333	.071
6b	n-Hexane	.323	.068
6e	n-Octane	.308	.000

The above listing of solvents in order of decreasing μ does not agree with the previous tabulation of the solvents in order of decreasing v_2. This difference points out a flaw in the basic method (but not in the theory) used by Geoffrey Gee for determining δ_2, the solubility parameter of the polymer (pages 69-70, Progress Report 10).

According to Gee's method, Figure B-12, page 38, shows the relation of swell (here the inverse, since v_2 is plotted) to the solubility parameter of the solvent. Points are lettered according to the particular test number for each solvent. To draw a smooth curve representative of the points involved considerable approximation, and minimum v_2 (corresponding to maximum swell) defined δ_2 only vaguely.

Despite this poor representation of data, a value of $\delta_2 = 7.50$ was assumed and according to Gee's refinement, Figure B-13, page 39, was prepared with v_2 plotted versus $\sqrt{V_1}\,(\delta_1 - 7.50)$. The representation here was better than in Figure B-12 and was certainly as good as has been exhibited by Gee in his discussion of the method(2). Nevertheless, even this supposed refinement does not define δ_2 accurately.

As an alternative to the above methods of Gee for determination of δ_2, a more accurate and equally simple technique was devised which is presented in Figure B-14, page 40; as in Gee's method, the proposed improvement required only the knowledge of v_2, V_1 and δ_1. The present technique involved the use and the theory of Flory's equation and the qualitative application of various equations relating μ to $(\delta_1 - \delta_2)$. On page 44 were calculated approximations of M_c in terms of a uniform function, $(\frac{1}{2} - \mu)$. These values were plotted against δ_1 for the various solvents and, although there was some scatter, a sharp peak was defined at $\delta_1 = \delta_2$. This graph provided the value of $\delta_2 = 7.50 \pm .05$.

This approximation of Flory's equation would be absurd if used for calculation of M_c for some of the solvents since, for instance, with methyl ethyl ketone where $\mu > 0.5$, M_c would appear to be negative. Nevertheless, its use in the proposed method for determination of δ_2 is valid both in theory and in practice.

(2) Gee, G., "Thermodynamics of Rubber Solutions and Gels", in Advances in Colloid Science, Vol. II, Interscience Publishers, Inc., New York 1946, pp 145-195.

Using this value for the solubility parameter of polydimethylsiloxane, functions according to Gee's theories were calculated for the various solvents on page 44, $\frac{V_1 (\delta_1 - \delta_2)^2}{RT}$. The range of possible values of μ for the various polymer-solvent pairs were plotted versus this function in Figure B-15, page 41 , and provided a definite, but not linear, relation.

In order to ascertain whether the rate of swell of silicone elastomer might be a function of the rate of diffusion of solvent into the rubber, Figure B-16, page 42, was prepared in which the coefficient of the logarithmic rate of swell equation was plotted versus ηV_1 (where η = viscosity, V_1 = molal volume) which was assumed to be related to the liquid diffusivity. No correlation was found to exist.

Further correlation was attempted in Figure B-17, page 43, where the slope of the rate of swell curve was plotted versus the equilibrium value of v_2 for all samples of Tests 3, 4 and 6. The resulting "path" was indicative that the rate of swell might be related to the free energy driving force which is, in turn, a complicated function of the changing v_2 and the constant μ and molal volumes. Of particular interest was the fact that the three samples of Test 3 (in which only M_c varied) provided an approximately linear relation of ($-A_1$ to v_2). In this graph the points are noted according to the test number.

Conclusions: The solubility parameter, or cohesive energy density, of polydimethylsiloxane is 7.50 ± 0.05 $(\text{cal./c.c.})^{\frac{1}{2}}$.

The theories of Geoffrey Gee relating the polymer-solvent interaction coefficient to the solvent molal volume and solubility parameter and the polymer solubility parameter have been at least qualitatively substantiated.

The polymer-solvent interaction coefficient, μ, for Flory's swelling equation does not correspond to the similar function in Huggins' osmotic pressure equation, μ_1, for the polymer-solvent pair of polydimethylsiloxane and methyl ethyl ketone.

A method for the determination of polymer solubility parameter has been devised which in this test was as convenient to use and more accurate in results than the conventional methods of Gee. The proposed procedure might be applied to published results of the swelling of other elastomers in various solvents in order to test its general worth for providing sharp definition of δ_2.

Values of M_c and μ have been defined within sufficiently narrow limits for comparative purposes; more accurate determination of the latter term is to be desired in order to correlate theory properly.

The rate of swell of silicone elastomer is probably dependent upon free energy factors rather than upon the rate of liquid diffusion into the elastomer. However The latter would probably become the rate-controlling factor, [redacted], if an extremely viscous liquid were to be used, such as a high molecular weight polymer.

The reasonable values of M_c and μ along with the aforementioned theoretical correlations add to the substantiation of P. J. Flory's equation for the swelling of polymers.

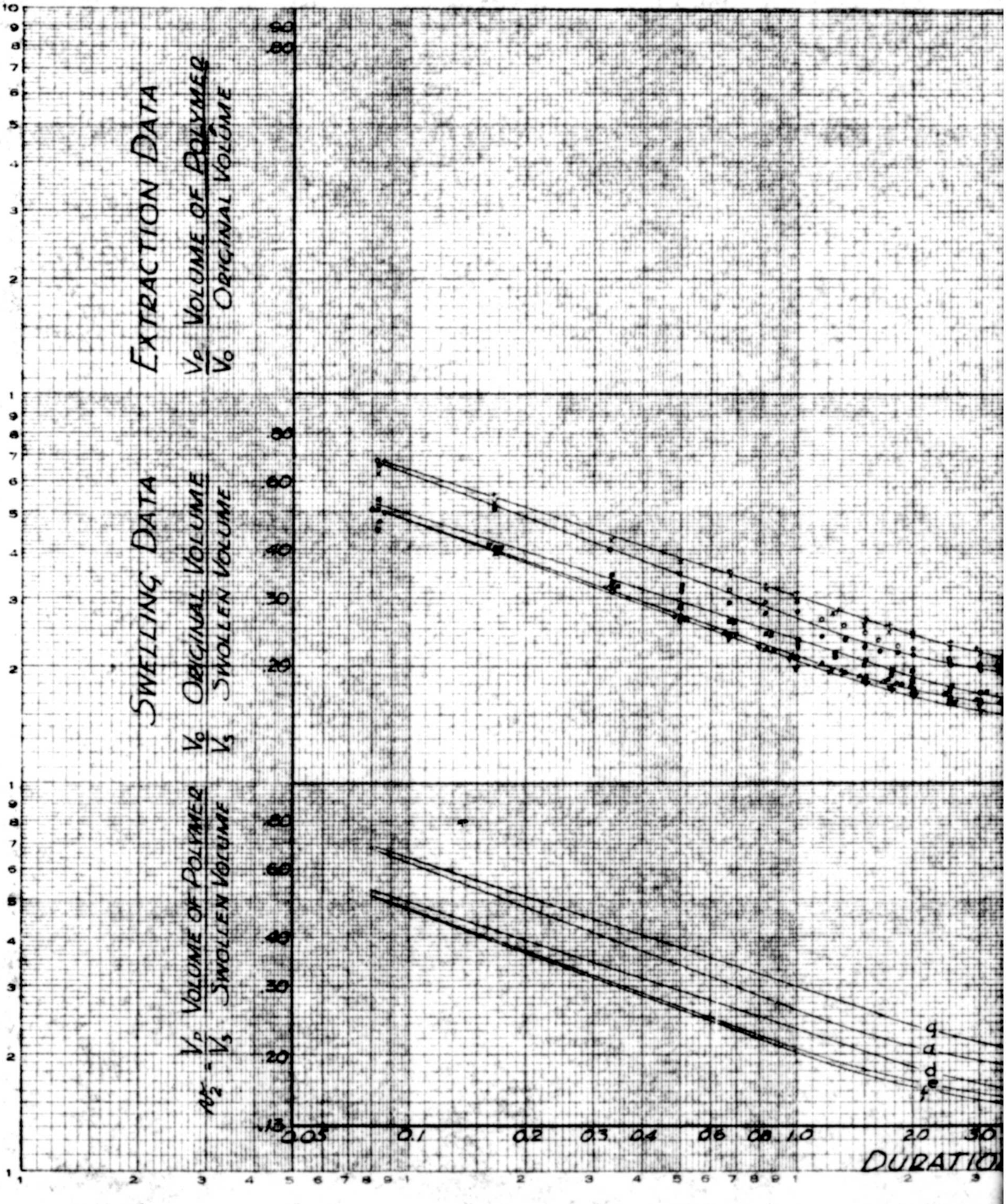
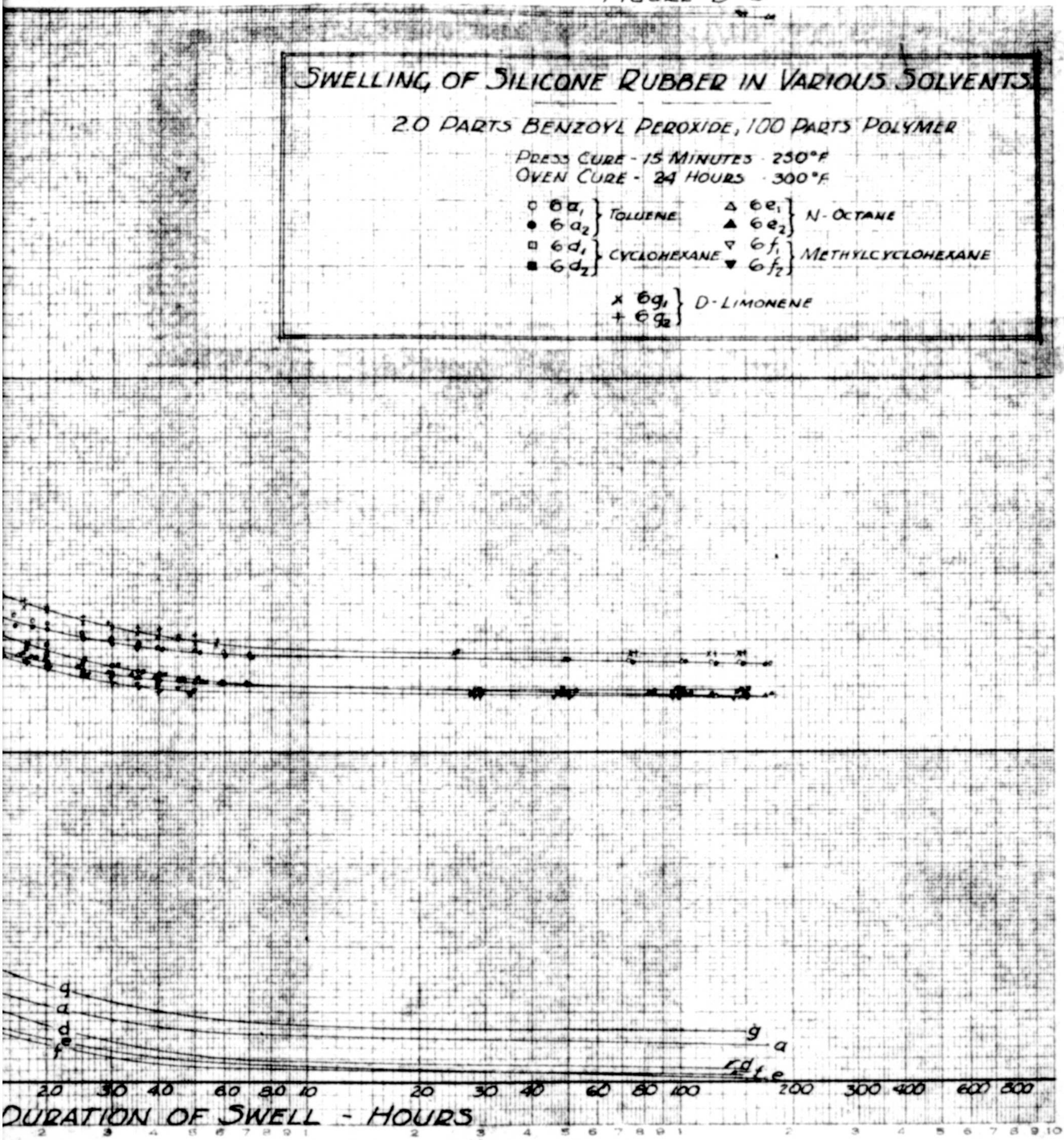

EXTRACTION DATA
$\frac{V_P}{V_O}$ = VOLUME OF POLYMER / ORIGINAL VOLUME
SWELLING DATA
$\frac{V_O}{V_S}$ = ORIGINAL VOLUME / SWOLLEN VOLUME
$\frac{\Delta K}{K_2} = \frac{V_P}{V_S}$ = VOLUME OF POLYMER / SWOLLEN VOLUME
.90
.80
.80
.60
.40
.30
.20
.80
.60
.40
.30
.20
.15
0.05
0.1
0.2
0.3
0.4
0.6
0.8
1.0
2.0
3.0
DURATIO
g
a
d
e
f

FIGURE B-8



SWELLING OF SILICONE RUBBER IN VARIOUS SOLVENTS

2.0 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER

PRESS CURE - 15 MINUTES - 230°F
OVEN CURE - 24 HOURS - 300°F

2

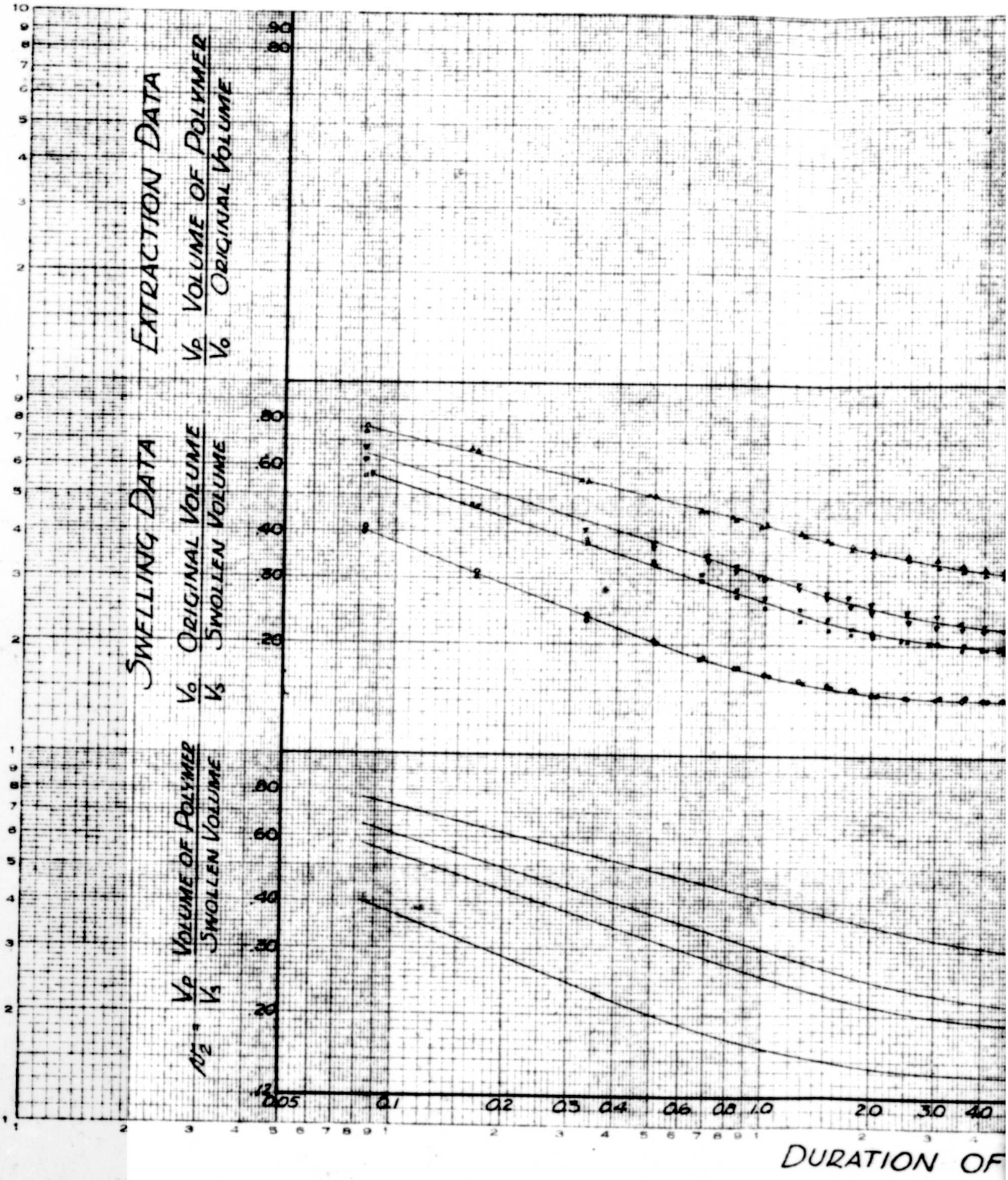
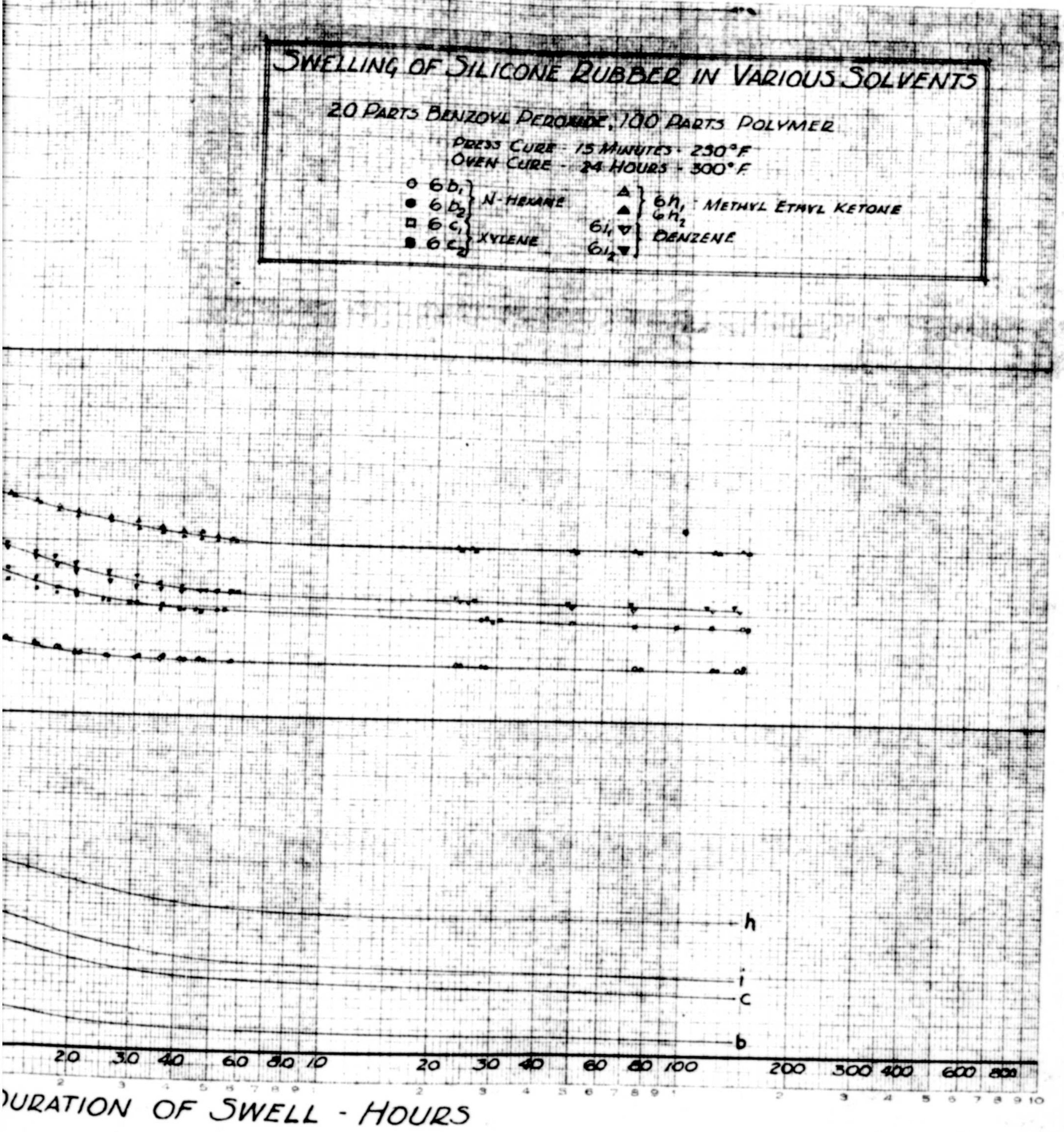

EXTRACTION DATA
$\frac{V_P}{V_O}$ VOLUME OF POLYMER / ORIGINAL VOLUME
.90
.80
SWELLING DATA
$\frac{V_O}{V_S}$ ORIGINAL VOLUME / SWOLLEN VOLUME
.80
.60
.40
.30
.20
$\nu_2 = \frac{V_P}{V_S}$ VOLUME OF POLYMER / SWOLLEN VOLUME
.80
.60
.40
.30
.20
.12
0.05
0.1
0.2
0.3
0.4
0.6
0.8
1.0
2.0
3.0
4.0
DURATION OF

FIGURE B-9



SWELLING OF SILICONE RUBBER IN VARIOUS SOLVENTS

2

TABLE B-2

Rate of Swell Equations for Test 6

Test and Solvent	Initial Period	Incremental Period
6a Toluene	.083 to 1.0 hours $\ln v_2 = -.380 \ln(t) -1.347$	7 to 175 hours $\ln v_2 = -.0222 \ln(t) -1.705$
6b n-Hexane	.083 to .40 hours $\ln v_2 = -.393 \ln(t) -1.833$	6 to 145 hours $\ln v_2 = -.0093 \ln(t) -1.971$
6c Xylene	.083 to 1.0 hours $\ln v_2 = -.327 \ln(t) -1.370$	10 to 145 hours $\ln v_2 = -.0147 \ln(t) -1.218$
6d Cyclohexane	.083 to 1.5 hours $\ln v_2 = -.331 \ln(t) -1.581$	7.0 to 145 hours $\ln v_2 = -.0138 \ln(t) -1.890$
6e n-Octane	.083 to 1.0 hours $\ln v_2 = -.359 \ln(t) -1.5702$	10 to 175 hours $\ln v_2 = -.133 \ln(t) -1.339$
6f Methylcyclohexane	.083 to 1.0 hours $\ln v_2 = -.372 \ln(t) -1.604$	7 to 145 hours $\ln v_2 = -.0119 \ln(t) -2.054$
6g d-Limonene	.083 to 1.5 hours $\ln v_2 = -.378 \ln(t) -1.327$	20 to 145 hours $\ln v_2 = -.0085 \ln(t) -1.689$
6h Methyl ethyl ketone	.083 to 1.5 hours $\ln v_2 = -.244 \ln(t) -.877$	20 to 145 hours $\ln v_2 = -1.255$
6i Benzene	.083 to 1.5 hours $\ln v_2 = -.310 \ln(t) -1.194$	6 to 144 hours $\ln v_2 = -.0187 \ln(t) -1.537$

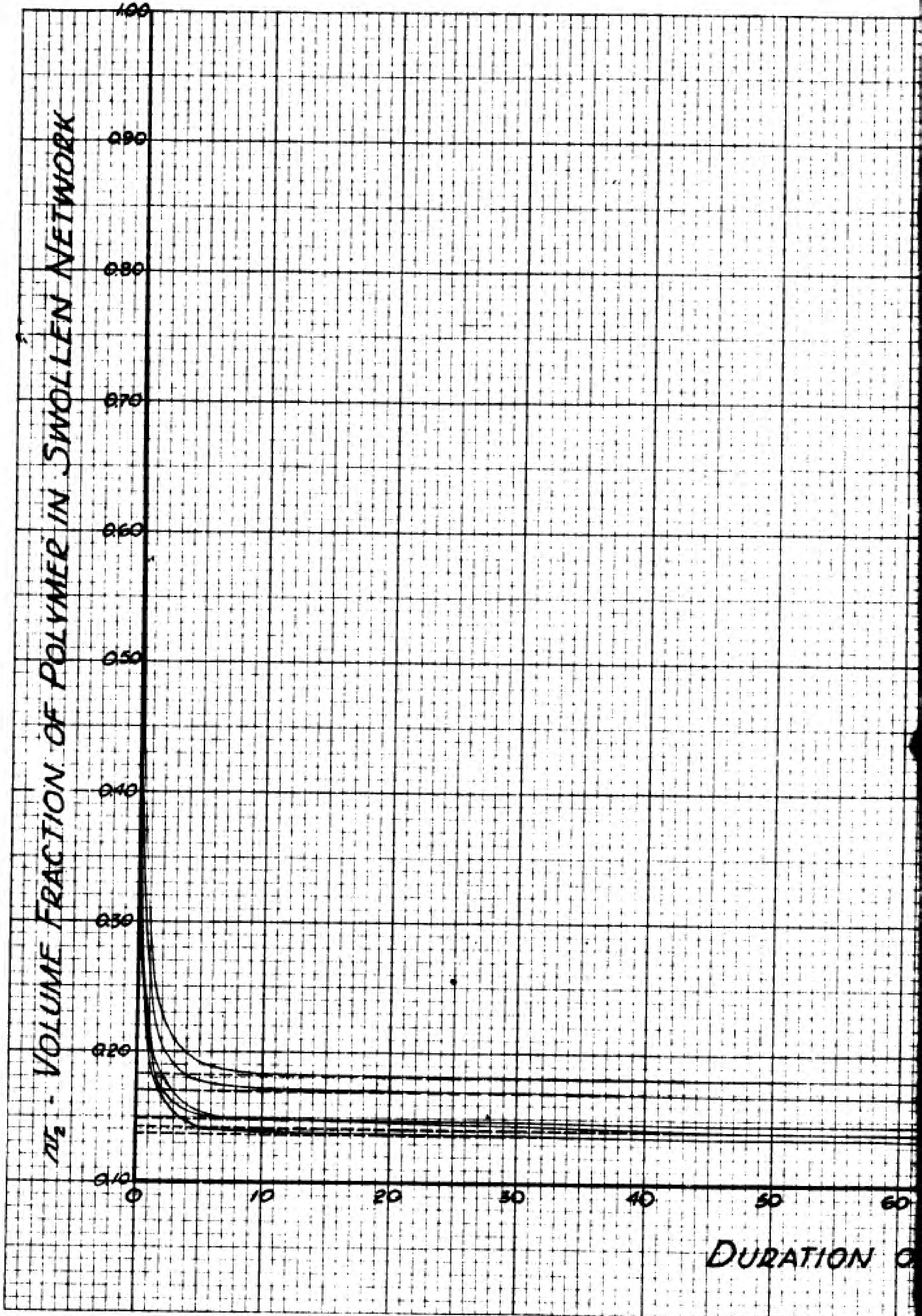
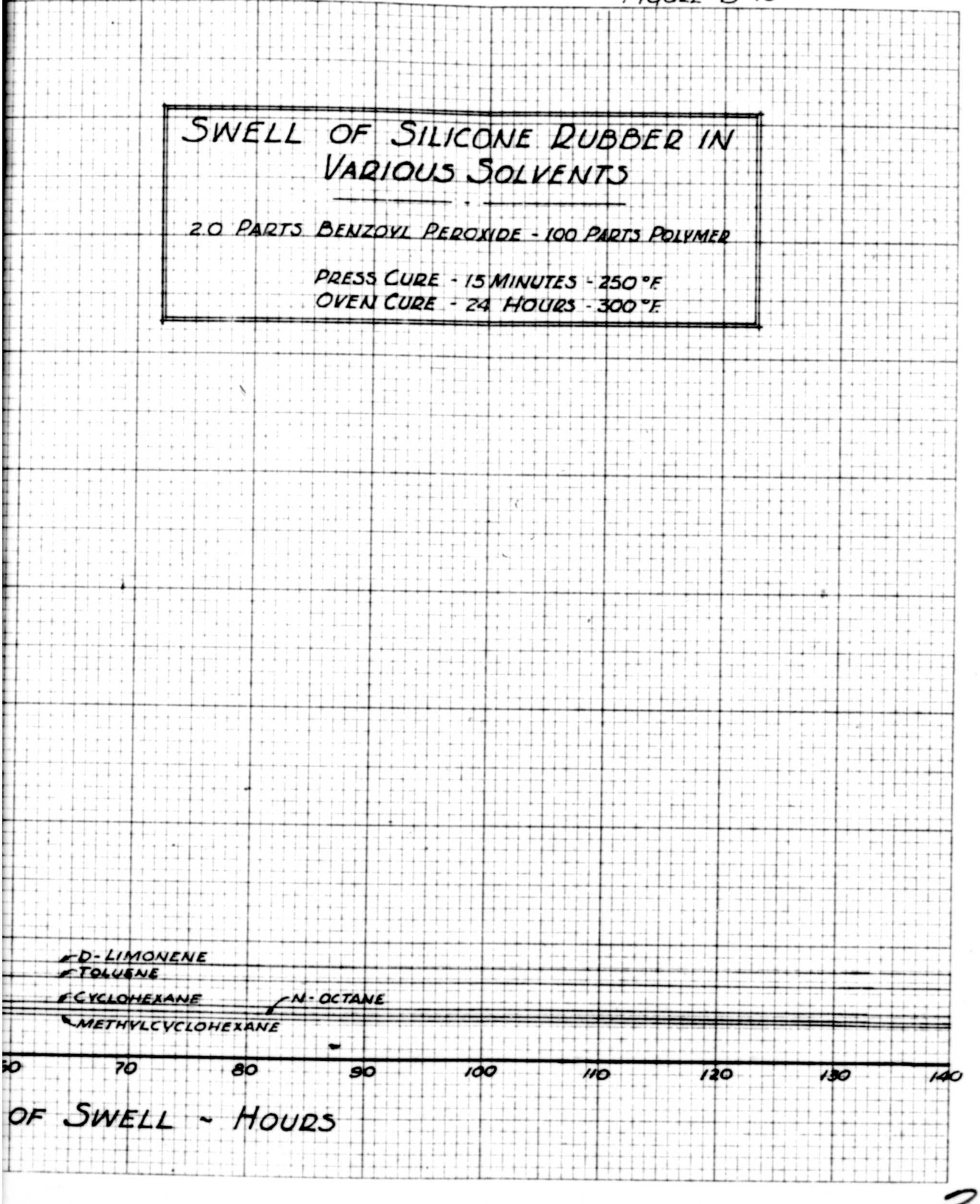

v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
10
20
30
40
50
60
DURATION O

FIGURE B-10



SWELL OF SILICONE RUBBER IN VARIOUS SOLVENTS

2.0 PARTS BENZOYL PEROXIDE - 100 PARTS POLYMER

PRESS CURE - 15 MINUTES - 250 °F.
OVEN CURE - 24 HOURS - 300 °F.

2

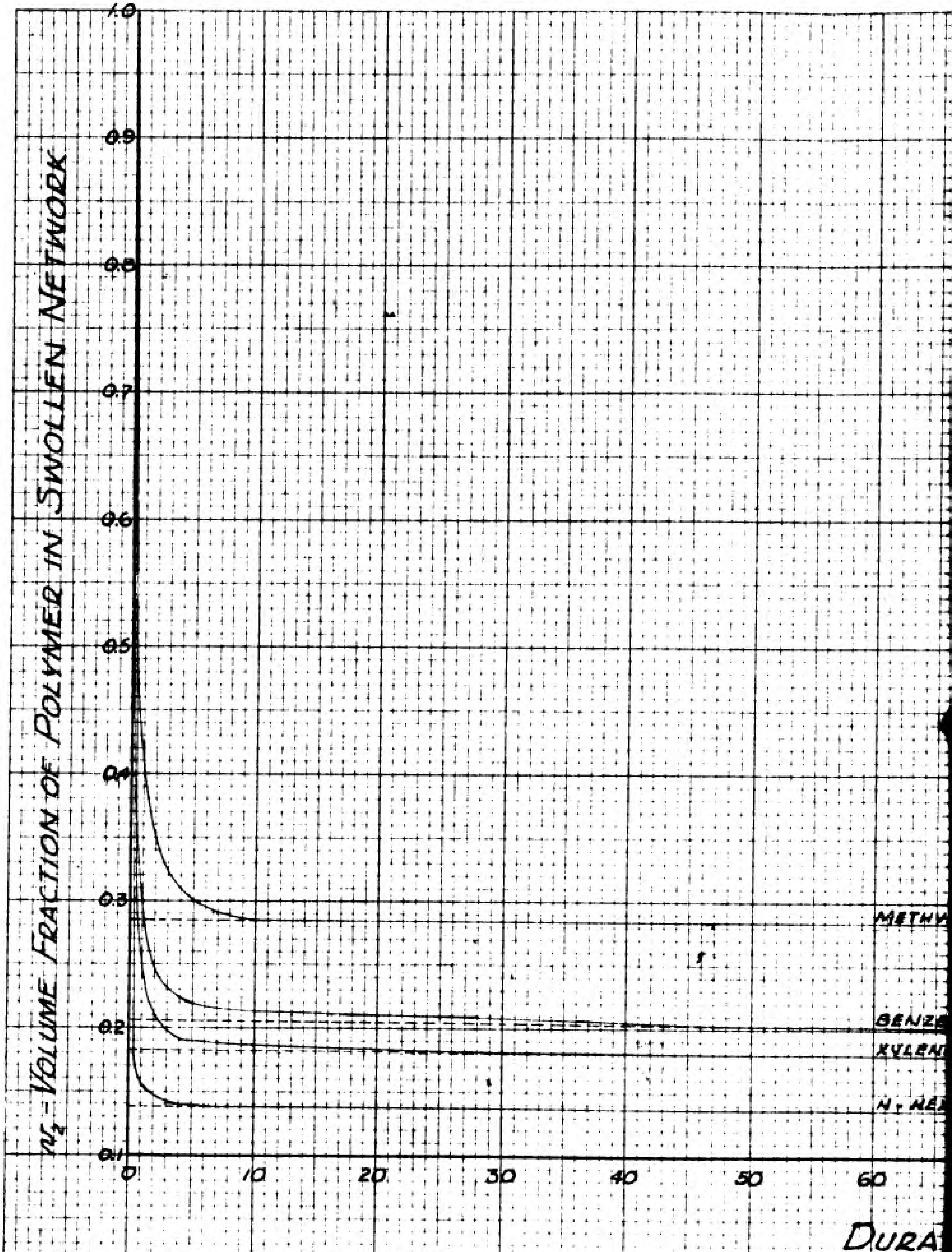
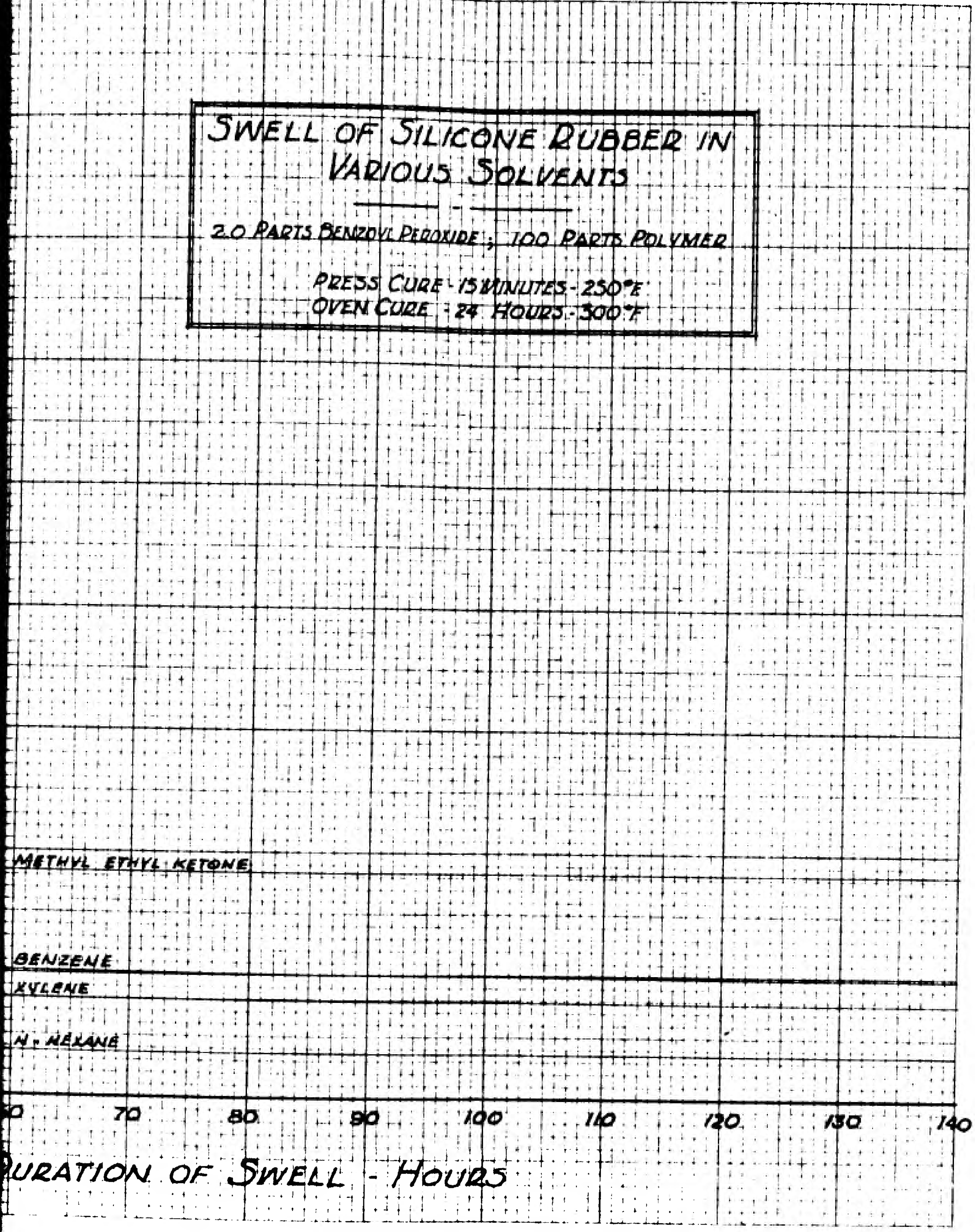

v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
METHY
BENZE
XYLEN
N-HEX
DURA

FIGURE B-11


SWELL OF SILICONE RUBBER IN VARIOUS SOLVENTS
2.0 PARTS BENZOYL PEROXIDE ; 100 PARTS POLYMER
PRESS CURE - 15 MINUTES - 250°F
OVEN CURE - 24 HOURS - 300°F
METHYL ETHYL KETONE
BENZENE
XYLENE
N - HEXANE
0
70
80
90
100
110
120
130
140
URATION OF SWELL - HOURS

2

FIGURE B-12

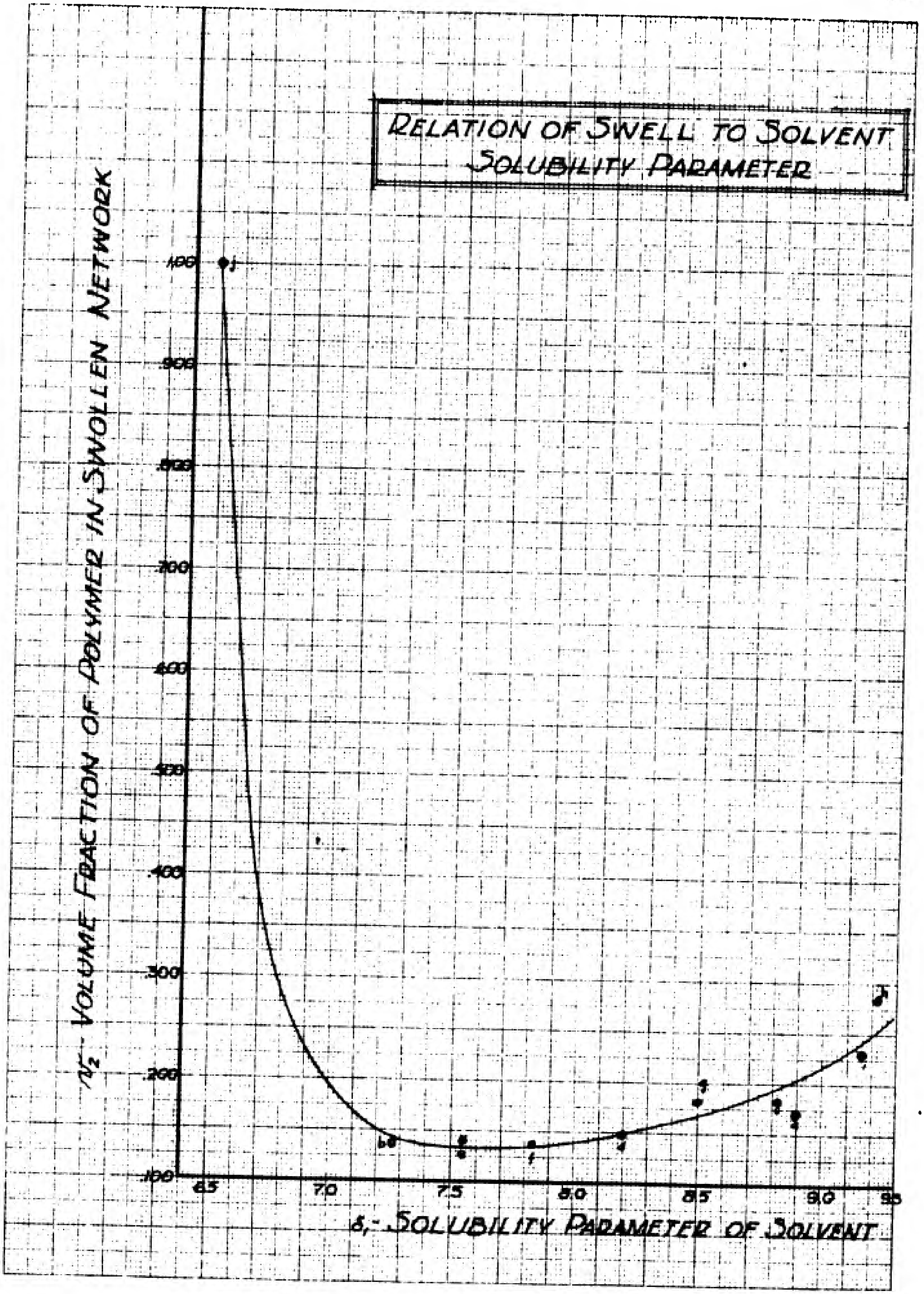

RELATION OF SWELL TO SOLVENT SOLUBILITY PARAMETER
v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
δ_1 - SOLUBILITY PARAMETER OF SOLVENT
1.00
.900
.800
.700
.600
.500
.400
.300
.200
.100
6.5
7.0
7.5
8.0
8.5
9.0
9.5
j

FIGURE B-13

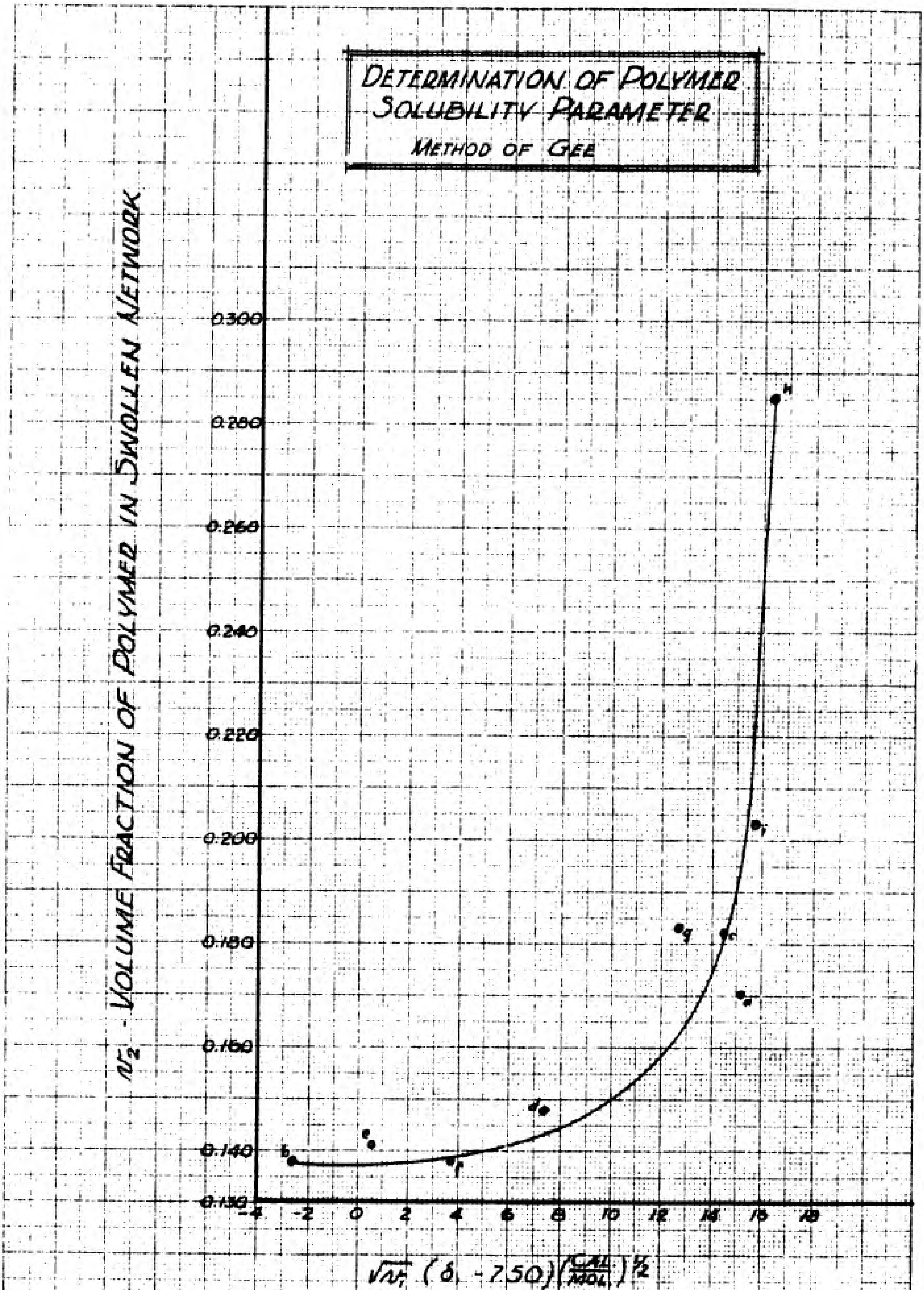
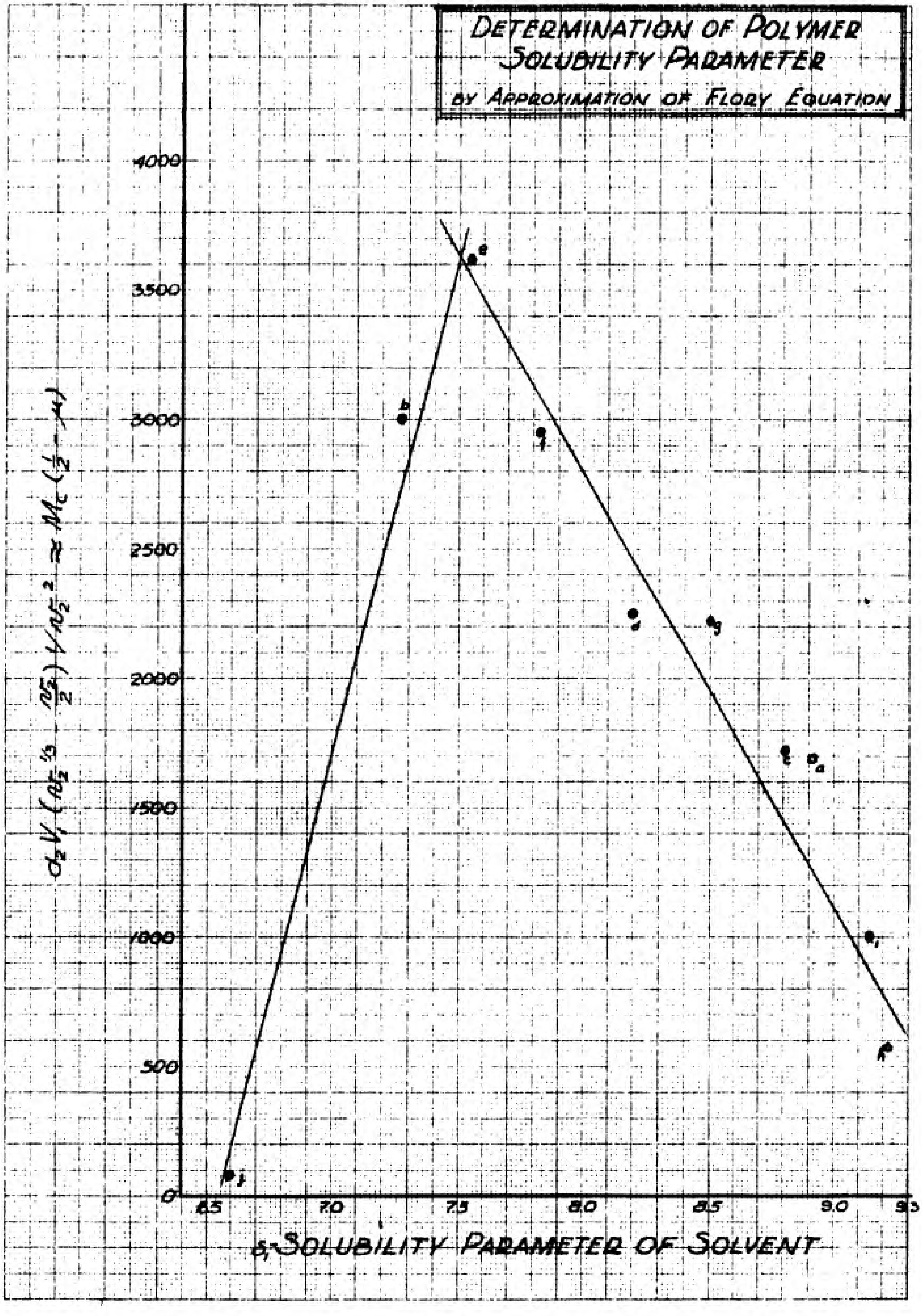

DETERMINATION OF POLYMER SOLUBILITY PARAMETER
METHOD OF GEE
v_2 - VOLUME FRACTION OF POLYMER IN SWOLLEN NETWORK
0.300
0.280
0.260
0.240
0.220
0.200
0.180
0.160
0.140
0.130
-4
-2
0
2
4
6
8
10
12
14
16
18
$\sqrt{v_1}\,(\delta_1 - 7.50)\left(\frac{CAL}{MOL}\right)^{1/2}$
b
e
f
d
g
c
a
i
H

FIGURE B-14


DETERMINATION OF POLYMER SOLUBILITY PARAMETER
BY APPROXIMATION OF FLORY EQUATION
σ2 V1 (ν2^1/3 - ν2/2) / ν2^2 ≈ Mc (1/2 - μ)
4000
3500
3000
2500
2000
1500
1000
500
0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
δ1 SOLUBILITY PARAMETER OF SOLVENT
e
b
f
d
g
c
a
i
k
j

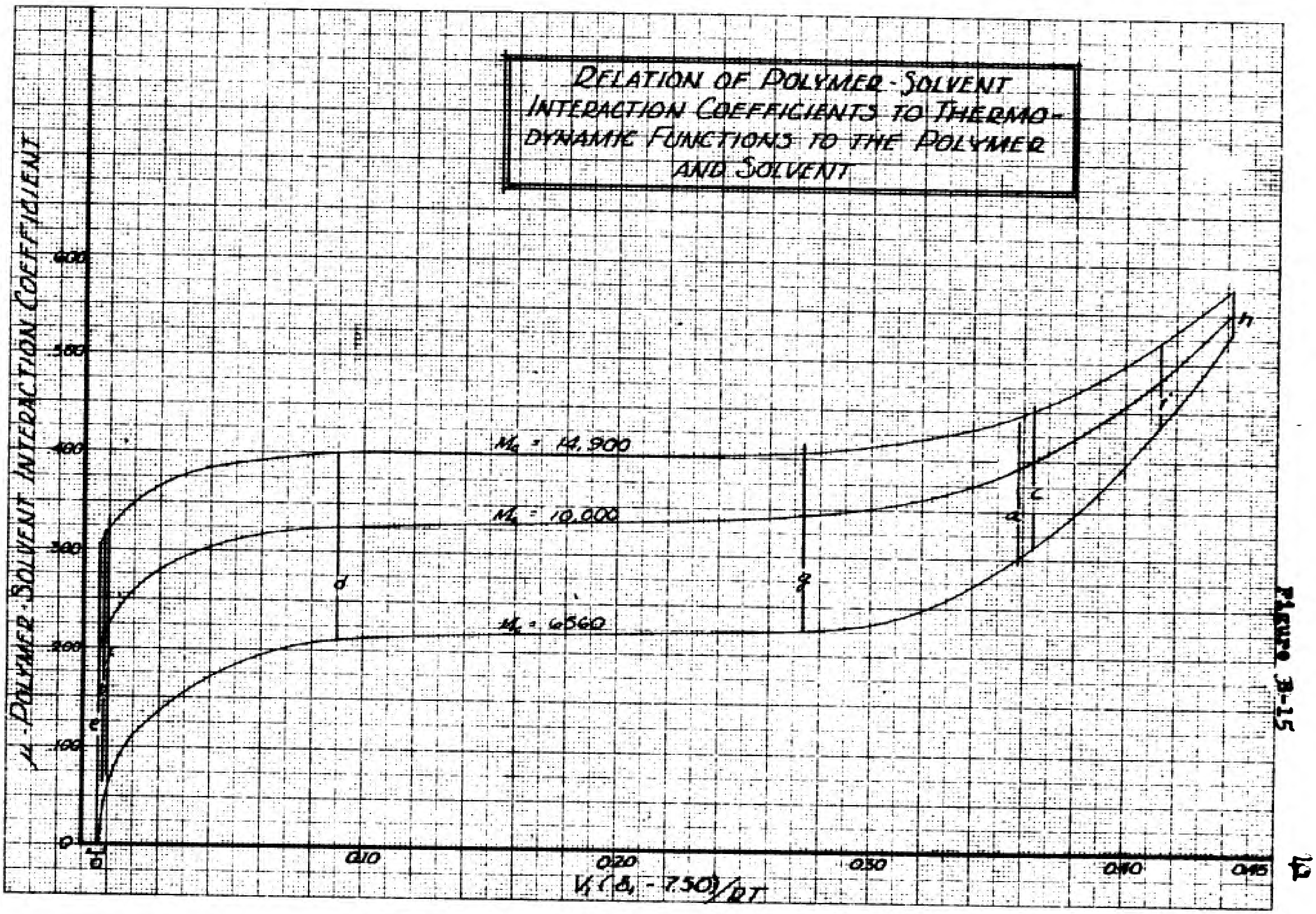
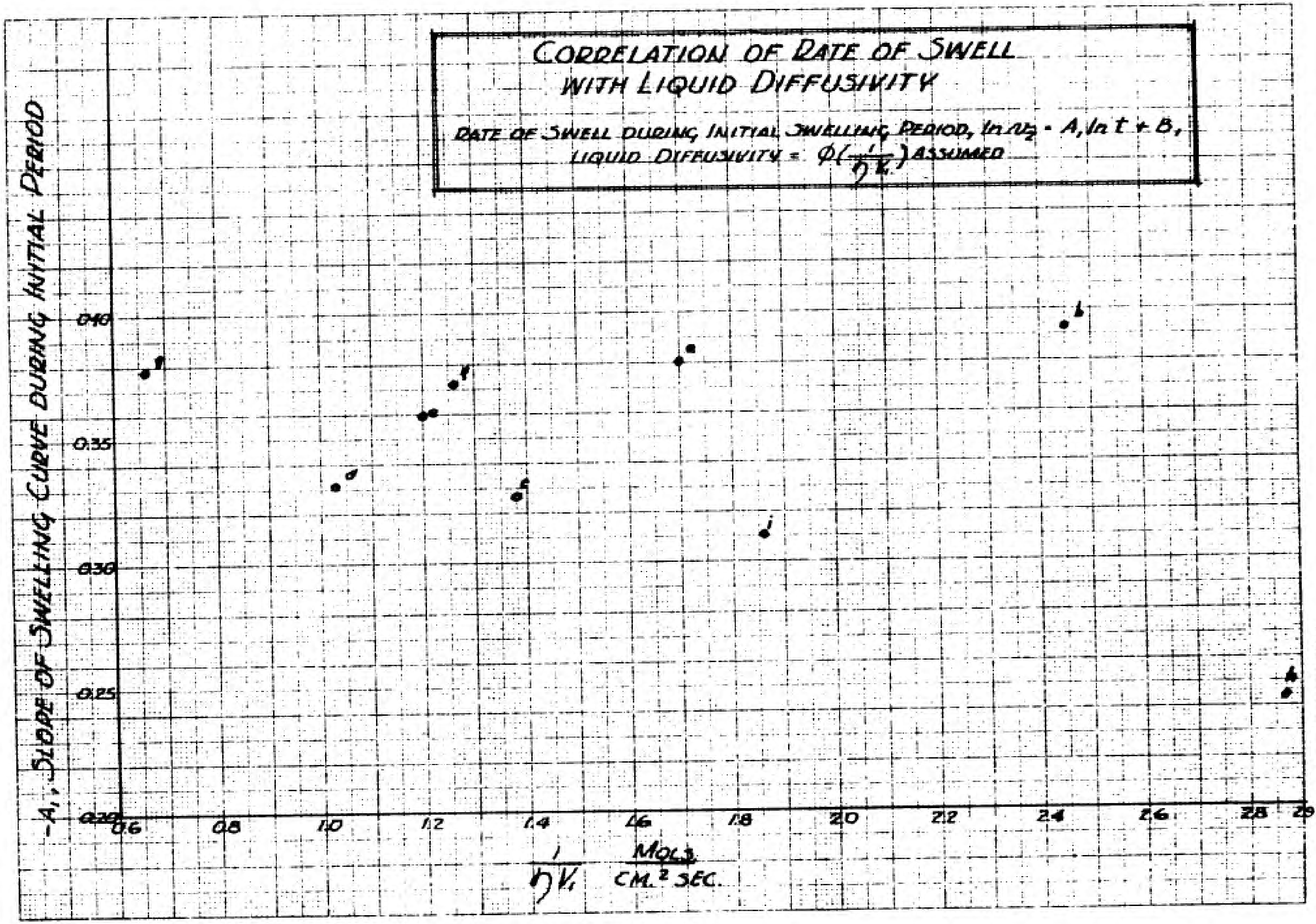

RELATION OF POLYMER-SOLVENT INTERACTION COEFFICIENTS TO THERMODYNAMIC FUNCTIONS TO THE POLYMER AND SOLVENT

Figure B-15

FIGURE B-16

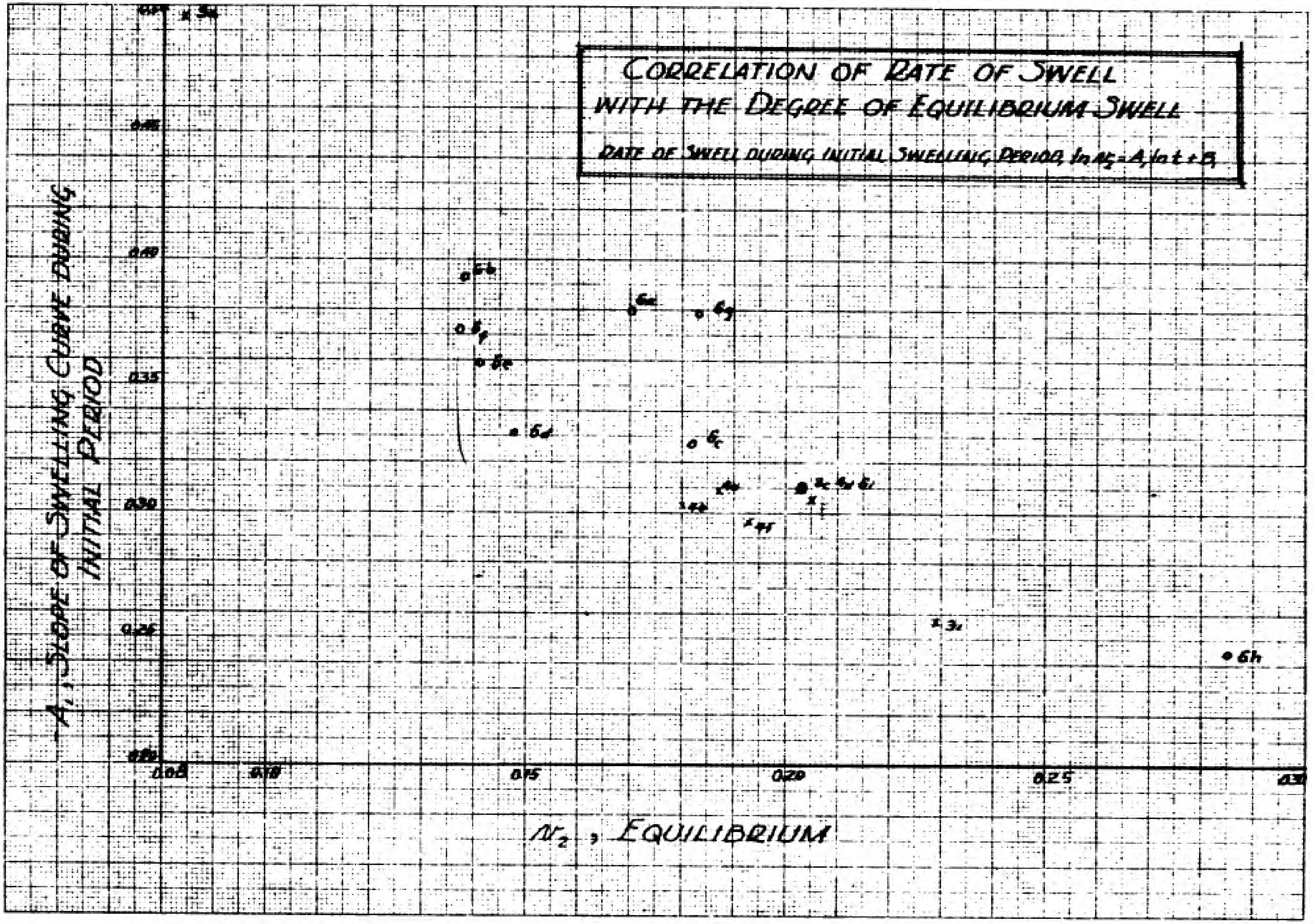


CORRELATION OF RATE OF SWELL WITH LIQUID DIFFUSIVITY

RATE OF SWELL DURING INITIAL SWELLING PERIOD, $\ln n_2 = A_1 \ln t + B_1$

LIQUID DIFFUSIVITY = $\phi\left(\frac{1}{\eta V_1}\right)$ ASSUMED

FIGURE B-17



CORRELATION OF RATE OF SWELL WITH THE DEGREE OF EQUILIBRIUM SWELL

RATE OF SWELL DURING INITIAL SWELLING PERIOD, $\ln \nu_2 = A_1 \ln t + B_1$

CALCULATIONS OF THE MOL

Test	Solvent	Molal Vol.	v_2 equil.	$v_2^{1/3}$	$\frac{v}{2}$	$v^{1/3}-\frac{v}{2}$	$1-v_2$	$\ln(1-v_2)$	$\ln(1-v_2)$ $+v_2$
3a	Benzene	89.40	.084	.438	.042	.396	.916	-.0877	-.0037
3c	Benzene		.206	.591	.103	.488	.794	-.2307	-.025
3i	Benzene		.229	.611	.1145	.4965	.771	-.2601	-.031
4a	Benzene	89.40	.187	.572	.0935	.4785	.813	-.2070	-.020
4b	Benzene		.205	.590	.1025	.4875	.795	-.2294	-.024
4c	Benzene		.193	.578	.0965	.4815	.807	-.2144	-.021
4d	Benzene		.206	.591	.103	.488	.794	-.2307	-.025
4e	Benzene		.180	.565	.090	.475	.820	-.1984	-.018
4f	Benzene		.195	.580	.0975	.4825	.805	-.2169	-.022
6a	Toluene	106.85	.170	.554	.085	.469	.830	-.1863	-.016
6b	n-Hexane	131.60	.138	.516	.069	.447	.862	-.1485	-.010
6c	Xylene	123.46	.182	.567	.091	.476	.818	-.2009	-.019
6d	Cyclohexane	108.74	.148	.529	.074	.455	.852	-.1602	-.012
6e	n-Octane	163.52	.141	.521	.0705	.4505	.859	-.1520	-.011
6f	Methyl-cyclohexane	128.33	.137	.515	.0685	.4465	.863	-.1473	-.010
6g	d-Limonene	162.2	.183	.568	.091	.477	.817	-.202	-.019
6h	Methyl ethyl ketone	90.16	.285	.658	.1425	.5155	.715	-.3355	-.050
6i	Benzene	89.40	.206	.591	.103	.488	.794	-.2307	-.025
6j	Perfluoro-(methylcyclohexane)	173.3	1.00	1.00	0.50	0.50	0.00	$-\infty$	

* by approximate Flory equation $M_c = \dfrac{0.976\ V_1(v_2^{1/3} - \frac{v_2}{2})}{v_2^2\ (\frac{1}{2}-\mu)}$

TABLE B-3

ALCULATIONS OF THE MOLECULAR WEIGHT BETWEEN CROSS-LINKS AND THE POLYMER-SOLVENT INTERACTION COEFFICIENTS

$1-v_2$	$\ln(1-v_2)$	$\ln(1-v_2)+v_2$	v_2^2	M_c* approx	M_c**	M_c max.	M_c min.	μ max.	μ min.	δ_1	$\delta_1-7.50$	$\frac{V_1(\delta_1-7.50)^2}{RT}$
.916	-.0877	-.0037	.0071	$\frac{4890}{\frac{1}{2}-\mu}$	$\frac{4890}{.525-\mu}$	10^6	24,200	.521	.436			
.794	-.2307	-.025	.0425	$\frac{1000}{\frac{1}{2}-\mu}$	$\frac{1000}{.588-\mu}$	14,900	6560					
.771	-.2601	-.031	.0524	$\frac{838}{\frac{1}{2}-\mu}$	$\frac{838}{.591-\mu}$	12,000	5400					
.813	-.2070	-.020	.0350	$\frac{1210}{\frac{1}{2}-\mu}$	$\frac{1210}{.571-\mu}$	24,200	8970	.521	.436			
.795	-.2294	-.024	.0420	$\frac{1025}{\frac{1}{2}-\mu}$	$\frac{1025}{.571-\mu}$	20,500	7600					
.807	-.2144	-.021	.0372	$\frac{1140}{\frac{1}{2}-\mu}$	$\frac{1140}{.565-\mu}$	25,900	8840					
.794	-.2307	-.025	.0425	$\frac{1000}{\frac{1}{2}-\mu}$	$\frac{1000}{.588-\mu}$	14,900	6560					
.820	-.1984	-.018	.0324	$\frac{1295}{\frac{1}{2}-\mu}$	$\frac{1295}{.555-\mu}$	38,000	10,900					
.805	-.2169	-.022	.0380	$\frac{1120}{\frac{1}{2}-\mu}$	$\frac{1120}{.579-\mu}$	19,300	7830					
.830	-.1863	-.016	.0289	$\frac{1695}{\frac{1}{2}-\mu}$	$\frac{1695}{.553-\mu}$	14,900	6560	.439	.295	8.91	1.41	.359
.862	-.1485	-.010	.0190	$\frac{3000}{\frac{1}{2}-\mu}$	$\frac{3000}{.525-\mu}$			.323	.068	7.27	-.23	.0012
.818	-.2009	-.019	.0331	$\frac{1728}{\frac{1}{2}-\mu}$	$\frac{1728}{.574-\mu}$			.458	.311	8.82	1.32	.364
.852	-.1602	-.012	.0219	$\frac{2210}{\frac{1}{2}-\mu}$	$\frac{2210}{.548-\mu}$			.400	.211	8.20	0070	.090
.859	-.1520	-.011	.0199	$\frac{3625}{\frac{1}{2}-\mu}$	$\frac{3625}{.552-\mu}$			.308	.000	7.55	0.05	.0007
.863	-.1473	-.010	.0188	$\frac{2960}{\frac{1}{2}-\mu}$	$\frac{2960}{.532-\mu}$			.333	.071	7.83	0.33	.0023
.817	-.202	-.019	.0335	$\frac{2250}{\frac{1}{2}-\mu}$	$\frac{2250}{.567-\mu}$			.416	.224	8.5	1.0	.27
.715	-.3355	-.050	.0813	$\frac{558}{\frac{1}{2}-\mu}$	$\frac{558}{.616-\mu}$			.577	.531	9.22	1.72	.451
.794	-.2307	-.025	.0425	$\frac{1000}{\frac{1}{2}-\mu}$	$\frac{1000}{.588-\mu}$			.521	.436	9.16	1.66	.415
0.00	$-\infty$			$\frac{85}{\frac{1}{2}-\mu}$				not defined		6.5	-1.0	.29

$$= \frac{0.976\ V_1(v_2^{1/3}-\frac{v_2}{2})}{v_2^{1/3}(\frac{1}{2}-\mu)}$$

** by exact Flory equation $M_c = \frac{0.976\ V_1(v_2^{1/3}-\frac{v_2}{2})}{\ln(1-v_2)+v_2+\mu v_2^2}$

C. DISCUSSION

Without delving into extensive theoretical assumptions, it has been possible to calculate within a fairly close range possible values of M_c and of μ for polydimethylsiloxane swelled in various solvents. In addition, the effects of various conditions of preparation, i.e. benzoyl peroxide concentration and press and oven cure temperatures, have been discerned in their relation to the number of cross-links of vulcanized silicone elastomer.

Further work will be directed toward both theoretical and very practical considerations of this problem. From homogeneous molecular weight fractions of silicone elastomer it will be possible to define more closely the possible values of M_c max. and M_c min., and hence the values of μ will be defined within narrower limits for the various polymer-solvent pairs. By treating swelling measurements in the proper manner, it will be possible to study rigorously the degree to which pigments reinforce silicone rubber and it may be possible to discern the mechanism of this reinforcement. A preliminary experiment has shown that swelling is reduced by pigments by a dilution effect and by a reinforcing action. Further studies will attempt to show the effect of various volume loadings of pigment on these swelling characteristics and various pigment types and sizes will be studied.

Of particular interest toward both theoretical and practical considerations will be a study of samples compounded with DuPont GS199S pigment to which no benzoyl peroxide has been added. This study should provide knowledge of the number of cross-links effected by the coated pigment and it should similarly permit differentiation of the reinforcing effect due to particle size and that due to the organic surface coating of the pigment.

Swelling measurements with the apparatus used in this study and with the unique procedure for graphical calculations should provide a valuable tool for future study of the physical as well as the thermodynamic properties of elastomeric polymers.

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SUPPLEMENTARY

INFORMATION

TAB No. 70-3 1 February 1970

IDENTIFICATION	*FORMER STATEMENT*	*NEW STATEMENT*	*AUTHORITY*
AD-494 888 Connecticut Hard Rubber Co., New Haven. Progress rept. no. 11, 5 Dec 51-4 Jun 52. 5 Jun 52 Contract DA-44-109-QM-64	DDC users only.	No limitation	USAMC ltr, 19 Jun 69