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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
SEPTEMBER 5, 1951 to DECEMBER 4, 1951

REPORT No. 10

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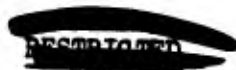
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ALBERT E. HINDMARSH
Captain, USN
Deputy Director, Security

THE CONNECTICUT HARD RUBBER COMPANY NEW HAVEN, CONNECTICUT

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

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Progress Report for the Period
September 5, 1951, to December 4, 1951



May 8, 1952.

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SUMMARY OF RESULTS

1. Activated Alumina F-10, ground glass filter paper and Celite 800 were tested as pigments in silicone rubber and found to be of little value. Si-O-Lite gave moderate reinforcement.
2. Santocel C has been studied further as a reinforcing agent in silicone rubber and found to have a maximum loading capacity of between 27.5 and 30 volumes per 100 of gum. Maximum reinforcement, as judged by tensile strength, is achieved at 20 volumes.
3. The rate of cure of silicone rubber compounds has been studied both with respect to the press cure and the oven cure. The recommended press cure based on this study is a 10-minute rise to 230°F. Lower cures result in lower tensile strengths, higher elongations, lower hardness and decreased compression set; higher press cures result in lower elongations, increased hardness and increased compression set.

With the recipe studied, the maximum stiffness, hardness and tensile strength was obtained with an 8-hour oven cure at 300°F. Compression set and elongation become lower as the oven cure is increased.
4. Moisture has been shown to have little effect on the physical properties of Santocel C compounds. "Bone dry" samples produced slightly stiffer and harder stocks. This pigment sinters when heated at 1500°F. and gives much reduced physical properties.
5. Alon is likewise insensitive to the moisture content except that the elongation tends to be much higher if the sample has not been dried. Thoroughly dehydrated Alon (at 1500 or at 1700°F.) becomes alkaline and

results in softer stocks with increased elongation and tensile strength.

6. Eleven pigments have been retested after strong heating and in some cases with preheating of pigment and rubber before addition of the benzoyl peroxide. Generally, drying of the pigment resulted in harder, stiffer stocks although this was not true with Whitcarb R, Super Multiflex, Celite 505 and zinc oxide with which the heating of the pigment had a deleterious effect. Preheating the pigment with the rubber before adding benzoyl peroxide generally enhanced the reinforcement.

7. The improvement resulting from preheating pigment with rubber before addition of benzoyl peroxide has been shown to persist even after extended oven curing. Preheating reduced shrinkage during oven cure substantially.

8. Alteration of the pH of the surface of Titanox R.A.N.C. resulted in softer stocks on either side of the neutral point.

9. Very fine particle size anatase titanium dioxide pigments were not outstanding reinforcing pigments. When activated by heating they tended to prevent cure with benzoyl peroxide.

10. Spheron 6 and Micronex 4-6 gave greater reinforcement than Sterling L or Furnex carbon blacks. Tertiary butyl perbenzoate was used as the curing agent. Spheron 6 gave best results when used to the extent of 40 volumes per 100 of rubber with 4 percent of tertiary butyl perbenzoate. Tensile strength was 424 pounds per square inch, elongation 175 percent and Shore A hardness 68.

11. A commercial silicone oil and a depolymerized silicone rubber oil stabilized with ammonia were used to coat several pigments, including Celite 800, Santocel C, Titanox R.A.N.C. and Spheron 6. In some cases superior tensile strengths and elongations resulted from the use of the silicone oil. In other cases the use of the ammonia-stabilized oil appeared to result in increased stiffness and tensile strength. The improvements that were noted do not appear to be sufficient to be worthy of practical evaluation.

12. In cooperation with the Linde Company, pigments were coated by them and by us with vinyl and methyltrichlorosilane and with dimethyldichlorosilane. Following this treatment, the coating was hydrolyzed and the coated pigment dried. Out of thirteen trials only one made an apparent improvement in the reinforcing action of the pigment. In this one case vinyltrichlorosilane enhanced the reinforcing action of Spheron 6.

13. A new reinforcing silica pigment known as DuPont GS199S has been submitted by the Grasselli Division of that company. It bears an organic coating which renders it hydrophobic and organophilic. The ultimate particle diameter is of the order of 100 A. Greatly superior reinforcing properties have been observed with this pigment with tensile strengths lying between 700 and 2000 pounds per square inch and elongations from 100 to 1000 percent. The superior reinforcing property of this pigment over Santocel C, for example, is attributed to superior wetting. Reinforcement is so great that high temperature cures tend to produce brittle samples. Electron microscope pictures have been taken showing the 100 A ultimate particles and the presence of aggregates of 5000 to

20,000 Å diameter.

14. Vulcanization with benzoyl peroxide has been studied in solution in n-heptane. It is concluded from the preliminary work reported herein that most of the decomposition of the peroxide is due to heat and interaction with the solvent. Carbon dioxide and benzoic acid were measured quantitatively and benzene was determined qualitatively among the products of the decomposition. Vulcanization was measured by increase in viscosity of the solution. It was demonstrated that mercurous oxide tends to act as a scavenger for the benzoic acid which is a deleterious by-product. A program for further study of this reaction is recommended.

15. Solubility of benzoic acid in silicone rubber is estimated to be 0.4 percent at room temperature. The addition of mercurous oxide to a system containing silicone rubber and benzoic acid was demonstrated to have removed the benzoic acid.

16. Ditertiarybutyl-diperphthalate peroxide was found to be a poor curing agent.

17. A very thorough study of the mechanism of swelling of silicone rubber in solvents has been carried out. A preliminary (approximately one-half) report is included herein.

18. Silicone rubber swells rapidly in benzene, for example, during the first 10 hours at 25°C. After this time swelling continues gradually up to 1000 hours and shows no sign of reaching a stationary state. Continued incremental swelling is attributed to breaking of the molecular

structure.

19. 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.

20. 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 percent but there is very little difference in the polymers which are cured with 2 and 8 percent benzoyl peroxide.

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

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

23. 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.

24. Analysis of General Electric SE-76 transparent silicone gum has been repeated, both with infrared and chemical analysis. This work shows definitely that the SE-76 polymer is essentially a dimethylsiloxane polymer. $\left[(\text{CH}_3)_2\text{SiO}\right]_n$

25. In Appendix I, data have been included on GS199S in GR-S, natural rubber and Neoprene as furnished by the DuPont Company.

INTRODUCTION

A high point in the progress of the research on silicone rubber has been reached during the period covered by this report. A pigment known as DuPont Silica GS199S came to the attention of Dr. C. M. Doede, Vice President of The Connecticut Hard Rubber Company, because of his oft expressed conviction that a method of improving silicone rubber would be found when a pigment was discovered that would be sufficiently finely divided and would be wet by the silicone rubber. This optimism has been fully justified.

The physical tests obtainable from silicone rubber comprising dimethylsiloxane (General Electric SE-76) have now been raised from less than 600 pounds per square inch tensile strength and 250 percent elongation (see Report No. 7, March, 1951) to approximately 2000 pounds per square inch tensile strength and 500 / percent elongation. These results have, it is true, been obtained with only one pigment; but the important point is that silicone rubber need no longer be avoided and discarded for those applications where strength or resistance to wearing and abrasion are necessary. Silicone rubber like the butadiene-styrene copolymers does not crystallize readily and consequently exhibits little or no strength in the unreinforced state. Therein, of course, lies the secret of its excellent low temperature properties. It is proven now that reinforcement of silicone rubber with a proper pigment will provide ample strength.

High price and lack of aromatic solvent resistance are the two remaining defects of silicone rubber. It also appears that increased

volume and continuing development of manufacturing methods of the polymer will sooner or later result in a much reduced market price for the silicones. Many ideas have been put forth but to date no solutions have been found for the lack of aromatic solvent resistance of the silicones. As would be expected, improved reinforcement with GS199S silica has shown a slight improvement in this property, though not enough to be considered outstanding. The cohesive energy density of the silicone rubbers place them close to that of the aromatic solvents. Strong reinforcement and a high degree of cross-linking can reduce the effect of such solvents but cannot prevent swelling.

A progress report on the study of swelling of silicone rubber is included in this report. Accurate methods have been developed enabling us to follow the progressive swelling of silicone rubber over periods up to 1000 hours. The effect of extracted polymer has been noted, and equations set up for calculating the value of M_c , the molecular weight of the polymer existing between cross-links.

A study also of the curing reaction with benzoyl peroxide is reported. When the portion of benzoyl peroxide which causes cross-linking can be measured, we can relate this to the number of cross-links formed as established by swelling measurements to prove whether this vulcanization reaction is a chain reaction involving free radicals or a simple oxidation of adjacent methyl side chains of the polymer.

The coating of carbon black and various silicas with silane and silicone coatings has been reported herein with no outstanding discoveries having been noted to date. A few additional new pigments have

been investigated with none coming even close to the interesting results obtained with GS199S.

A correction of a previous analysis of General Electric 81176 (SE-76) is included herein. The new data correlates well with infrared examination of the polymer proving definitely that it is essentially a dimethyl silicone and not one in which part of the siloxane linkages have been replaced by methylene linkages as had been suspected.

A detailed study of the time and temperature of press and oven curing of silicone stocks is reported herein. Optimum conditions for carrying out these curing operations have been arrived at and the importance of careful observations of time and temperature specifications especially in press curing has been demonstrated.

EXPERIMENTAL PART

I. REINFORCEMENT OF SILICONE RUBBER.

A. New Pigments in General Electric SE-76 Silicone Gum.

Four new pigment materials have come to our attention and have been evaluated as reinforcing pigments for General Electric SE-76 silicone gum. Data on the compounding and physical tests of stocks prepared from these pigments are given in Table I-A-1, page 5. It is evident that none of these finely divided materials can be classed as good reinforcing pigments, although Si-O-lite shows moderate reinforcement at intermediate volume loadings.

Activated Alumina F-10, supplied by the Aluminum Company of America, is a sample of fine dehydrated alumina. Its chemical composition is very nearly pure Al_2O_3 , in the gamma crystalline state. Its pH in water was found to be 5.0, indicating the absence of excess foreign acidic or basic materials. Its particle size is less than 40 microns (325 mesh) but since it is a product of grinding, it does not appear to be down in the size range for good reinforcing action.

The data in Table I-A-1 indicate a maximum reinforcement of 185 p.s.i. at 20 volume loading when compounded with 2 percent benzoyl peroxide. Preheating the milled pigment and gum prior to addition of peroxide and cure made it possible to obtain cures at 20 and 30 volume loading, whereas this was not possible without preheating. The low degree of reinforcement shown by this material, as compared to the action of Alon (a pure alumina pigment of less than 0.05 μ particle size discussed in our previous Report No. 9) is probably due to its relatively large particle size and low degree of porosity.

TABLE I-A-1

New Pigments in G.E. 81176 Silicone Gum with 2.0% Benzoyl Peroxide

Pigment	Treatment	Compd. No.	Vol. per 100 vol. Gum	St. @ 200%	Physical Properties ⁴		
					Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
Activated Alumina F-10	---	1980-5	10	82	104	283	22
	Preheated ¹		--	--	132	175	32
	---	1980-1	20	No Cure ²	---	---	--
	Preheated		--	--	185	138	30
	---	1980-2	30	No Cure	---	---	--
	Preheated		--	131	141	358	37
	---	1980-3	40	No Cure	---	---	--
	Preheated		--	No Cure	---	---	--
Glass Filter Paper	---	1999	5	--	154	50	47
	Pigment heated 500°F ³	1999-1	--	127	127	100	40
	---	1999-2	10	--	264	50	55
	Pigment heated 500°F	1999-3	--	--	239	75	46
Celite 800		2101	10	77	229	438	19
		2101-1	20	--	42	63	16
		2101-2	30	--	120	50	56
Si-O-Lite		2074	15	226	386	325	35
		2074-1	20	368	434	263	46
		2074-2	25	378	432	238	49
		2074-3	40	--	245	63	71

A somewhat different type of material suggested as a possible reinforcing agent was a new glass filter paper manufactured by the Cambridge Corporation, Syracuse, New York. This paper will pass only 0.02 percent of particles in the 0.2 μ range when employed as an air filter, and thus must be a very fine fibrous network. It showed less than 5 percent weight loss on ignition, and gave a pH of 5 to 6 indicating no foreign acidic or basic substances.

The glass filter paper was milled into SE-76 silicone gum with ease at 5 and 10 volume loading. The paper broke up as anticipated and good dispersion was obtained. Physical test data show that definite reinforcement was obtained, though this was not great, with tensile strengths up to 260 p.s.i. This is as good reinforcement as has been obtained with some of the less effective silicas such as Hi-Sil and is interesting in view of the difference in physical form of this fibrous glass paper from that of usual pigments.

Celite 800 is a very fine diatomaceous earth furnished by the Johns Manville Corporation. Its average particle size is 0.02 μ , as compared to about 0.5 to 1.0 μ for other grades such as Celite 505. Its true density is 1.9 and its pH in water 9 to 10. This pigment was given a preliminary evaluation as reported in Table A of Report No. 9; however, it was felt desirable to repeat this in view of later work. The data on Celite 800 in Table I-A-1 indicate that the pigment has best reinforcing properties in the low loading range. The absence of reinforcement at 20 volumes is unexplainable, but was also observed in another series of Celite 800 compounds. In general, this fine diatomaceous earth does not appear promising.

TABLE I-A-2

Santocel C in G.E. 81176 Gum Alone and with 2.0% Benzoyl Peroxide

Compd. No.	Vol. per 100 vol. Gum	Benzoyl Peroxide Wt. Percent	Oven Cure	St., ¹ 200%	Physical Properties ¹		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
1962	5 (Preheated) ²	2.0 "	1 Hr. @ 300°F.	101 133	168 145	300 183	27 34
1962-1	10 (Preheated)	" "	1 Hr. @ 300°F.	212 257	586 353	333 242	40 45
1962-2	15 (Preheated)	" "	1 Hr. @ 300°F.	390 598	862 897	342 225	50 55
1962-3	20 (Preheated)	" "	1 Hr. @ 300°F.	481 700	887 838	308 225	61 65
1962-4	25	" "	1 Hr. @ 300°F. 24 Hrs. @ 400°F.	533 ---	576 429	225 125	71 75
1962-5	27.5	" "	1 Hr. @ 300°F. 24 Hrs. @ 400°F.	582 785	694 785	263 200	73 75
1962-6	30	"	1 Hr. @ 300°F.			No Cure	

¹ Press cure 15 min. @ 230°F. Oven cure as noted in column 4.² Milled pigment and gum preheated 1 hr. @ 300°F. before addition of peroxide and cure.

Si-O-Lite is a by-product material produced by the Mallinckrodt Chemical Works. It is obtained as a by-product in the manufacture of a specialty grade of silica. The average particle size of Si-O-Lite is claimed to be 0.8μ with, however, 4 to 5 percent being as high as 15μ . Complete information on it is not available. However, it was found to contain less than 10 percent of water of hydration which is lost on ignition. It may be seen in Table I-A-1 that Si-O-Lite imparts moderately good reinforcement, although it is doubtful that it would prove to be superior in any respect to the Celites (see previous reports).

Santocel C was considered in detail in Report No. 9. Because of our interest in DuPont GS Silica, it was desirable to extend our knowledge of Santocel C especially with respect to volume loadings at higher concentrations in the 20 to 30 volume percentage range. The data are shown in Table I-A-2 and it will be noted that the maximum reinforcement is obtained in the range from 15 volumes to 27.5 volumes per 100 of rubber. Above 27.5 volumes the batch becomes very dry indicating that the porous Santocel C absorbs so much rubber within its pores that there is insufficient left over to bond the slab together. A comparison of the direct mix with the preheated mixes in which the pigment and rubber were mixed and preheated together for 1 hour at 300°F . shows the effect of this variation on the method of mix.

B. Rate of Cure of Silicone Rubber Compounds.

A study of the rate of decomposition of benzoyl peroxide in a solvent such as toluene or heptane shows that it decomposes rapidly as soon as the solvent is heated to a temperature of approximately 200°F .

At this temperature decomposition is virtually complete in about one hour. This indicates that press curing of silicone compounds containing benzoyl peroxide in the range from 200 to 300°F. probably accomplishes the complete decomposition of the benzoyl peroxide and the establishment of cross-links between molecules which constitutes vulcanization. If this assumption is correct, the oven cure following the press cure is applied for some purpose other than the formation of the cross-links. It was deduced, therefore, that an accurate study of the effect of time and temperature of press curing should be made to determine whether variations in the press cure would cause variations in the ultimate properties of the compound.

Sufficient General Electric 81223 compound, which contains approximately 16 volume percentage of Santocel C and 1.6 percent on the rubber of benzoyl peroxide, was selected to carry out all of the cures reported in Tables I-B-1 and I-B-2 and shown graphically in Figures 1-B-1 and I-B-2.

Silicone rubber compounds are customarily cured starting with a cold mold and part of the cure takes place during the rise time to the selected curing temperature. Therefore, as will be seen in Table I-E-1, the first two cures were obtained during the time required to raise the mold to 210 and 230°F., respectively. Then the curing time was increased at 230°F. through the cure labelled "E". Subsequent cures were carried out at 250 and 300°F. Thus, the time and temperature were both increased from the start to the end of the series tested. All temperatures were measured by means of a mercury thermometer inserted to the center of the bottom part of the mold. All slabs were given a thorough oven cure following the press cure. This consisted of a 40-hour gradually rising temperature cycle ending at 480°F.

TABLE I-B-1

Press Curing of G. E. 81223 Stock

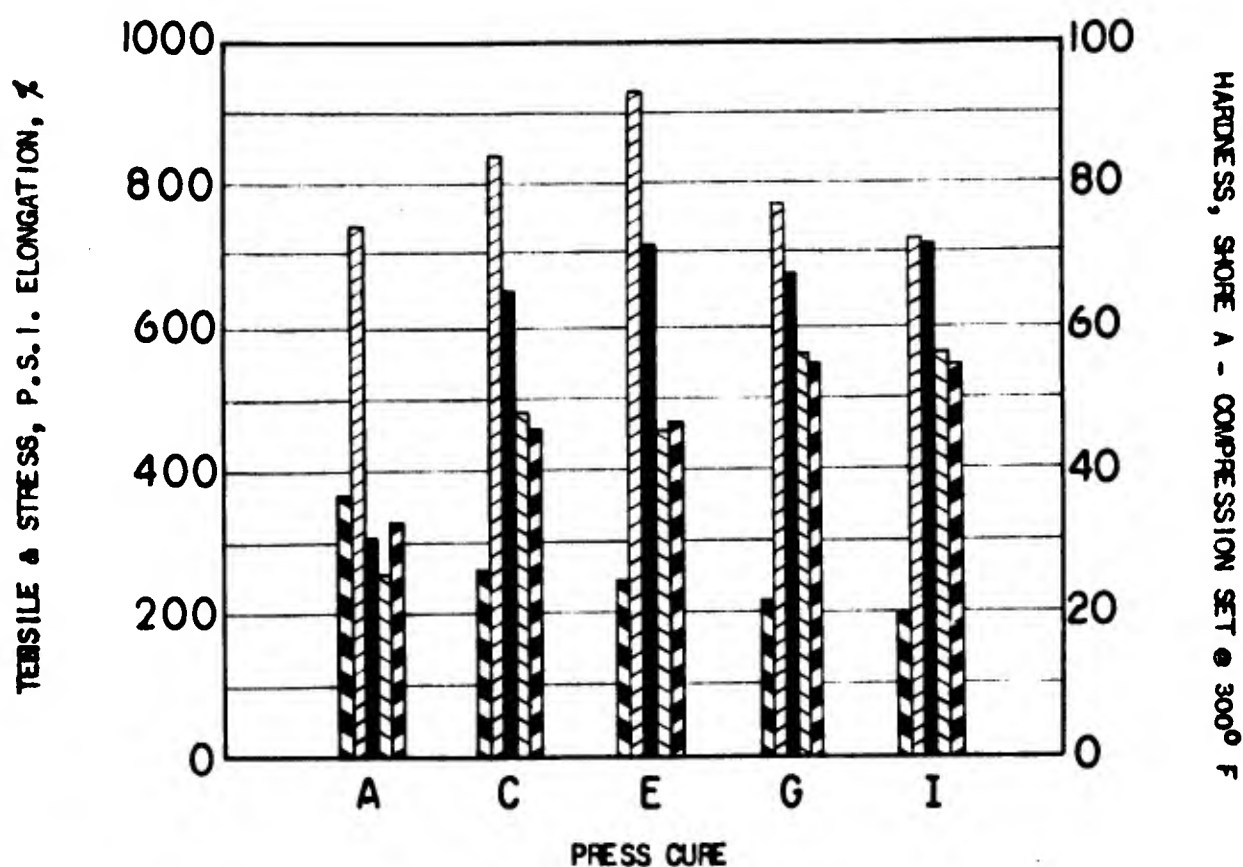
Sample No.	Time & Temp. ¹ of Oven Cure	St @ 200%	Tensile Strength p.s.i.	Physical Properties ²		
				Elongation Percent	Hardness Shore A	Comp. ³ Set %
A	5 min. rise to 210°F.	308	743	375	34	25.0
B	10 min. rise to 230°F.	627	764	250	47	37.4
C	10 min. rise to 230°F. / 5 min. @ 230°F.	652	842	263	46	47.9
D	10 min. rise to 230°F. / 10 min. @ 230°F.	679	839	263	47	45.6
E	10 min. rise to 230°F. / 15 min. @ 230°F.	710	932	250	47	46.2
F.	10 min. rise to 250°F. / 5 min. @ 250°F.	641	914	275	55	57.5
G	10 min. rise to 250°F. / 10 min. @ 250°F.	675	763	225	56	56.9
H	10 min. rise to 250°F. / 15 min. @ 250°F.	667	758	250	55	56.0
I	15 min. rise to 300°F. / 5 min. @ 300°F.	715	715	200	55	56.6
J	15 min. rise to 300°F. / 10 min. @ 300°F.	675	675	200	55	58.5

¹ Thermometer was placed in platen to measure temperatures.

² All slabs oven cured using 48-hr. factory cycle up to 480°F. before measuring physical properties.

³ Compression set according to A.S.T.M. D-395-49T (Method B) 22 hours at 300°F.

FIG. I-B-1



PHYSICAL PROPERTIES VS. PRESS CURE G.E. 81223 SILICONE RUBBER COMPOUND

OVEN CURE: 48 HRS CYCLE TO 480° F.

PRESS CURES

- A 5' RISE TO 210° F
- C 10' RISE TO 230° F + 5' @ 230° F
- E 10' RISE TO 230° F + 15' @ 230° F
- G 10' RISE TO 250° F + 10' @ 250° F
- I 15' RISE TO 300° F + 5' @ 300° F

LEGEND

- TENSILE
- ELONGATION
- STRESS @ 200%
- COMPRESSION SET @ 300° F
- HARDNESS

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It will be noted that the maxima in stress at 200 percent elongation and tensile strength were reached with a 10-minute rise to 230°F. and a 15-minute cure at this temperature. A maximum hardness was reached only with a slightly greater cure, 10 minutes rise to 250°F. plus 5 minutes at 250°F. It is interesting to note also that more satisfactory compression set results were obtained with low degrees of heating as shown in the first two cures (A and B).

The importance of careful measurement of time and temperature during press curing is obvious from Table I-B-1. The difference between the slabs marked "D" and "G" might be pointed out. Slab "D" has higher tensile strength and higher elongation but 9 points lower hardness and 11 percent less compression set, these differences being caused by the difference between 230 and 250°F. as a curing temperature. The difference between 250°F. and 300°F. as a press curing temperature is much smaller. Since maximum stiffness and tensile strength and moderate compression set were obtained with the 10-minute rise to 230°F. plus 15 minutes at 230°F., this cure was selected as a standard for future work.

Having established, as reported above, the importance of carefully measuring press cures and using the standard cure selected above, the oven cure was varied as shown in Table I-B-2. Maximum stiffness, tensile strength and hardness were obtained with an 8-hour cure at 300°F. and with an 8-hour cure at 300°F. plus 16 hours at 400°F. Cures which were less or more severe than these conditions resulted in slightly softer vulcanizates. The elongation became progressively shorter as would be expected. Compression set data were somewhat erratic. However, the most severe cure gave the lowest compression set. It is common experience

TABLE I-B-2

Oven Curing of General Electric 81223¹

Sample No.	Time & Temp. of Oven Cure	St. @ 200%	Physical Properties			
			Tensile Strength	Elongation Percent	Hardness Shore A	Comp. Set % ²
SA	1 hr. @300°F.	560	865	275	50	64.3
SB	8 hrs. @300°F.	704	933	225	55	58.3
SC	8 hrs. @500°F. / 16 hrs. @400°F.	729	786	238	55	52.3
SD	8 hrs. @300°F. / 16 hrs. @450°F.	658	726	225	52	52.1
SE	8 hrs. @300°F. / 2 hrs. @350°F. / 16 hrs. @400°F. / 8 hrs. @480°F.	637	699	238	49	59.9
SF	8 hrs. @300°F. / 2 hrs. @350°F. / 16 hrs. @400°F. / 8 hrs. @480°F. / 5 hrs. @400-500°F. / 2 hrs. @500°F.	673	685	213	50	50.3

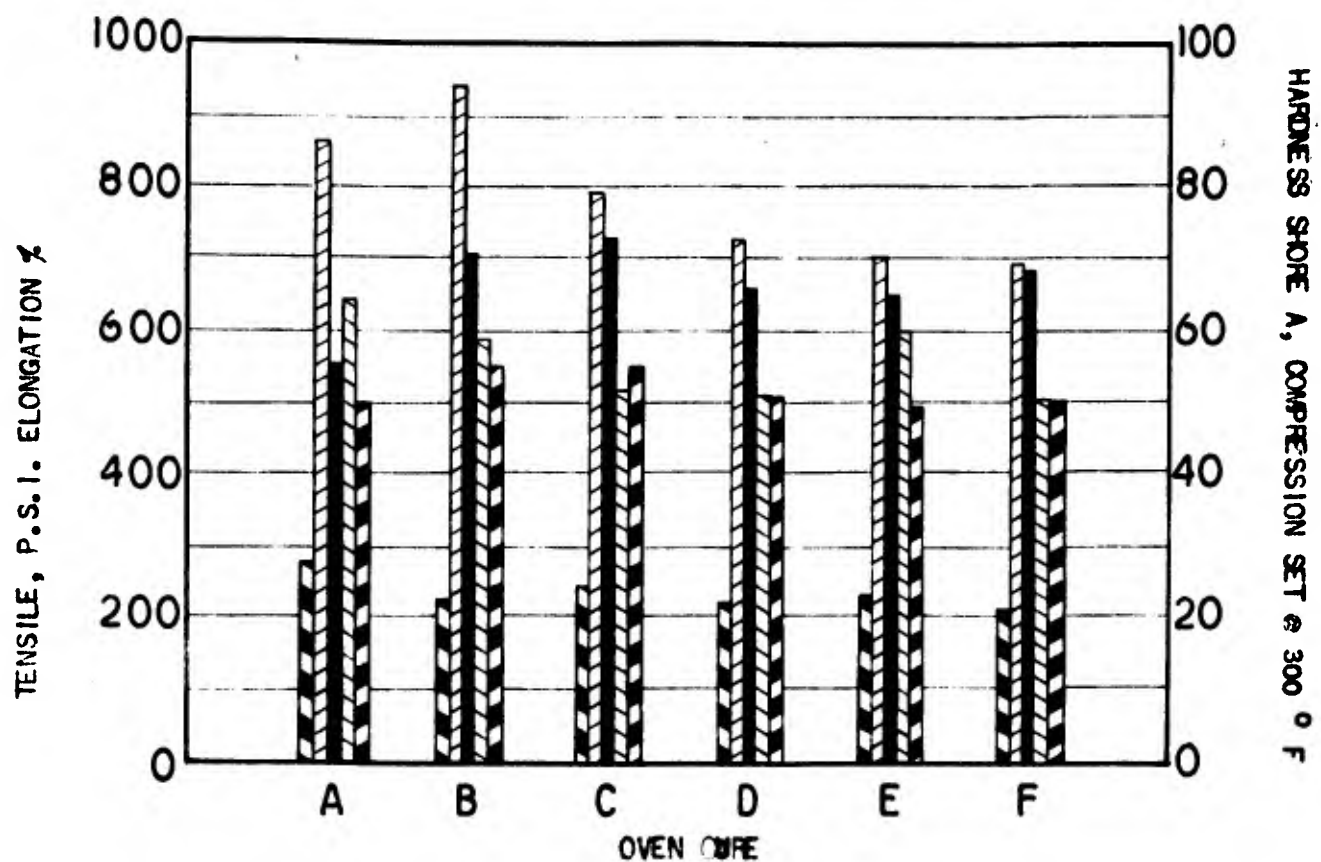
TABLE I-B-3

Oven Curing of Titanox R.A.N.C. Stock¹
(40 vol., 2.0% Benzoyl Peroxide)

Sample No.	Time & Temp. of Oven Cure	St. @ 200%	Physical Properties			
			Tensile Strength	Elongation Percent	Hardness Shore A	Comp. Set % ²
TA	1 hr. @300°F.	720	720	200	53	82
TB	8 hrs. @300°F.	---	663	175	55	80.6
TC	8 hrs. @300°F. / 16 hrs. @400°F.	---	662	175	55	65.5
TD	8 hrs. @300°F. / 16 hrs. @450°F.	---	607	163	51	63.0
TE	8 hrs. @300°F. / 2 hrs. @350°F. / 16 hrs. @400°F. / 8 hrs. @480°F.	---	365	125	52	66.0
TF	8 hrs. @300°F. / 2 hrs. @350°F. / 16 hrs. @400°F. / 8 hrs. @480°F. / 5 hrs. @400-500°F. / 2 hrs. @500°F.	---	600	150	55	55.4

¹ Press-cure 10 min. rise to 230° / 15 minutes @ 230°F.² Compression set according to ASTM D-395-49T (Method B) 22 hrs. @ 300°F.

FIG. I-B-2



PHYSICAL PROPERTIES VS. OVEN CURE G.E. 81223 SILICONE RUBBER COMPOUND

OVEN CURES

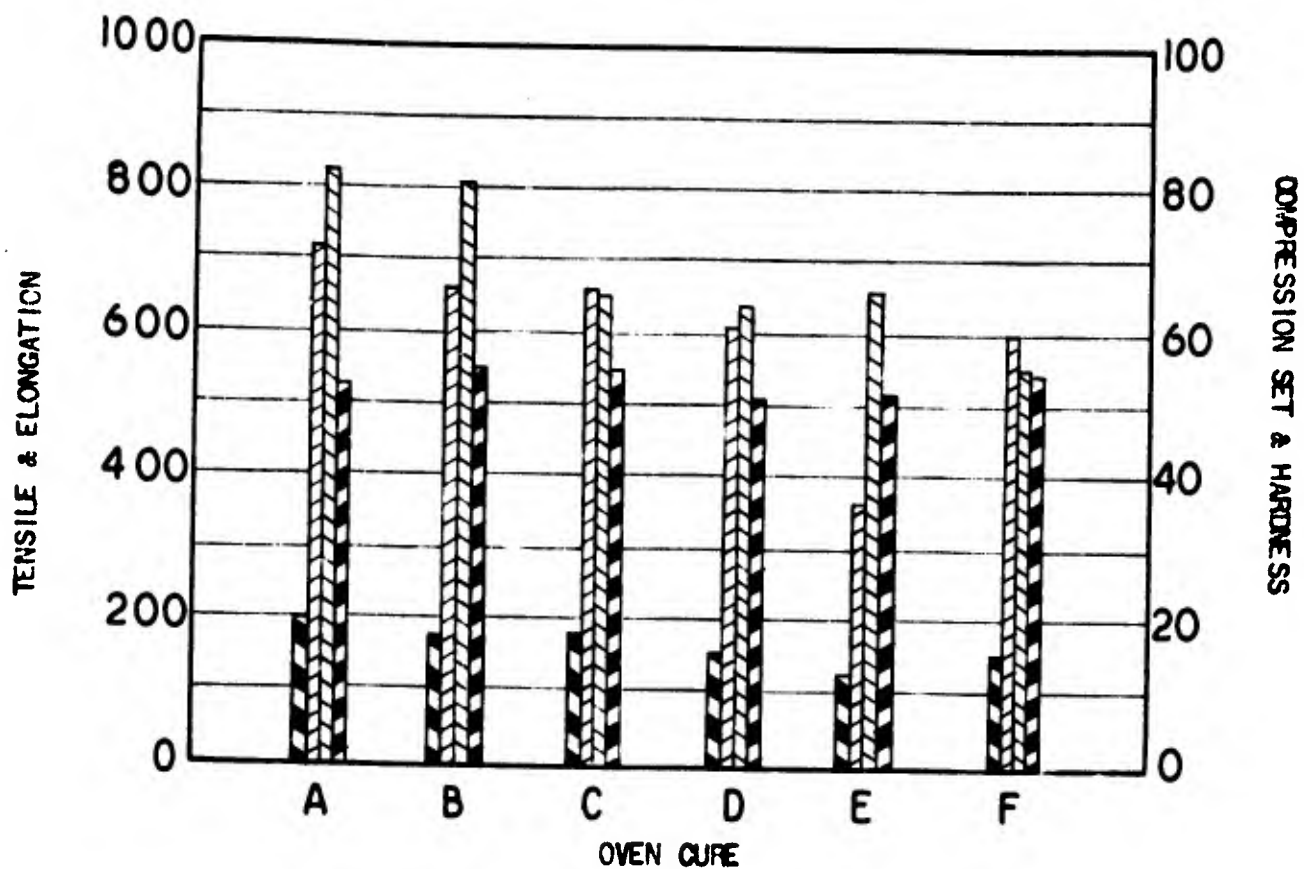
- A 1 HR @ 300° F
- B 8 HRS @ 300° F
- C 8 HRS @ 300° F + 16 HRS @ 400° F
- D 8 HRS @ 300° F + 16 HRS @ 450° F
- E 8 HRS @ 300° F + 2 HRS @ 350° F
16 HRS @ 400° F
8 HRS @ 450° F
- F 8 HRS @ 300° F + 8 HRS @ 480° F
5 HRS @ 400-500° F
2 HRS @ 500° F

LEGEND

- TENSILE
- ELONGATION
- STRESS @ 200 %
- COMPRESSION SET @ 300° F
- HARDNESS

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FIG. I-B-3



PHYSICAL PROPERTIES VS. OVEN CURE
40 VOLUMES TITANOX RANC IN G.E. 81176 GUM
2.0% B.P.

OVEN CURES

A 1 HR @ 300° F

B 8 HRS @ 300° F

C 8 HRS @ 300° F + 16 HRS @ 400° F

D 8 HRS @ 300° F + 16 HRS @ 450° F

E 8 HRS @ 300° F + 2 HRS @ 350° F

16 HRS @ 400° F

8 HRS @ 480° F

F 8 HRS @ 300° F + 8 HRS @ 480° F

5 HRS @ 400-500° F

2 HRS @ 500° F

LEGEND



TENSILE



ELONGATION



COMPRESSION SET @ 300° F



HARDNESS

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that this should be true. It is not usually recognized, however, that the shortest press cures shown in Table I-B-1 accompanied by a thorough oven cure result in lower compression set values.

Table I-B-3 gives a picture of the effect of the same variations in oven curing as shown in Table I-B-2, except that they are applied to a Titanox stock loaded with 40 volumes and cured with 2 percent of benzoyl peroxide. It will be recalled that Table I-B-2 is concerned with a 16-volume Santocel C compound cured with 1.6 percent benzoyl peroxide. Maxima in stiffness, tensile strength and hardness were obtained with the same oven cures as before; namely, 8 hours at 300°F. or 8 hours at 300°F. plus 16 hours at 400°F. It is noteworthy that in the longest and hottest cure, the 40-volume Titanox compound has properties which are quite similar to those obtained on 81223. (See also Figure I-B-3). Faulty action of the temperature regulator in the last cures of both tables occurred during the heating at 480°F.

From this study of oven curing it appears that moderate cures at 300° or 400°F. are most satisfactory for obtaining high physical properties with the exception of compression set. Lowest compression set values can be obtained with long oven cures and short press cures.

C. Effect of Moisture Content on Reinforcement.

We reported in Report No. 9 a decided advantage to be gained by preheating mixtures of pigment and gum before adding the curing agent. Some of the observed improvement was felt to have come from the elimination of moisture on the surface of the pigment during the preheating process. For this reason Santocel C and Alon were studied carefully with a wide range of moisture contents. In Table I-C-1 and I-C-2 on the

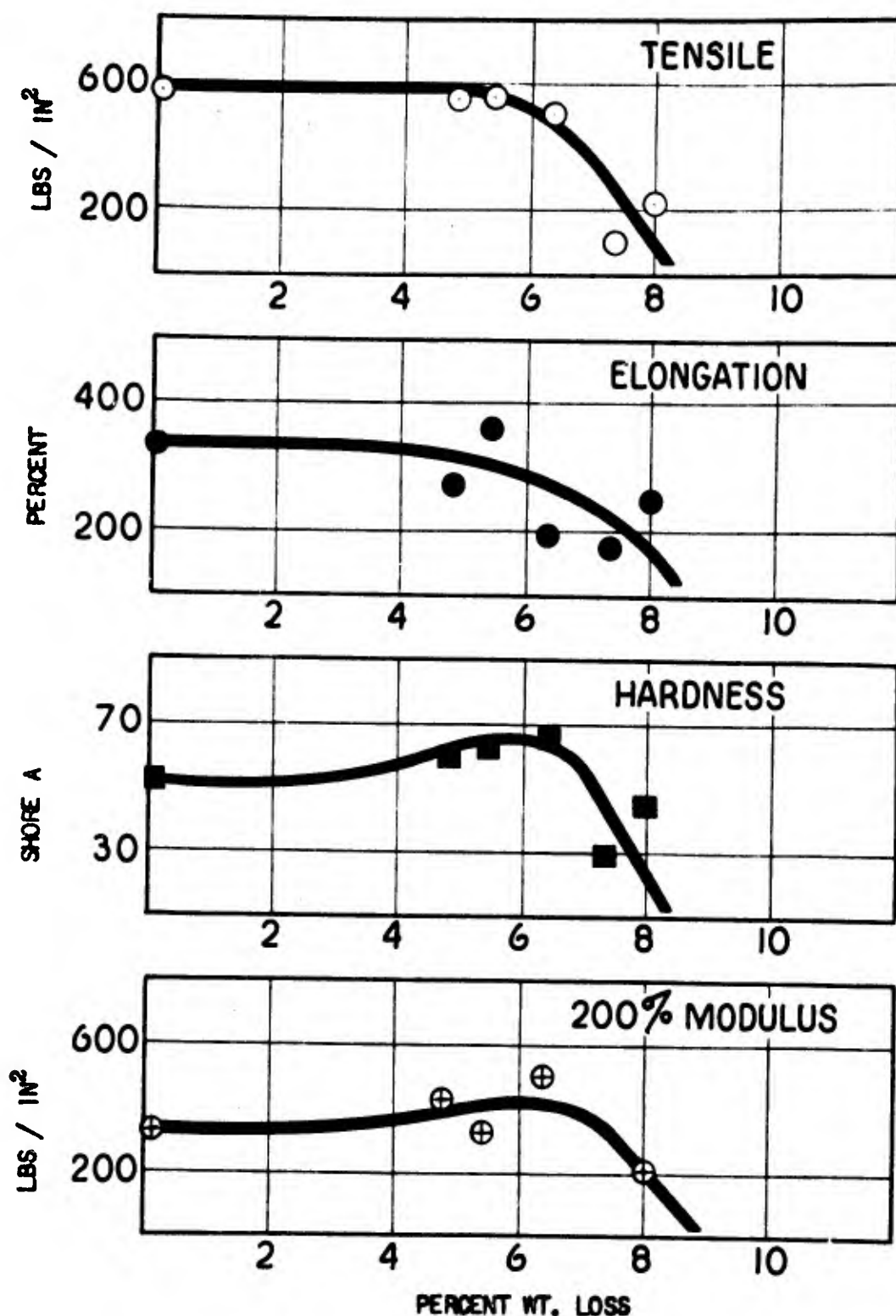
TABLE I-C-1

Santocel "C" with Varying Water Content¹

Samples No.	Time & Temp. of Heating (°F)	Pigment Wt. Loss (%)	Pigment ³ pH (H ₂ O)	Physical Properties ²				
				Compd. No.	St. F 200%	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
S-88	Not heated.	---	3.88	1993	333	576	333	53
S-89	6 Hrs. @ 220°	5.40	3.86	1993-1	367	577	325	62
S-90	4 Hrs. @ 500°	4.82	3.85	1993-2	421	559	275	60
S-91	3 Hrs. @ 1000°	6.38	4.23	1993-3	506	506	200	66
S-92	3 Hrs. @ 1500°	8.00	6.20	1993-4	202	234	250	45
S-93	1 Hr. @ 1700°	7.35	8.17	1993-5	---	101	175	30

¹ Compounded with G.E. 81176 silicone Gum. 15 vols. per 100 vols. gum, 2.0% benzoyl peroxide.² Press cure 15 minutes 250°F. Oven cure 1 hour 300°F.³ pH of 0.5 gms. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0).

FIG. I-C-1



**PHYSICAL PROPERTIES VS. WT. LOSS OF PIGMENT
ON HEATING AT 200°-1700°F.**

SANTOCEL-C IN 81176 SILICONE GUM, 15 VOLUMES 2.0% B.P.

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first line, there is reported the results obtained with pigment as taken from the laboratory supply and not heated in any way. Results in the rest of both tables were obtained after the pigment had been thoroughly wet with moisture in a covered dish and exposed to water vapors at room temperature. Following this treatment which lasted 24 hours, samples were heated for varying lengths of time at varying temperatures as shown in the two tables. It may be seen in Table I-C-1 that approximately 6.4 percent of moisture was driven off by heating at 500 and also at 1000°F. It is believed that heating in this temperature range produced the maximum reinforcement as judged by the stress at 200 percent elongation and the Shore hardness. Water on the surface of Santocel C had little effect on pH until the 1000°F. heating temperature was exceeded. Heating at 1500 and 1700°F. resulted in the formation of a more alkaline surface on the pigment. Heating at these temperatures was also accompanied by sintering of the Santocel C aerogel and resulted in a drastic reduction in the apparent volume of the pigment.

Maximum stiffness and hardness were attained by heating Alon for 3 hours at 500°F. The maximum amount of water was removed, however, by heating at 1000°F. or higher. When Alon was heated at 1500 or 1700°F. the surface became more basic, but the pigment form did not appear to change appreciably. It may be that the increased basicity of the pigment surface accounts for the increased elongation and reduced hardness and stiffness. If Alon were commercially available, it would be interesting to pursue further the results that could be obtained by heating the pigment at these high temperatures. The results tabulated in I-C-1 and

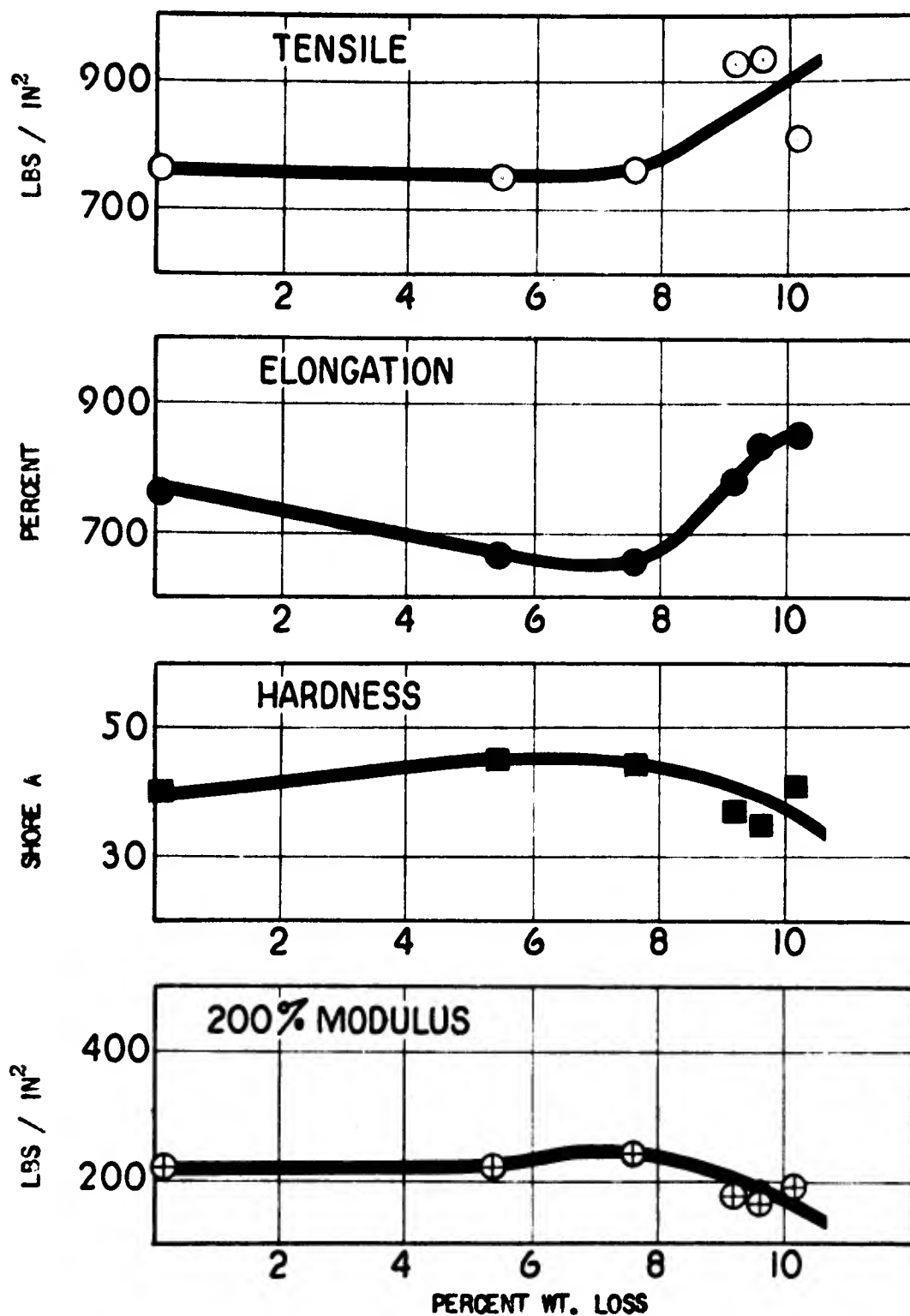
TABLE I-C -2

Alon with Varying Water Content¹

Sample No.	Time & Temp. of Heating (°F.)	Pigment Wt. Loss (%)	Pigment pH (H ₂ O) ³	Compd. No.	St. @ 200%	St. @ 400%	Physical Properties ²		
							Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
S-99	Not heated.	---	5.05	1994	206	439	767	763	40
S-100	5 Hrs. @ 220°	5.48	4.92	1994-1	220	483	751	663	45
S-101	3 Hrs. @ 500°	7.61	5.76	1994-2	245	503	763	650	45
S-102	2 Hrs. @ 1000°	10.19	5.70	1994-3	189	405	810	850	41
S-103	3 Hrs. @ 1500°	9.63	7.85	1994-4	164	416	938	838	35
S-104	1 Hr. @ 1700°	9.19	7.80	1994-5	171	428	925	775	37

¹ Compounded with G.E. 81176 silicone gum, 15 vols. per 100 vols. gum, 4.0% benzoyl peroxide.² Press cure 15 min. @ 2500°F. Oven cure 1 hr. @ 300°F.³ pH of 0.5 gm. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0)

FIG. I-C-2



**PHYSICAL PROPERTIES VS. WT. LOSS OF PIGMENT
ON HEATING AT 200°-1700°F.**

ALON IN 81176 SILICONE GUM. 15 VOLUMES 4.0% B.P.

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I-C-2 have also been shown in Figures I-C-1 and I-C-2. It will be recalled that Chart I in Report No. 9 showed a significant increase in elongation and reduction in hardness at a pH of 6 to 7 when Alon was treated with ammonia.

Extending the study of the effect of removal of moisture on the reinforcement of silicone rubber, Table I-C-3 presents effect of heating eleven different pigments on the physical properties obtained in 81176 with 2 percent benzoyl peroxide and a 1-hour oven cure. In some cases the effect of preheating the pigment and rubber mixture is also shown. The results varied with the pigment that was treated. With Hi-Sil, Celite Superfloss, Alon, Santocel C and Davison's Silica the heated or dried pigment produced a harder, stiffer stock as compared with the unheated pigment. In several cases, however, the preheating treatment of pigment and rubber together gave superior results. With Whitcarb R, Super Multiflex, Celite 505 and zinc oxide heating at 500°F. had a deleterious effect in one way or another, reducing either tensile strength, stiffness or hardness or even preventing cure at all. Alon II was not greatly affected by heating the pigment, but the stiffness of the cured compound was improved by preheating the pigment and rubber together. Complete elucidation of the mechanism of preheating pigment and rubber together is not yet possible, but it is clearly a preferred treatment with most pigments.

The results obtained by preheating Titanox R.A.N.C. with gum before adding benzoyl peroxide were so outstanding that further study was made with this pigment and also with Hi-Sil and hydrated alumina in which the pigment itself was heated at 500° or 1000°F. In some cases, the heated

TABLE I-C-3

Heating and Preheating Various Pigments¹

Pigment	Treatment	Pigment ⁵ Wt. Loss (%)	Pigment ⁶ pH (H ₂ O)	Compd. No.	Vol. per 100 vol. gum.	St. @ 200%	Physical Properties ²		
							Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
Hi-Sil	None		8.90		15	217	261	283	37
	Preheated ³					354	456	258	40
	Pigment heated ⁴	16.8	8.65	1975		---	276	192	50
Whitcarb R	None		10.60		40	159	252	700	32
	Preheated					137	177	458	34
	Pigment heated	1.6		1974		No Cure			
Titanox RANC	None		7.70		40	197	434	417	41
	Preheated					507	581	267	45
	Pigment heated	1.6		1969		287	670	450	40
Celite Super Floss	None		9.52		40	456	466	208	58
	Preheated					---	497	150	66
	Pigment heated	0.8	9.63	1972		---	539	175	60
Alon C-52	None		4.79		15	131	511	950	35
	Preheated					319	770	475	43
	Pigment heated	6.4	5.10	1964		362	722	483	51
Santocel C	None		4.15		15	387	737	383	52
	Preheated					676	826	275	56
	Pigment heated	3.4	4.05	1965		640	660	225	59
Alon II	None		8.20	1961-3	30	108	216	375	30
	Preheated			1961-3		---	223	163	43
	Pigment heated	0.8	5.55	1979		106	378	500	27

TABLE I-C-3 (Cont.)

Heating and Preheating Various Pigments¹

Pigment	Treatment	Pigment ⁵ Wt. Loss (%)	Pigment ⁶ pH (H ₂ O)	Compd. No.	Vol. per 100 vol. gum	St. ⁶ 200%	Physical Properties ²		
							Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
Davison Silica	None		8.20	1966-1	20	183	218	283	37
	Preheated			1966-1		340	369	225	45
	Pigment heated	4.9	7.30	1976		244	252	213	43
Zinc Oxide	None		7.15	1823	40	---	436	507	52
	Pigment heated	0.4	6.85	1970		126	269	442	29
Celite 505	None		7.60	1792	20	---	417	138	60
	Pigment heated	1.3	7.65	1971		350	388	250	42
Super Multiflex	None		9.40	1828	20	---	218	638	35
	Pigment heated	2.9	10.16	1973		125	138	275	35

¹ Compounded with G.E. 81176 silicone gum. Vol. loading as indicated in Column 6. All with 2.0% benzoyl peroxide.

² Press cure 15 min. 250°F. Oven cure 1 hr. @ 300°F.

³ Milled pigment and gum preheated 1 hr. @ 300°F. before addition of peroxide and cure.

⁴ Pigment heated in air 16 hrs. @ 500°F. and kept dry.

⁵ Wt. loss of pigment during heating.

⁶ pH of 0.5 gm. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0)

pigment was also preheated in contact with the rubber. The first part of Table I-C-4 shows increased stiffness to result from the regular preheating treatment or from heating the pigment alone, or from a combination of the two treatments. Tests were run at 30, 40 and 50 volumes of pigment in an effort to secure results using Titanox R.A.N.C. which might be comparable to those obtained earlier with Alon or Santocel C. The maximum tensile strength and stiffness were obtained with a 50-volume loading using heated pigment and the preheating treatment as well. With Hi-Sil the best results were obtained by heating the Hi-Sil for 2 hours at 1000°F. before using it in the rubber. The preheating treatment was not used in this case. Hydrated alumina which contains a theoretical 34 percent of combined water was not improved at all by heating at 500 or 1000°F. Under these conditions of heating, the pigment apparently becomes excessively alkaline and fails to cure with the benzoyl peroxide. This may also have been the case with Whitcarb R reported in Table I-C-3.

In all the work that has been done on preheating pigments with the rubber, only short 1-hour at 300°F. cures have been studied. In order to see whether the desirable advantages obtained through preheating carry through in long cures, the results in Table I-C-5 were obtained. Since Alon shows a remarkably great improvement on preheating, it was selected for this work. The data show that in using a 1-hour at 300°F. cure preheating has increased tensile strength by 470 percent. A long cure without preheating increased the tensile from 121 pounds to 368 pounds, but the long cure with preheating resulted in 975 pounds tensile strength. These results definitely show that advantages gained

TABLE I-C-4 (Cont.)

Heating Various Pigments at 500° and 1000°F.¹

Pigment	Sample No.	Pigment treatment	Pigment loss (%)	Pigment pH (40)5	Compd. No.	Vol. Loading	St. @ 200%	Physical Properties ²		
								Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
Hydrated Alumina C-730	S-110	None		9.38	1989	40	14.8	279	613	33
	S-111	Heated 3 hrs. @ 500°F.	13.2	10.20	1989-1			No Cure		
	S-112	Heated 2 hrs. @ 1000°F.	34.4	10.25	1989-2			No Cure		

¹ Compounded with C. E. 81176 silicone gum. Vol. loading as indicated in Column 7, all with 2.0% benzoyl peroxide.

² Press Cure 15 min. 250°F. Oven cure 1 hr. @ 300°F.

³ Milled pigment and gum preheated 1 hr. @ 300°F. before addition of peroxide and cure.

⁴ Wt. loss of pigment during heating.

⁵ pH of 0.5 gm. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0)

TABLE I-C-5

Effect of Preheating Alon in G.E. 81176 Gum
with 3.0% Benzoyl Peroxide
(15 Volume Loading)

Compd. No.	Oven Cure	Physical Properties				
		Vol. Shrinkage During Oven Cure	St.@ 400%	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
2138	1 hr. @ 300°F.	9.6	112	121	437	27
2138-2	Preheated ¹	6.1	400	692	675	31
2138-1	24 hrs. @ 400°F.	12.2	316	368	425	39
2138-3	Preheated	6.1	840	975	450	42

¹ Milled pigment and gum preheated 1 hour at 300°F. before addition of peroxide and cure.

through preheating are preserved when long cures are used.

An additional important result achieved through preheating is shown in column three of Table I-C-5 in that the preheated batches showed a volume shrinkage of only 6 percent. This was half as great as that shown on the fully cured but not preheated slab. Inasmuch as mold shrinkage is a troublesome feature of silicone molded articles, the reduction obtained through the preheating is important.

D. Effect of pH on Pigments.

Supplementing earlier work with Alon and Santocel C on the effect of pH on the surface of the pigment, there is shown in Table I-D-1 the effect of treating Titanox R.A.N.C. with ammonia and HCl vapors followed by evacuation and heating to drive off excess gas. The pH range covered is not very broad, but the most acid sample, S-127, and one of the most alkaline pigments, S-128, show the highest elongations indicating that maximum stiffness or reinforcement is obtained with a neutral surface. The most acid pigment is also slightly inferior with respect to compression set. The data are shown graphically in Figure I-D-1.

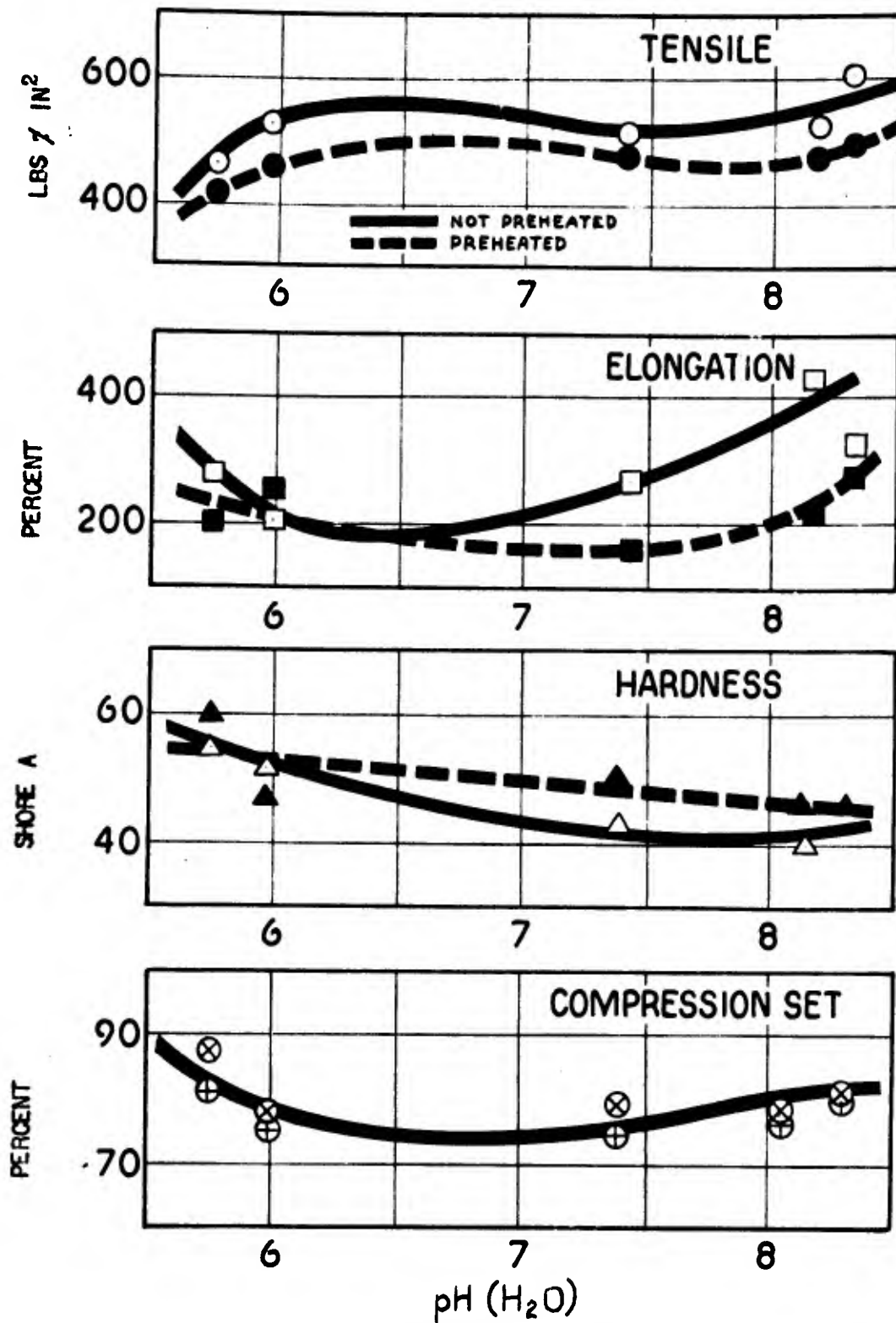
TABLE I-D-1

Titanox RANC at Varying pH¹

Sample No.	Treatment	Pigment pH (H ₂ O) ⁴	Compd. No.	Vol. Loading	St. ^a 200%	Physical Properties ²			
						Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Comp. Set (%)
S-125	Heated to 500°F. only Preheated ³	7.40	2048	40	405	511	263	43	79.3
S-126	HCl, Evac., Heated ⁵ Preheated	5.97	2048-1	40	527 390	485 456	163 200 250	50 52 47	74.7 76.9 75.6
S-127	HCl, Heated Preheated	5.75	2048-2	40	361 400	465 426	275 200	55 60	86.8 81.3
S-128	NH ₃ , Evac., Heated Preheated	8.15	2048-3	40	530 565	579	425 213	40 46	77.7 78.5
S-129	NH ₃ , Heated Preheated	8.31	2048-4	40	405 476	606 595	325 275	46 46	80.6 79.2
S-129	NH ₃ , Heated Preheated	8.31	2048-5	50	371	610 381	275 100	49 65	
S-129	NH ₃ , Heated Preheated	8.31	2048-6	60	419	458 504	100 163	54 65	
S-129	NH ₃ , Heated Preheated	8.31	2048-7	70	---	516 484	163 63	70 89	

¹Compounded with G.E. 81176 gum at indicated vol. loading and 2.0% benzoyl peroxide.²Press cure 15 min. 250°F. Oven cure 1 hr. 300°F.³Milled pigment and gum preheated 1 hr. 300°F. before addition of peroxide and cure.⁴pH of 0.5 gm. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0).⁵Pigment heated to 500°F. after NH₃ or HCl treatment.

FIG. I-D-1



PHYSICAL PROPERTIES VS. pH OF PIGMENT
TITANOX RANC IN G.E. 81176 SILICONE GUM
40 VOLS. 2.0% B.P.

As indicated previously, some interest was felt in the more alkaline varieties of Alon. For this reason, further tests were run on sample S-129, the most alkaline of the treated Titanox samples. In these tests the volume loading was raised to see if a superior compound would result. Despite the possibility of obtaining stretchier compounds with an alkaline surface as shown on samples S-128 and S-129, higher volume loadings appeared to be beyond the point of maximum reinforcement. After treating the pigment with ammonia and removing the excess, the best results were obtained on sample S-129 at 40 volumes loading.

E. Titanium Dioxides.

Continuing to show interest in titanium dioxide pigments because of some similarity to Alon and because of their greater availability, samples of very fine particle size as shown in Table I-E-1 were examined. These fine titanium dioxide pigments were obtained from the National Lead Company and they were of the Anatase crystalline form, whereas the rutile form is that most generally used in reinforcement studies. No outstanding results are shown in Table I-E-1. It was observed that these pigments tended to react with benzoyl peroxide and prevent cure. Unfortunately, it was impossible to run preheating tests with this series of pigment because the laboratory supply was exhausted when the tests shown in Table I-E-1 had been run. Additional samples were ordered and will be reported in future reports.

F. Carbon Blacks.

It is well known that carbon black cannot be used as a reinforcing agent with silicone rubber in the presence of benzoyl peroxide. However, tertiary butyl perbenzoate has been claimed to act as a curing agent in the presence of carbon black. The preliminary results attained

TABLE I-E-1

Anatase Titanium Dioxide Pigments of Varying Particle Size¹

Sample No.	Particle Size Microns	Pigment Treatment	Pigment Wt. Loss (%)	Compd. No.	Vol. Loading	Benzoyl Peroxide(%)	Physical Properties ²			
							St. @ 200%	Tensile Strength p.s.i.	Elong. %	Hardness Shore A
MP-561-1	0.06-0.3	None		1990	20	4.0	---	107	150	38
"		Heated 15 hrs. @ 500°F.	0.64	1991			194	194	213	40
MP-561-2	0.01-0.12	None		1990-1			206	403	398	43
MP-561-3	0.01-0.06	None		1990-2				No Cure		
MP-561-1	0.06-0.3	None		1987	40	2.0	99	No Cure	750	32
"		Heated 15 hrs. @ 500°F.	0.64	1986						
MP-561-2	0.01-0.12	None		1987-1				No Cure		
"		Heated 15 hrs. @ 500°F.	1.01	1986-1				No Cure		
MP-561-3	0.01-0.06	None		1987-2				No Cure		
"		Heated 15 hrs. @ 500°F.	8.65	1986-2				No Cure		

¹ Compounded with G.E. 81176 silicone gum as indicated.² Press cure 15 min. 250°F. Oven cure 1 hr. 300°F.

TABLE I-F-1

Carbon Blacks in G.E. 81176 Cured
with 2.0% Tertiary Butyl Perbenzoate
(25 Volume Loading)

<u>Pigment</u>	<u>Compound No.</u>	Physical Properties ²		
		<u>Tensile Strength p.s.i.</u>	<u>Elongation Percent</u>	<u>Hardness Shore A</u>
Micronex W-6	1957-1	112	92	35
	Preheated ¹	119	117	35
Sterling L	1958-1	40	88	20
	Preheated	77	142	22
• Furnex	1959-1	89	463	15
	Preheated	188	458	18
Spheron 6	1960-1	168	150	41
	Preheated	159	150	43

¹ Milled pigment and gum preheated 1 hour at 300°F. before addition of perbenzoate and cure.

² Press cure 15 min. at 250°F.; oven cure 16 hours at 395°F.

in Table I-F-1 were obtained using 25 volumes of four different types of carbon black when cured with 2 percent of tertiary butyl perbenzoate. Cures were obtained but they were very weak. Micronex W-6 and Spheron 6 gave the most reinforcement. The preheating process appeared to have no effect.

Spheron 6 was selected for further study at lower and higher volume loadings and with varying percentages of tertiary butyl perbenzoate. Practically no reinforcement was observable until a volume loading of 25 percent with 4 percent of tertiary butyl perbenzoate were used. From this level increased percentages of either black or tertiary butyl perbenzoate increased the stiffness and hardness of the resulting

TABLE I-F-2

Spheron 6 Black at Varying Loadings Cured
with Tertiary Butyl Perbenzoate¹

Compd. No.	Treatment	Vols., per 100 vol.-cum.	Tertiary Butyl Perbenzoate Wt. (%)	St.%, 100%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
1995	None Preheated ³	15	1.0	---	11 20	200 200	11 11
1995-1	None Preheated	15	2.0	27 27	27 27	150 150	14 16
1995-2	None Preheated	15	3.0	32 38	53 54	200 175	18 18
1995-3	None Preheated	20	2.0	21 53	21 80	125 163	22 24
1995-4	None Preheated	20	3.0	40 27	40 27	100 100	23 20
1995-5	None Preheated	20	4.0	72 97	107 202	175 238	30 32
1995-6	None Preheated	25	2.0	82 --	96 77	150 75	34 36
1995-7	None Preheated	25	3.0	76 --	76 53	100 63	34 35
1995-8	None Preheated	25	4.0	131 178	258 191	200 150	39 46

TABLE I-F-2 (Cont.)

Spheron 6 Black at Varying Loadings Cured
with Tertiary Butyl Perbenzoate¹

Compd. No.	Treatment	Vols. per 100 vol. gum	Tertiary Butyl Perbenzoate Wt. (%)	St. @ 100%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
1995-9	None Preheated	25	5.0	168 211	298 268	225 163	44 50
1995-10	None Preheated	40	3.0	236 261	300 346	150 163	65 65
1995-11	None Preheated	40	4.0	310 312	424 350	175 138	68 68
1995-12	None Preheated	40	5.0	348 312	348 312	113 100	70 74
1995-13	None Preheated	40	6.0	304 ---	304 335	100 75	75 75
1997	Pigment heated 40 16 hrs. @ 500°F.		6.0	---	260	75	--

¹ Compounded with G.E. 81176 silicone gum as indicated.

² Press cure 15 min. @ 250°F. Oven cure 16 hrs. @ 400°F.

³ Milled pigment and gum preheated 1 hr. @ 300°F. before addition of peroxide and cure.

compounds. The best results were obtained with 40 volumes of Spheron 6 and 4 percent of tertiary butyl perbenzoate. However, tests as good as these are readily obtainable with several mineral fillers, and it appears to be true that carbon black is not a good reinforcing pigment for silicone rubber.

G. Coated Pigments.

The next six tables are concerned with modification of the surface characteristics of pigments by coating with silicone oils, silanols, alcohols and hydrocarbons. It should be pointed out at this time that no outstanding results from this investigation have been obtained, although it will be seen that moderate improvement in some of the physical properties has been accomplished in some cases.

Table I-G-1 shows what happens when a low volume loading of pigment, Celite 800 in this case, is coated with silicone oil and then used in 81176 silicone rubber. The silicone oils were deposited on the pigment from carbon tetrachloride solution and the carbon tetrachloride removed by drying in an oven. In Samples S-131, S-132, S-134 and S-135 no correction for the consumption of benzoyl peroxide by the coating itself was applied because the extra benzoyl peroxide that would be needed was a negligible amount. Where 100 percent of coating was applied to the surface of the pigment, additional benzoyl peroxide was included in the recipe. Allowance also was made for the increased weight of the pigment due to the coating on it. Thus a larger amount of coated pigment was incorporated in S-133 than in S-130, for example. There seems to be a stronger bond between pigment and rubber with Sample S-132 when 10 percent of a silicone oil was deposited on Celite 800, as may be seen from the physical tests in Table I-G-1. The oil

TABLE I-G-1

Celite 800 Coated with Silicone Oils¹
(25.0 Volumes, 2.0% Benzoyl Peroxide)

Sample No.	Coating	Coating Wt. (%)	Compd. No.	St. @ 200%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
--	None	--	1912-1	---	138	158	46
S-130	CCl ₄ only	--	2051	---	52	50	35
S-131	G.E. 9981LT-4	1	2051-1	---	83	75	40
S-132	"	10	2051-2	290	295	213	42
S-133	"	100	2051-3	172	172	213	35
S-134	NH ₃ Oil	1	2051-4	---	99	113	43
S-135	"	10	2051-5	---	71	100	35
S-136	"	100	2051-6	179	248	313	--

¹ Compounded with G.E. 81176 silicone gum.

² Press cure 15 min. 230°F. Oven Cure 1 hr. 300°F.

used in this case was a stabilized silicone oil which is commercially available.

The ammonia-stabilized oil in the lower portion of Table I-G-1 was prepared by depolymerizing General Electric 9979-G gum followed by neutralizing with ammonia. It is known to repolymerize in the presence of benzoyl peroxide. Here again, it appears that a stronger bond has formed between the pigment and the rubber when a coating of ammonia-stabilized oil was present on the Celite 800. It was felt that these promising results indicated further study.

In Table I-G-2 Santocel C, which is a better reinforcing agent than Celite 800, was also coated with silicone oils using 20 and 30 volumes of pigment which gives better physical properties to start with. Necessary adjustment in benzoyl peroxide concentration due to the presence of silicone oils was made and the necessary reduction in volume of rubber was made when high volumes of silicone oils were present. Samples S-139 and S-140 containing 10 and 100 percent of silicone oil on the surface of Santocel C resulted in a stronger bond between pigment and rubber as shown in the higher elongation figures which in turn resulted in higher tensile figures in these two compounds. It cannot be said that greater reinforcement resulted since the hardness is reduced as is the stress at 200 percent. As pointed out previously, sufficient benzoyl peroxide was present to vulcanize the silicone oil as well as the rubber. It is inferred that the high degree of porosity of Santocel C and the low viscosity of the oil applied has given rise to a more rubbery bond between pigment and 81176 rubber.

TABLE I-G-2

Santocel "C" Coated with Silicone Cils¹
(20 and 30 volumes, 2.0% Benzoyl Peroxide)

Sample No.	Coating	Coating Wt. (%)	Compd. No.	Vol. Loading	St. 200%	Physical Properties ²		
						Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
---	None ³	---	1962-3	20	475	669	289	72
S-137	CCl ₄ only	---	2052		635	635	200	70
S-138	G.E. 9981LT-4	1	2052-1		---	398	163	65
S-139	"	10	2052-2		498	703	300	65
S-140	"	100	2052-3		319	1025	500	60
S-141	NH ₃ Oil	1	2052-4		468	612	263	68
S-142	"	10	2052-5		718	1000	275	65
S-143	"	100	2052-6		---	740	100	85
S-140	G.E. 9981LT-4	100	2072-1	30	177	804	638	61
S-142	NH ₃ Oil	10	2072		600	925	325	84

¹ Compounded with G.E. 81176 silicone gum.

² Press cure 15 min. 230°F. except in the case of 1962-3 where the cure was 15 min. at 250°F. Oven cure 1 hour at 300°F. except in the case of 2072 and 2072-1 where the cure was 24 hours at 400°F.

³ Control pigment dried at 500°F.

With the ammonia-stabilized oil a similar result was obtained on Sample S-143, except that in this case the coating appears to have polymerized or hardened strongly so that there is no increase in elongation, and the stress at 200 has been increased. With 30 volumes of pigment and 100 percent coating of General Electric silicone oil, it appears that the maximum concentration of pigment has been exceeded since the results are not as good as those obtained at 20 volumes. It is interesting to note that 30 volumes of Santocel C cannot be used in the absence of the coating without producing a batch which is too dry to mold.

With 30 volumes of pigment and 10 percent of ammonia-stabilized oil as a coating, the results were not greatly different from those obtained with 20 volumes of pigment except for a slightly increased hardness.

In Table I-G-3 tests are reported on Titanox R.A.N.C. coated with the same two silicone oils. The optimum concentration of Titanox R.A.N.C. is 40 volumes of pigment per 100 of rubber. Due to its smooth surface Titanox R.A.N.C. does not readily absorb as much oil as Santocel C so that the range of coatings applied is lower. Suitable corrections in the amount of benzoyl peroxide and the ratio of rubber to pigment were applied in this work as in the work reported in the two previous tables. Possibly due also to the lack of porosity of Titanox R.A.N.C., the addition of the coating on the pigment appeared to have less effect. The only exception to this is a slight improvement in tensile strength observed when a very light coating of ammonia-stabilized oil (Sample S-148) was applied. Even this result could not be confirmed at the 60

TABLE I-G-3
Titanox RANC Coated with Silicone Oils¹
(40 and 60 Volumes, 2.0% Benzoyl Peroxide)

Sample No.	Coating	Coating wt. (%)	Compd. No.	Vol. Loading	St. @ 200%	Physical Properties ²		
						Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
--	None ³	--	1982-1	40	545	611	250	55
S-1144	CCl ₄ only	--	2053		316	331	250	48
S-1145	G.E. 9981LT-4	0.3	2053-1		507	650	275	50
S-1146	"	3	2053-2		---	447	175	50
S-1147	"	30	2053-3		196	336	338	33
S-1148	NH ₃ Oil	0.3	2053-4		565	710	263	53
S-1149	"	3	2053-5		177	191	225	30
S-1150	"	30	2053-6		---	216	100	45
S-1145	G.E. 9981LT-4	0.3	2073-1	60	301	463	288	59
S-1148	NH ₃ Oil	0.3	2073		---	426	138	67

¹ Compounded with G.E. 81176 silicone gum.

² Press cure 15 min. 230°F. except in the case of 1982-1 where the cure was 15 min. at 250°F. Oven cure 6 hrs. at 300°F.

³ Pigment dried at 500°F.

volume loading. Any advantage using silicone oils as coatings for the silica-type pigments such as Santocel C does not appear to carry through to titanium dioxide.

Silicone oil coatings were also applied to Spheron 6, the carbon black which had been selected as the best for study in silicone rubber compounding. No beneficial effect was observed either with General Electric silicone oil or with the ammonia-stabilized gum. As a matter of fact, a 30 percent coating of the oil inhibited cure completely even though the curing agent used was tertiary butyl perbenzoate which is the most satisfactory curing agent for use in the presence of carbon black. The results are shown in Table I-G-4.

The Linde Corporation has proposed the use of monoalkyltrichlorosilanes as coating materials for pigments. Following addition of these silanes to the surface of a pigment, it is exposed to water vapor thus hydrolyzing the chlorine groups. Upon heating, it is supposed that the silanols thus formed condense to make a siloxane coating on the surface of the pigment. We have applied methyl, dimethyl and vinyltrichlorosilanes to the surface of Santocel C, Celite 800, Titanox R.A.N.C. and Spheron 6. The range of gains in weight of the pigments due to the deposition of siloxanes on the surface was 0.1 to 8.0 percent by weight. Where it was possible to record the exact gain in weight, these data are tabulated below for the following sample numbers:

<u>Sample No.</u>	<u>Pigments Coated with Silanes</u>		<u>Percent Wt. Gain After Treatment</u>
	<u>Pigment</u>		
S-120	Santocel C		4.2
S-121	Celite 800		8.0
S-122	Titanox R.A.N.C.		0.1
S-123	Spheron 6		---

Data on these experiments are given in Table I-G-5.

TABLE I-G-4

Spheron 6 Coated with Silicone Oils¹
(25 Volumes, 4.0% Tertiary Butyl Perbenzoate)

Sample No.	Coating	Coating Wt. (%)	Compd. No.	St. 200%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
--	None	--	1995-8	258	258	200	39
S-151	CCl ₄ only	--	2056	240	270	250	42
S-152	G.E. 9981LT-4	1	2056-1	259	304	275	40
S-153	"	10	2056-2	207	219	238	42
S-154	"	100	2056-3		No cure		
S-155	NH ₃ Oil	1	2056-4	230	274	263	40
S-156	"	10	2056-5	139	145	213	33
S-157	"	100	2056-6		No cure		

¹ Compounded with G.E. 81176 silicone gum.

² Press cure 15 min. 230°F, except in the case of 1995-8 where the cure was 15 min. at 250°F. Oven cure 16 hrs. at 400°F.

TABLE I-3-5

Pigments Coated with Silanes ¹							
Sample No.	Silane Coating	Compd. No.	Recipe	St. @ 200%	Physical Properties ²		Hardness Shore A
					Tensile Strength p.s.i.	Elongation Percent	
<u>SANTOCCEL C</u>							
S-120	None	1962-2					
	Vinyltrichloro (CHR)	2000*	15 Vol.	390	862	342	50
S-160	"	2075	2.0% B.P.	464	499	275	75
	"	2075-1		309	548	325	42
S-161	(Linde)	2082		113	281	313	44
S-164	(CHR)	2081		235	360	363	55
	Methyltrichloro (CHR)	2083		398	723	325	50
	Dimethyldichloro (CHR)			387	720	325	47
<u>CELITE 800</u>							
	None	1962-3	20 Vol.	481	937	308	61
	Vinyltrichloro (CHR)	2075-2	2.0% B.P.	---	234	125	68
	"	2075-3		---	295	125	65
<u>TITANOX RANG</u>							
S-121	None	1912-1		---	188	158	46
	Vinyltrichloro (CHR)	2044	25 vols. 2.0% B.P.		No Cure		
S-122	None	1857		292	530	325	45
	Vinyltrichloro (CHR)	2047	40 Vols. 2.0% B.P.	269	395	263	44

TABLE I-G-5

Pigments Coated with Silanes¹

Sample No.	Silane Coating	Compd. No.	Recipe	St. @ 200%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
<u>SPHERON 6</u>							
S-123	None	1995-9		258	258	200	39
	Vinyltrichloro (CHR)	2058-1	25 Vols.. 4.0% T.B.P.B.	400	400	200	67
S-123	"	(CHR)	4.0% B.P.		No Cure		
S-123	None	1995-11	40 Vols.	---	424	175	68
	Vinyltrichloro (CHR)	2058-2	4.0% T.B.P.B.	---	339	100	73

¹ Compounded with G.F. 81176 silicone gum at indicated volume loading and cured with either benzoyl peroxide (b.p.) or tertiary butyl perbenzoate (T.B.P.B.).

² Press cure 15 min. 250°F. except in the case of compounds 2081, 2082 and 2083 where the cure was 15 min. at 230°F. Oven cure 1 hour at 300°F. except Spheron 6 and tertiary butyl perbenzoate, 16 hours at 400°F.

* Compounded with 20 volumes of pigment.

In some cases, vinyl coatings were deposited on Mantocel C by the Linde Corporation through arrangements made by Dr. Juan Montermoso.

No outstanding improvement in reinforcement was obtained in any of this work. With Sample S-120 the coating applied by us produced increased hardness as compared to the control, but this result was not duplicated on a second test nor was it duplicated when the coating was applied by the Linde Corporation. Very little difference was observed whether methyltrichlorosilane or dimethyldichlorosilane was used.

When Spheron 6 was used at 20 volumes or at 40 volumes loading, the addition of a vinyl siloxane coating showed definite improvement in the reinforcement as judged by the higher stress and hardness figures, with low elongations. Even though the carbon black was masked by the coating, it was still impossible to cure with benzoyl peroxide. Should time permit, it would be interesting to pursue further the possibility of using carbon black as a reinforcing pigment after treatment with vinyltrichlorosilane and water.

II. REINFORCEMENT OF SILICONE RUBBER WITH DUPONT GS199S SILICA.

DuPont GS199S Silica in General Electric SE-76.

Late in the year 1951, there came to the attention of Dr. C. M. Doede, Connecticut Hard Rubber Company, one of the most finely-divided pigments ever proposed for the reinforcement of rubber compounds. This pigment is known commercially as DuPont GS199S Silica. It has already been extensively evaluated by the DuPont Company as an inorganic thickening agent for oils to make lubricating greases. The structure of the pigment has not yet been revealed. The product information sheet put out by Grasselli Chemical Department, E. I. duPont de Nemours Company, states that GS199S Silica has the following properties:

1. Extremely small ultimate particle size.
2. High specific surface area.
3. Pronounced hydrophobic and organophilic properties.
4. Ease of dispersion in organic systems using conventional milling procedures.
5. Low bulk density.

Other obvious characteristics may be listed:

6. An organic constituent to the extent of approximately 10 percent which is removable by heating at 480°F.
7. A pronounced capacity for taking up static charges.

Other properties disclosed by DuPont include the following:

- | | |
|--|--------------------------------|
| 1. Surface area by nitrogen absorption | 250-300m ² /g. |
| 2. Bulk density | 7 lb./ft. ³ average |

3. SiO_2	84-88%
4. pH in 50-50 methanol-water mixture	7.5-9.5
4. Physical form of silica	Amorphous

It is also revealed that the pigment is chemically stable at ordinary temperatures except in the presence of alkalies and hydrogen fluoride. It is subject to attack by oxygen above 220°F. with loss of its hydrophobic properties.

It is also revealed that GS199S Silica has a strong reinforcing effect in natural rubber and in standard CR-S, Cold CR-S and Neoprene GN. Data supplied by the DuPont Company are given in Appendix I.

Dr. C. M. Doede has long held the view that outstanding reinforcement of silicone or other rubbers would result with the preparation of pigments with particle diameters of 100 Å or smaller solely on the basis that such particles begin to be of the same order of magnitude as the molecules of rubber. The arrival of DuPont GS199S Silica made it possible to test this idea in silicone rubber.

The pigment was first tested in 5, 10, 15 and 20 volume loadings shown in Table II-A-1. These results showed nothing very unusual except that it was noticed that unusually high elongations were being obtained with a silica-type pigment. Hence, it was decided to go to higher volume loadings of 25, 30 and 40 percent. In this second part of the experiment astonishingly high tensile strengths were found. Repeat tests on the low volume loadings at a later date indicate that there may have been some error in the mixing of the 5, 10, 15 and 20 volume loadings reported in Table II-A-1 since the later tests gave better physical tests (see, for example, Tables II-A-2, II-A-3 and

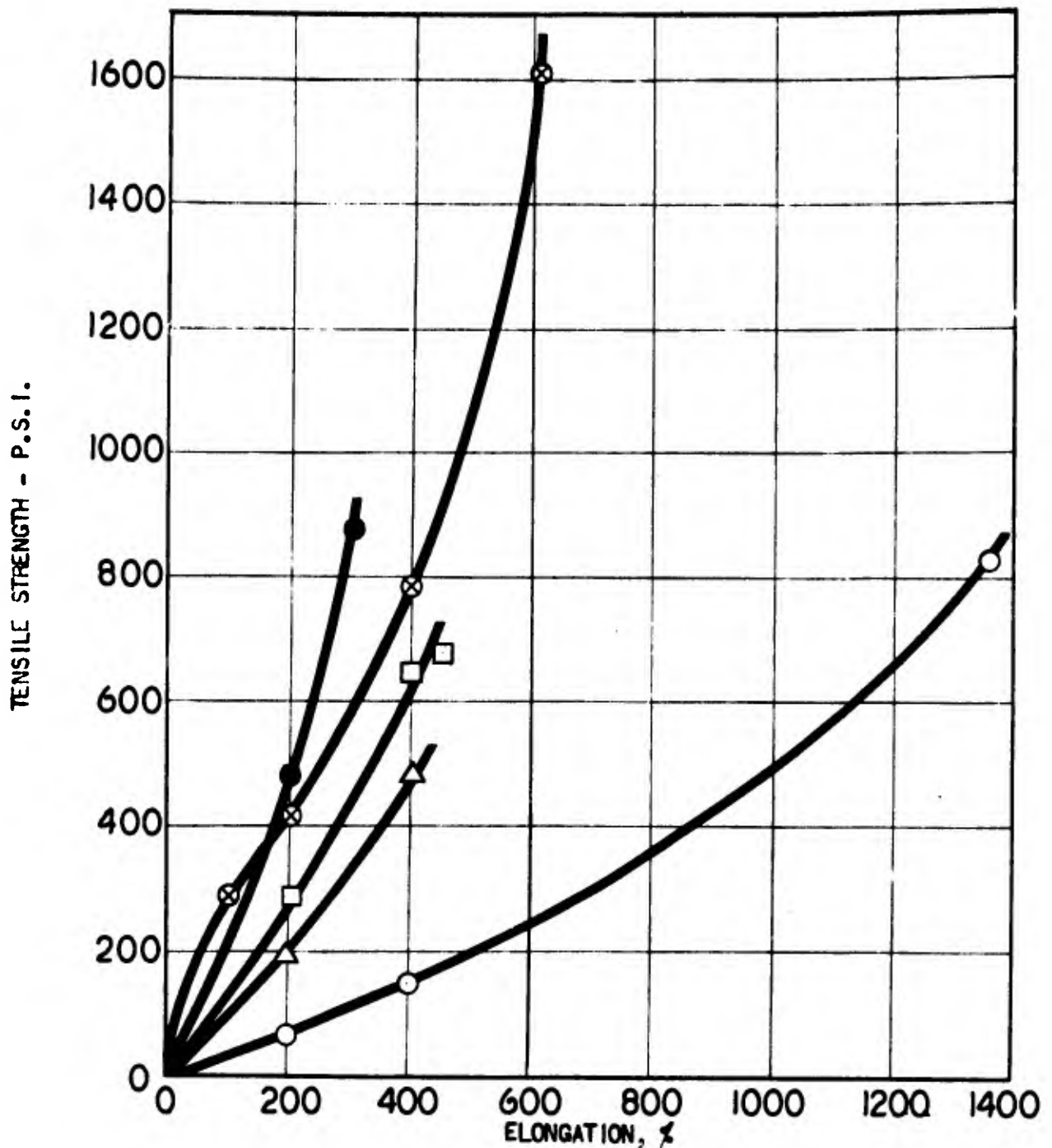
TABLE II-A-1

RL-1 Silica at Varying Loading¹

Compd. No.	Vol. Pigment per 100 gum	St. @ 200%	Physical Properties ²		
			Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
1967	5	56	111	400	19
	Preheated	53	64	300	19
1967-1	10	85	226	475	23
	Preheated	104	195	338	25
1967-2	15	172	289	375	37
	Preheated	171	247	300	40
1967-3	20	203	591	563	43
	Preheated	248	321	275	43
1967-4	25	335	1285	625	70
	Preheated	379	1400	563	70
1967-5	30	485	1365	525	80
	Preheated	361	1096	500	70
1967-6	40		Too much pigment. n		
	Preheated				

¹ Compounded with G.E. 81176 silicone gum with 2.0% benzoyl peroxide.² Press cure 15 min. @250°F. Oven cure 1 hr. @300°F.³ Milled pigment and gum preheated 1 hr. @300°F. before addition of peroxide and cure.

FIG. II-A-1



STRESS-STRAIN CURVES
VARIOUS PIGMENTS IN 81176 GUM, 2.0 PERCENT B.P.

- 15 VOLUMES OF ALON
- △ 40 VOLUMES OF TITANOX RANC
- 40 VOLUMES OF TITANOX RANC, HEATED
- ⊗ 25 VOLUMES OF RL-1
- 20 VOLUMES OF SANTOCEL-C

PRESS CURE: 15 MIN @ 250° F
OVEN CURE: 1 HOUR @ 300° F

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA-44-109 -QM-64

II-A-5). It is surmized that the mill operator failed to secure adequate dispersion of the benzoyl peroxide and thus failed to get a sufficient degree of cure in the earlier tests.

Throughout the rest of this report, the DuPont GS199S Silica is referred to as RL-1 Silica, this being the number placed upon it in our laboratory. The observation on Compound 1967 that there was too much pigment present to allow a slab to be formed is no longer considered correct. Later tests have shown that it is possible to incorporate 52.5 volumes of RL-1 Silica in 100 volumes of gum. This is close to the limit, however. With 52.5 volumes of silica, it appears that the pigment has used up all of the available rubber on the surface and there is none left over to allow a slab of the compound to mold during the cure.

The values obtained for tensile strength and elongation on the 25 and 30 volume recipes are obviously outstanding as compared with any heretofore found and reported with any other pigment when used in General Electric SE-76 (81176) rubber. It is interesting to note that the preheating treatment discovered earlier in this report and in Report No. 9 appears to be of no value here. It is concluded that the RL-1 pigment is thoroughly wetted by the silicone rubber. In Figure II-A-1 stress strain curves are shown for a typical RL-1 compound, together with cures for the best compounds available with three other good pigments.

Table II-A-1 gives representative results obtained with 20 and 25 volumes of RL-1 Silica with a 1-hour cure at 300°F. Data shown in Table II-A-2 illustrate the effect of further curing at 300°F. and at higher temperatures. It will be seen that the longer cures tend to

TABLE II-A-2

RL-1 Silica with Varying Cures¹

Compd. No.	Benzoyl Peroxide Wt. (%)	Vol. Pigment per 100 Vol. Gum	Oven Cure	St., % 200%	Physical Properties ²		
					Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A
1967-2	2.0	15	24 hrs. @ 300°F.	573	782	313	69
			24 hrs. @ 300°F.	---	653	175	73
			15 hrs. @ 350°F.				
			24 hrs. @ 400°F.	675	650	188	73
1967-3	2.0	20	24 hrs. @ 300°F.	520	987	425	75
			24 hrs. @ 300°F.	730	1056	350	80
			15 hrs. @ 350°F.				
			24 hrs. @ 400°F.	---	589	75	84
1985	2.0	25	24 hrs. @ 300°F.	219	1415	800	65
			24 hrs. @ 300°F.	392	1160	600	73
			15 hrs. @ 350°F.				
			24 hrs. @ 400°F.	700	1035	350	82 ³
1985-1	1.7	25	24 hrs. @ 300°F.	285	1635	783	72
			24 hrs. @ 300°F.	539	1395	550	80
			15 hrs. @ 350°F.				
			24 hrs. @ 400°F.	---	731	88	93

¹ Compounded with G.E. 81176 silicone gum at indicated loadings and peroxide concentration.² Press cure 15 min. @ 250°F., oven cures as indicated.³ The data here show that under certain conditions the RL-1 Silica stock will stand high temperature curing.

result in increased hardnesses, lower elongations and higher tensile strengths up to a maximum beyond which the compounds begin to stiffen sufficiently so that the tensile strength falls off. This is particularly noticeable with higher volume loadings. It may be seen here that several cures at 400°F. have resulted in elongations less than 100 percent. These compounds were definitely brittle. In one case, however, the compound withstood curing for 24 hours at 400°F. without becoming brittle.

In Table II-A-3 the effect of adjustment of the benzoyl peroxide concentration was investigated. There was a slight reduction in the excessive stiffening effect, noted in the previous table, when lower concentrations of curing agent were used. This table shows also the advantage of high temperature curing to develop low compression set. The 400°F. cure in one case gives a compression set almost 50 percent lower than the 300°F. cure. There appears to be a definite advantage in using the lower concentrations of benzoyl peroxide from the standpoint of compression set. Similar data to those shown in Table II-A-3 were obtained and are reported in Table II-A-4 with 25 volume loading of RL-1 Silica. At this loading maximum reinforcement as judged by the combination of elongation and tensile strength is reached. The 1930 pound tensile strength figure is the best that we have ever recorded on silicone rubber. Again we note the effect of long cures at high temperatures in reducing elongation almost to the brittle point, and again we notice the improvement with long high-temperature curing in compression set.

Table II-A-5 shows the results obtained on 15 and 25 volume loadings

TABLE II-A-3
15 Vols. RL-1 Silica with Varying Benzoyl Peroxide and Cures¹

Compd. No.	Benzoyl Peroxide wt. (%)	Oven Cure	St. @ 200%	Physical Properties ²			Hardness Shore A	Comp. Set (%) ³
				Tensile Strength p.s.i.	Elongation Percent			
2050-1	1.0	24 hrs. @ 300°F.	374	840	175		63	85.5
		24 hrs. @ 400°F.	630	710	275		70	44.9
2050-2	1.5	24 hrs. @ 300°F.	437	960	100		65	83.0
		24 hrs. @ 400°F.	720	370	275		73	52.5
1967-2	2.0	24 hrs. @ 300°F.	597	975	350		68	83.1
		24 hrs. @ 400°F.	755	795	200		76	61.5

¹ Compounded with G.E. 81176 silicone gum at 15 vol. loading and indicated concentration of peroxide.

² Press cure 15 min. @ 250°F. Oven cures as indicated.

³ Compression set according to A.S.T.M. D-395-49T (Method B) 22 hrs. @ 300°F.

TABLE II-A-4

25 Volumes of PL-1 Silica with Varying¹
Benzoyl Peroxide and Cures

Benzoyl Peroxide and Cures								
Compd. No.	Benzoyl Peroxide Wt. (%)	Oven Cure	St. @ 200%	Physical Properties ²				Comp. Set (%) ³
				Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A		
1996	1.0	1 hr. @ 300°F.	276	1930	850	73		96.7
		24 hrs. @ 300°F.	554	1660	550	83		86.5
		24 hrs. @ 400°F.	---	795	63	93		42.1
1996-1	1.5	1 hr. @ 300°F.	308	1680	700	75		93.5
		24 hrs. @ 300°F.	610	1325	463	85		83.5
		24 hrs. @ 400°F.	---	795	75	94		43.3
1985	2.0	1 hr. @ 300°F.	419	1615	613	77		94.5
		24 hrs. @ 300°F.	684	1170	388	85		84.8
		24 hrs. @ 400°F.	---	795	75	93		49.0

¹ Compounded with C.F. 81176 silicone gum at 25 vol. loading and indicated concentration of peroxide.

² Press cure 15 min. @ 250°F. Oven cures as indicated.

³ Compression set according to A.S.T.M. D-395-49T (Method E) 22 hrs. @ 300°F.

TABLE II-A-5

Comparison of Three Batches of RL-1 Pigment¹

Compd. No.	Vol. Loading	Benzoyl Peroxide Percent	St. @ 200%	Physical Properties ²			Date
				Tensile Strength p.s.i.	Elong. %	Hardness Shore A	
<u>1st Shipment</u>							
1967-2	15	2.0	172	289	375	37	10/4/51
1985	25	2.0	419	1615	613	77	11/13/51
<u>2nd Shipment</u>							
1967-2	15	2.0	346	1008	525	61	12/5/51
1985	25	2.0	410	1670	625	80	12/19/51
<u>3rd Shipment</u>							
1967-2	15	2.0	242	1170	613	61	1/23/52
1985	25	2.0	320	1687	663	70	

¹ Compounded with G.E. 81176 silicone gum.

² Press cure for 1st and 2nd shipments was 15 min. at 250°F. and 15 min. at 230°F. for the 3rd shipment. Oven cure 1 hr. at 300°F.

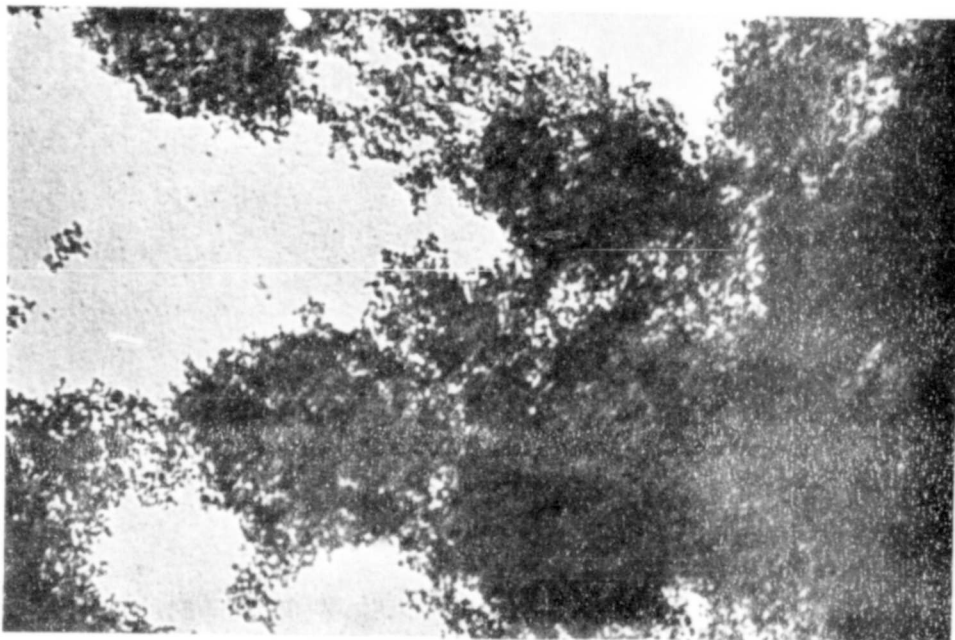
with 2 percent benzoyl peroxide on individual samples or shipments of the RL-1 Silica pigment. The first test shown in the table has been taken from Table II-A-1 and is a low test as pointed out on page 43. With this exception, the three shipments appear more uniform although the third shipment appears to have slightly less stiffening effect than the first two. This is felt to be an advantage and indicates that it is possible that the DuPont Company can adjust the properties obtainable from RL-1 Silica by changes in the method of manufacture. The third shipment, incidentally, was 100 pounds.

At the date of writing considerably more information has been obtained regarding compounding of silicone rubber with RL-1 Silica.

This will be reported in the next Quarterly Report. The results that have been presented herein are sufficiently outstanding to excite the imagination of compounders who have been accustomed to silicone rubber compounds having only 300 to 500 pounds tensile strength and 100 to 200 percent elongation. The often-expressed hope or conviction that silicone rubber compounding would eventually come of age with compounds showing physical properties at least comparable to those of some of the other special-purpose rubbers has now been realized. Compounding work to further develop the use of RL-1 Silica in silicone rubber is being emphasized under this contract. We are working closely with the Market Development Section of the Grasselli Chemical Department to improve properties obtainable, try out pilot plant samples and encourage them to put this pigment into production as rapidly as possible. End items where stronger silicone stocks are needed are being compounded and the effect of the better silicone compounds evaluated in laboratory tests.

Electron microscope pictures of RL-1 Silica in the 81176 polymer are shown on the following pages. These reveal the excellent dispersion of the ultimate particles of silica in the rubber but do not permit any conclusions as to why the superior physical tests are obtained. Insufficient data are available to relate particle size to reinforcement. We hope to be able to secure a range of sizes of DuPont 68199S Silica in order to carry out such a comparison.

ELECTRON MICROGRAPH OF GS-199S SILICA PIGMENT



34,000 X

Electron micrographs of GS-199S Silica pigment alone. Pigment
spark-dispersed on collodion membrane, shadowed with palladium.
Photographed with R.C.A. Model E.M.U. electron microscope, courtesy
of Yale University.

Micrograph shows 0.5 - 2.0 micron agglomerates of silica particles,
whose ultimate size appears to be 0.005 - 0.015 microns (50 - 150 Å).
This is in line with information received from the DuPont Company, which
claims particle sizes of 80 - 100 Å.

ELECTRON MICROGRAPH OF GS-199S SILICA
IN SE-76 SILICONE GUM



21,600 X

Electron micrograph of GS-199S Silica in SE-76 Silicone gum, 15 volume loading with 1 hour at 300°F. oven cure. This is a micrograph of a 100 Å thick microtome section of the cured rubber slab, prepared by sectioning a portion of the slab which had been embedded in butyl methacrylate polymer. The polymer was removed from the mounted section, and it was shadowed with palladium. Photographed with R.C.A. Model E.M.U. electron microscope, courtesy of Yale University.

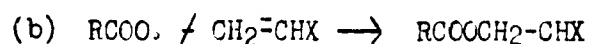
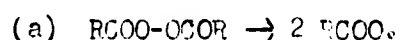
Micrograph shows an edge of the section on a collodion background. Extremely good dispersion is observed, with pigment agglomerates appearing to be of the order of 0.05 - 0.10 microns (500 - 1000 Å) only.

III. VULCANIZATION STUDIES.

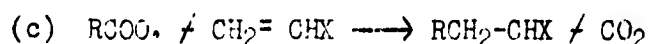
A. Mechanism of Vulcanization.

1. Introduction.

It has been reported by many authors after extensive research that dibenzoyl peroxide is one of the best general purpose sources of free radicals for initiating polymerization or vulcanization of various types of hydrocarbon rubbers. Hey and Waters¹ proposed the following mechanism by which dibenzoyl peroxide initiates the polymerization reaction in the case of vinyl monomers:



or



Bartlett and Cohen² corroborated the above-mentioned mechanism by finding benzoate fragments attached to the terminal groups of styrene which was polymerized by means of p-chlorodibenzoyl peroxide.

Dibenzoyl peroxide decomposes slowly at moderate temperatures³ with elimination of carbon dioxide to yield both free aryl radicals and free carboxylate groups, the latter capable of further similar decomposition. This decomposition into radicals (potential oxidation chain centers) provides a ready explanation of the autocatalysis observed in chain reactions.⁴

1) Hey and Waters, Chem. Rev. 21, 169 (1937)

2) Bartlett and Cohen, J.A.C.S. 65, 543 (1943)

3) Waters, "The Chemistry of Free Radicals," pg. 165-169, The Clarendon Press, Oxford (1948)

4) George and Walsh, Trans. Faraday Soc. 42, 94 (1946)

Dibenzoyl peroxide reacts readily with unsaturated rubbers at temperatures above 100°C.⁵ It decomposes thermally to give Ph and Ph-CO-O. radicals and these are able to attack an organic substance RH with formation of new compounds and new free radicals:

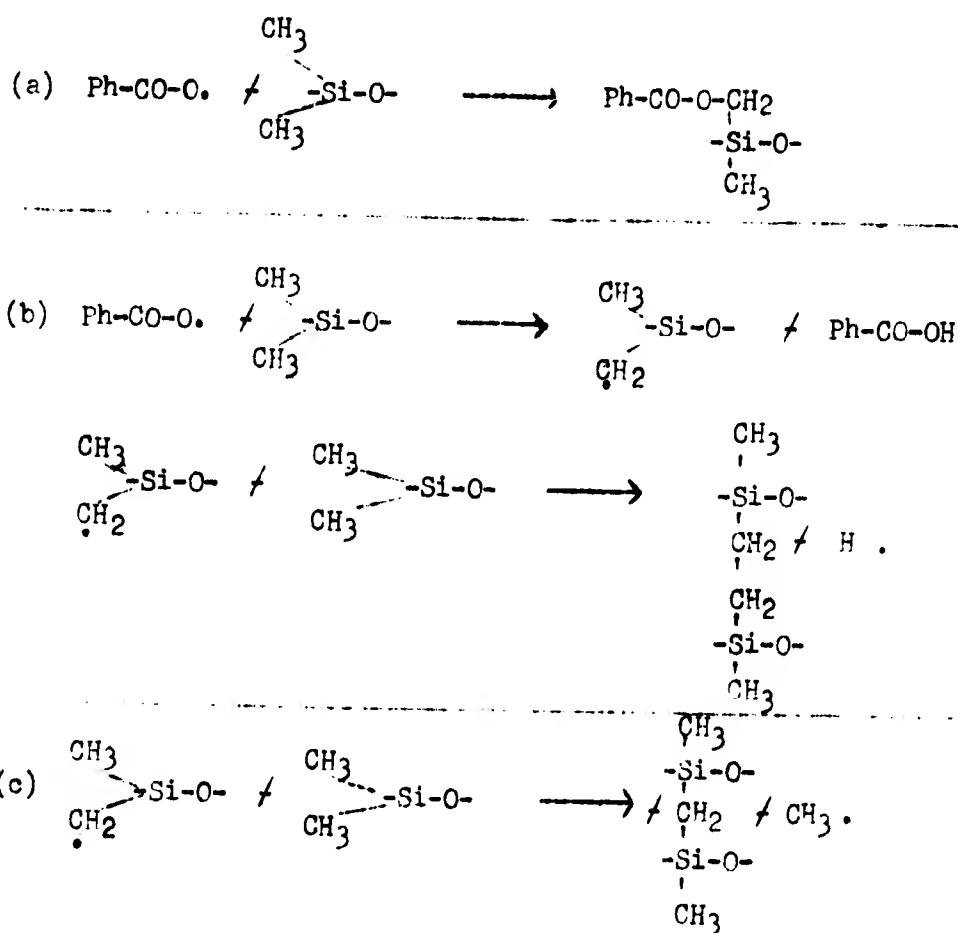
- (a) $\text{Ph} \cdot \nearrow \text{RH} \rightarrow \text{PhR} \nearrow \text{H} \cdot$
- (b) $\text{Ph} \cdot \nearrow \text{RH} \rightarrow \text{PhH} \nearrow \text{R} \cdot$
- (c) $\text{Ph-CO-O} \cdot \nearrow \text{RH} \rightarrow \text{Ph-CO-CR} \nearrow \text{H} \cdot$
- (d) $\text{Ph-CO-O} \cdot \nearrow \text{RH} \rightarrow \text{Ph-COOH} \nearrow \text{R} \cdot$
- (e) $\text{R} \cdot \nearrow \text{RH} \rightarrow \text{R-R} \nearrow \text{H} \cdot, \text{etc.}, \text{etc.}$

The new free radicals are available for further attack on the molecules present or, if their concentration permits, for intercombination. If reactant RH is present in very large excess the intercombination of free radicals must mainly give place to their attack on RH; therefore, potentially at any rate, the action of decomposing dibenzoyl peroxide is two-fold, comprising a substitution agency (reactions a and b) and a molecule linking or polymerization agency (reaction e). The vulcanization reaction of silicone rubber with dibenzoyl peroxide is likely to be a combination of cross-linking and substitution on the rubber chain as distinct from cross-linking and double bond addition as in sulfur vulcanization.

Although a very large amount of research has been directed toward the solution of the problem concerning the mechanism of polymerization and vulcanization of unsaturated rubbers by means of peroxides, little or nothing has thus far appeared in the chemical literature in regard to the polymerization and vulcanization mechanism of silicone gums

5) Farmer and Michael, J. Chem. Soc. 513, (1942)

catalyzed by peroxides. From the evidence obtained by Farmer⁶ that the cross-linking taking place during the curing of hydrocarbon rubbers seems to be due to an attack by the peroxidic free radicals principally at the α -methylene groups, the following scheme can be written in the attempt to interpret the vulcanization mechanism of a silicone polymer by means of dibenzoyl peroxide:



The object of the present research, of which this is a preliminary report, is to determine the mechanism through which dibenzoyl peroxide effects a cure of a silicone gum in solution and, finally, to establish a simple method along the same lines for evaluating various oxidants as to their curing properties for silicone gums.

6) Farmer et al., Trans. Faraday Soc. 38, 340, 348, 356 (1942)

2. Experimental Part.

The silicone gum used throughout the series of experiments was General Electric SE-76 which was soluble in n-heptane. The apparatus for the titration and viscosity measurements was a 500 cc. three-necked flask equipped with reflux condenser, glass-monel Hershberg stirrer and a cylindrical glass chamber for viscosity measurements. The latter were taken by means of calibrated 1 cc. pipettes which were brought to the temperature of the solution by insertion into the glass chamber within the flask. The peroxide titrations were run according to the standard sodium thiosulfate-potassium iodide method, and the acid titrations were made with standard sodium hydroxide solution, with phenolphthalein as indicator. All the samples to be titrated were first dissolved in isopropyl alcohol to make them water miscible. The temperature of the solution, measured at short time intervals, was constant enough (99°C.) to warrant reproducibility of the experiments, although a certain difference (1-2°C.) was observed between the temperatures of the solution containing peroxide and solvent alone and those containing solvent, peroxide and gum, the latter being somewhat lower.

Description of Graph Notations:

- ⊙ Benzoic acid (B.A.) in solution at time t, percent of theoretical yield based on dibenzoyl peroxide (B.P.) originally present.
- Dibenzoyl peroxide (B.P.) in solution at time t, percent of total originally present.
- ⊗ Percent of B.P. plus B.A. not titrated at time t.
- ▣ Relative viscosity of solution at time t, a measure of degree of vulcanization of silicone polymer.

The curves shown in Figure III-A-1 are the average of three control runs and two runs in the two experiments when gum was present.

Experiment I.

Data: 1 g. of dibenzoyl peroxide in 200 cc. of n-heptane.

Object: To follow the decomposition of dibenzoyl peroxide in n-heptane with no gum present.

Results: From Figure III-A-1 it is apparent that the percent of benzoic acid isolated gradually increased up to 18 percent. Then it leveled off, while the peroxide decreased continually. By a comparison of these two curves, it is seen that the amount of peroxide converted to acid is much less than the amount of peroxide decomposed. The amount of peroxide not accounted for as acid increased steadily with time. Complete decomposition was not reached within the reaction period.

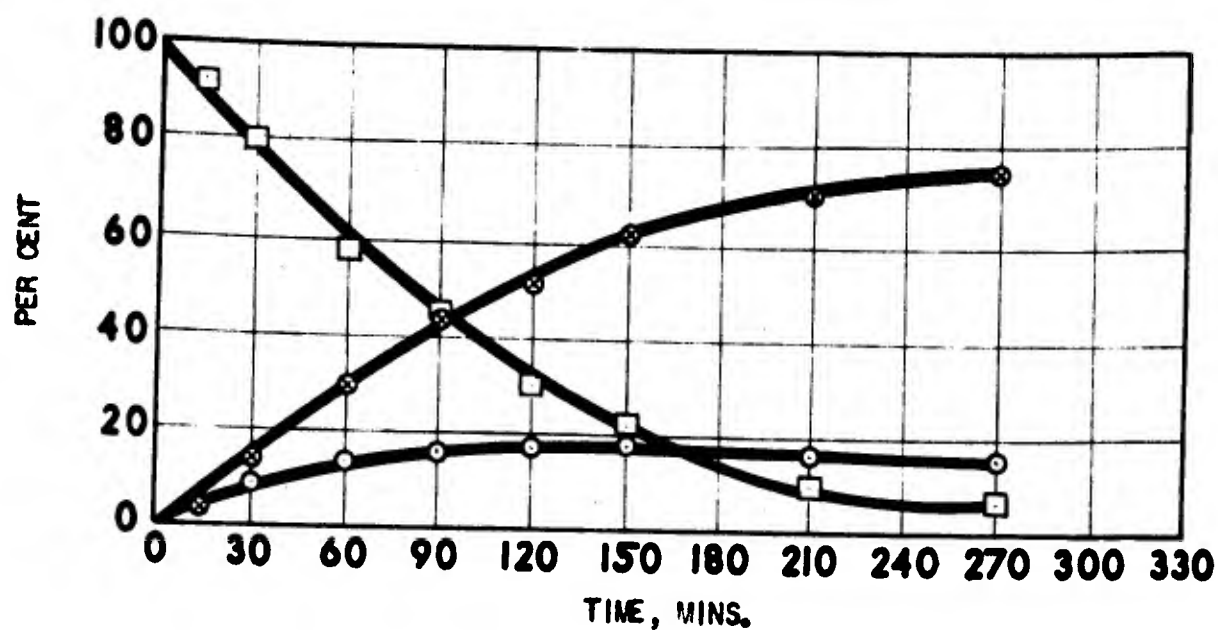
Experiment II.

Data: 1 g. of dibenzoyl peroxide, 20 g. of gum, 220 cc. of n-heptane.

Object: To follow the rate of decomposition of dibenzoyl peroxide (5 percent by weight of gum) in n-heptane in the presence of gum, and to investigate the rate of vulcanization of polymer through measurements of solution viscosity.

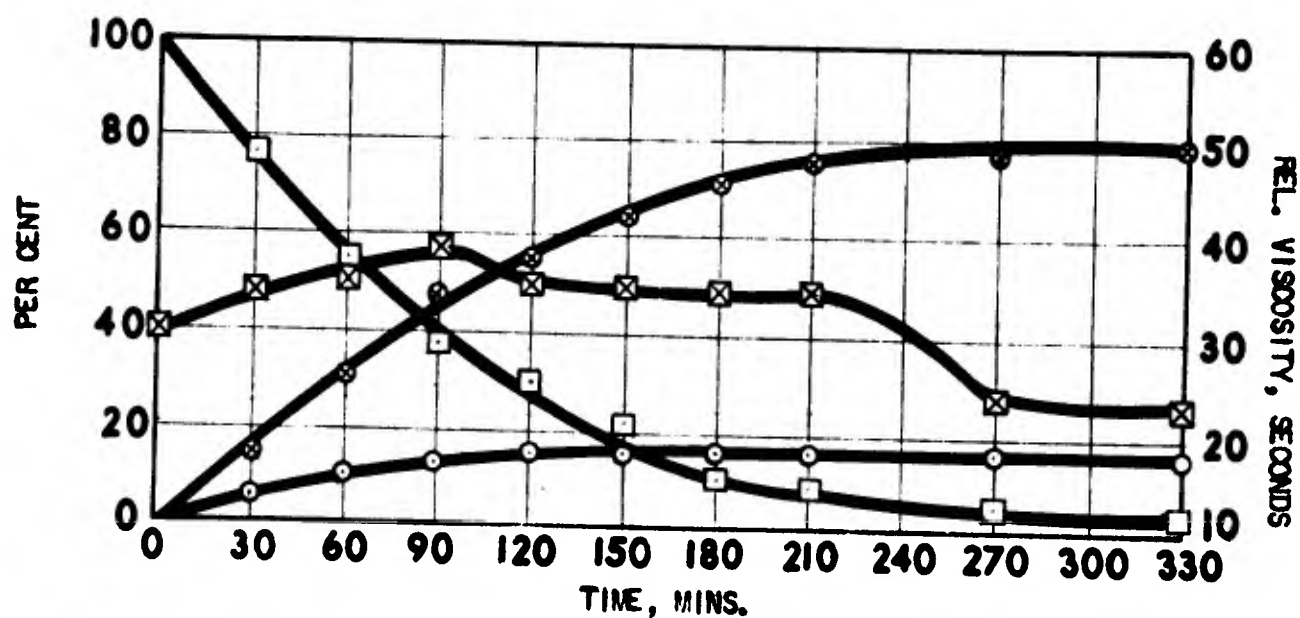
Results: (Figure III-A-2) The data show that in this case the values of the percent peroxide converted into acid were approximately 3 to 5 percent lower than the corresponding values in Experiment I; the curve expressing the percent peroxide decomposed followed closely the corresponding curve of Experiment I, being only 1 to 2 percent

FIG. III-A-1



EXP. I- DECOMPOSITION OF B.P. IN N-HEPTANE ALONE

FIG. III-A-2



EXP. II- DECOMPOSITION OF B.P. IN N-HEPTANE
IN THE PRESENCE OF GUM

- - B.A.
- - B.P.
- ⊙ - 100-(B.A.+B.P.)
- ⊠ - VISCOSITY

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

lower. The viscosity, measured in time of flow through a calibrated pipette, started at 31 seconds; 90 minutes after addition of peroxide it reached a maximum of 39 seconds, then it dropped, leveled off and dropped again to a value of 23 seconds after a total of 330 minutes. Complete decomposition was not reached within the reaction period.

Experiment III.

Data: 1 g. of dibenzoyl peroxide, 20 g. of gum, 0.5 g. of mercurous oxide, in 210 cc. of n-heptane.

Object: To follow the decomposition of dibenzoyl peroxide in n-heptane in the presence of gum and mercurous oxide.

Results: In Figure III-A-3 the curve expressing the amount of benzoic acid isolated increased more slowly than in either of the previous experiments, and it leveled off at a lower value; then it tended to drop off slowly. The peroxide curve followed the same trend as the previous peroxide curves but fell off more rapidly.

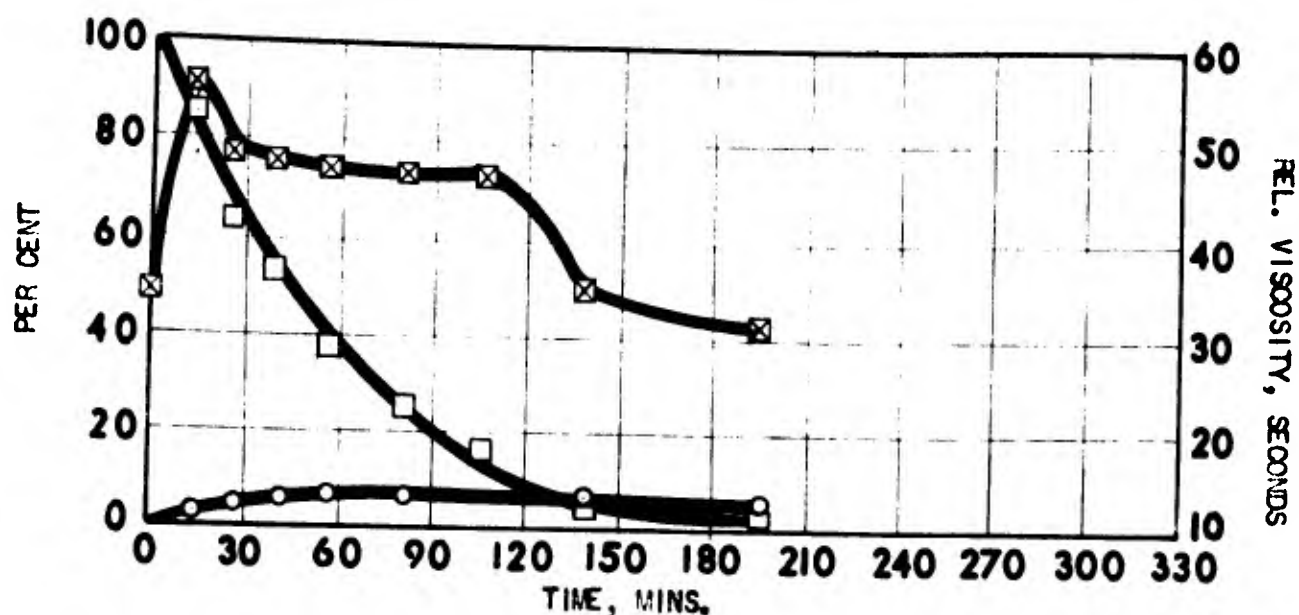
The viscosity, originally at 35 seconds, dropped but remained higher than the viscosity in the previous case.

Experiment IV.

Object: To isolate, characterize and determine quantitatively the products of complete decomposition of dibenzoyl peroxide in n-heptane, with and without polymer present.

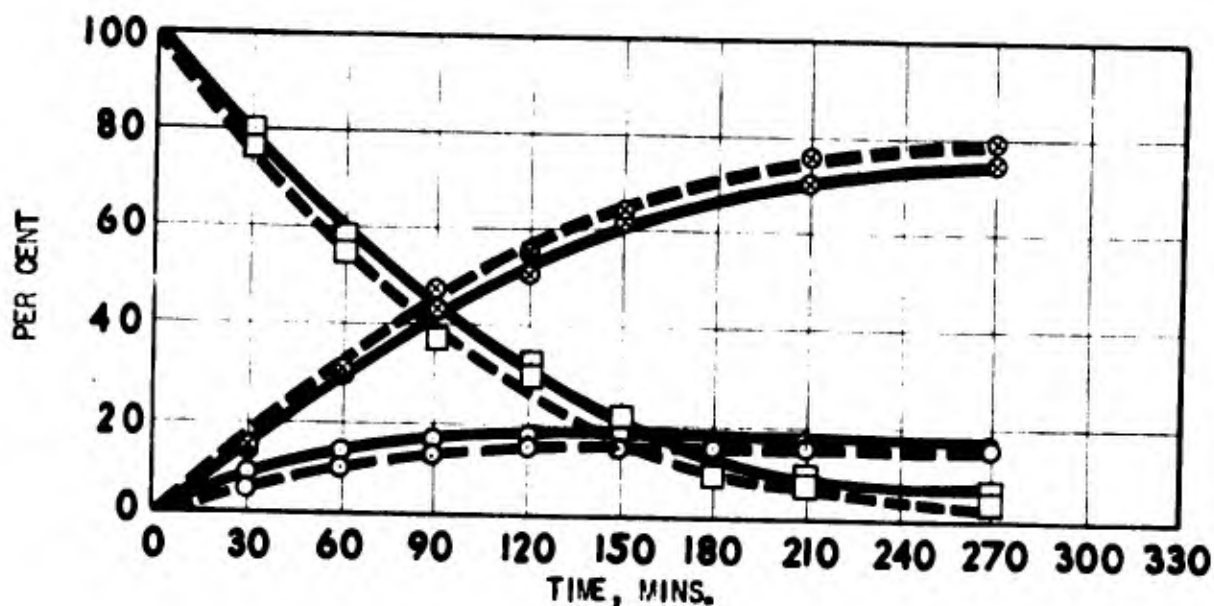
Results: benzene and benzoic acid were isolated and characterized as products of decomposition of dibenzoyl peroxide in solution with and without polymer present. Carbon dioxide was determined gravimetrically in the two cases.

FIG. III-A-3



EXP. III-DECOMPOSITION OF B.P. IN N-HEPTANE IN THE PRESENCE OF GUM AND MERCUROUS OXIDE.

FIG. III-A-4



COMPARISON OF GRAPHS III-A-1 AND III-A-2

— EXP. I

- - - EXP. II

- - B.A.
- - B.P.
- ⊗ - 100 - (B.A. + B.P.)
- ⊠ - VISCOSITY

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Data: (a) Dibenzoyl peroxide (9.4625 g.) was decomposed in 215 cc. of n-heptane at a constant temperature of 99°C. for a period of 10 hours. A stream of carbon dioxide-free and water-free nitrogen was passed through the reaction vessel and the carbon dioxide generated during the decomposition of the peroxide was collected in an absorption bottle filled with Ascarite. When no more peroxide was detected in the system, a sample of the solution was titrated to determine the amount of benzoic acid present at the end of the decomposition reaction. The mixture was then distilled and the refractive index of a sample of the distillate was taken. Another sample of the distillate was nitrated under mild conditions, and nitrobenzene was detected, first by means of its strong characteristic odor and then by reduction to aniline and identification of the latter. This proved the presence of benzene in solution. A small amount of yellow residue remained after the distillation, and benzoic acid was isolated from it and characterized by its melting point. A further small dark residue, possibly composed of polymeric products from the n-heptane-peroxide interaction,⁷ was not identified.

(b) 200 cc. of n-heptane was heated for 10 hours at 99°C. under the same conditions employed in case (a), in order to establish a correction factor for the carbon dioxide evolution. This factor was consistently applied to subsequent calculations for carbon dioxide.

(c) Dibenzoyl peroxide (9.889 g.) was decomposed in the presence of a solution containing 220 cc. of n-heptane and 20 g. of gum

7) Farmer and Moore, J.Chem.Soc. 1951, 131-41

at a temperature of 98°C. for 10 hours. The experiment was run under the same conditions as in case (a). Carbon dioxide was again collected in an absorption bottle and benzoic acid was titrated at the end of the decomposition reaction. The mixture was then distilled, benzene was identified in a sample of the distillate and the refractive index of the latter was taken. The reaction residue obtained after distillation of n-heptane and benzene exhibited a somewhat higher viscosity than the original polymer and was dissolved in benzene with more difficulty. It was extracted repeatedly with acetone and benzoic acid was isolated and recrystallized (m.p. 121°C.).

TABLE III-A-1

(a) Results from the Decomposition of Dibenzoyl Peroxide in the Absence of Polymer

0.0391 mols. of peroxide originally present	
0.01635 mols. of benzoic acid formed	.418 $\frac{\text{mols. B.A.}}{\text{mol. peroxide}}$
0.0268 mols. of carbon dioxide formed	.685 $\frac{\text{mols. CO}_2}{\text{mol. peroxide}}$

TABLE III-A-2

(c) Results from the Decomposition of Dibenzoyl Peroxide in the Presence of Polymer

0.0408 mols. of peroxide originally present	
0.0196 mols. of benzoic acid formed	.480 $\frac{\text{mols. B.A.}}{\text{mol. peroxide}}$
0.0306 mols. of carbon dioxide formed	.750 $\frac{\text{mols. CO}_2}{\text{mol. peroxide}}$

TABLE III-A-3

Comparison of Results Obtained from the
Decomposition of Dibenzoyl Peroxide in
Cases (a) & (c)

<u>Carbon Dioxide</u>	<u>Benzoic Acid</u>
Case (a) : 0.685 $\frac{\text{mols. CO}_2}{\text{mol. peroxide}}$	Case (a) : 0.418 $\frac{\text{mols. B.A.}}{\text{mol. peroxide}}$
Case (c) : 0.750 $\frac{\text{mols. CO}_2}{\text{mol. peroxide}}$	Case (c) : 0.480 $\frac{\text{mols. B.A.}}{\text{mol. peroxide}}$

A comparison of the relative amounts of benzene formed in the two cases and approximately determined by refractive index determination⁸ shows that more benzene is formed when the peroxide is decomposed in the presence of solvent alone than when it is decomposed in the presence of solvent plus polymer.

3. Discussion.

A study of Graphs III-A-1 and III-A-2 shows that when dibenzoyl peroxide is decomposed in solvent alone or in solvent in the presence of gum, the benzoic acid resulting from such decomposition is only a fraction of the theoretical yield based on peroxide originally present. This possibly indicates that the peroxide decomposition results not only in benzoate fragments which may take up one hydrogen atom from either the solvent or the polymer to become benzoic acid, but also in different fragments whose final form is not that of benzoic acid. The presence of benzene, probably formed through the decarboxylation of a benzoate radical and subsequent combination of the resulting phenyl radical with one hydrogen atom, and the evolution of carbon dioxide during the decomposition reaction may be examples of a different mode of decomposition.

8) Weissberger, "Physical Methods of Organic Chemistry," Vol. I, pg. 672-683, Interscience Pub., Inc., N.Y. (1945)

A comparison of the molar values expressing the benzoic acid concentrations found in solution and the amounts of carbon dioxide liberated during decomposition shows that the presence of silicone polymer favors the formation of benzoic acid and carbon dioxide but decreases the formation of benzene. This increase in the formation of benzoic acid in the presence of polymer is probably due to the vulcanization reaction taking place in the gum; the decarboxylation of the benzoate fragments is also favored by the presence of gum as shown by the increased amount of carbon dioxide collected; the resulting free phenyl radicals show less tendency to combine with hydrogen to form benzene but rather remain in the system, possibly attached to the silicone chain.

By comparing Figures III-A-1 and III-A-2 (Figure III-A-4), it is seen that a slight difference is present between the peroxide and acid curves in the case of peroxide decomposed in solvent alone and the corresponding curves in the case of the peroxide decomposed in the presence of gum. This phenomenon is probably due to the lower temperature when gum was present, as already mentioned. The higher temperature in the case of peroxide decomposed in solvent alone may cause a higher percent of the peroxide to be converted into acid.

The viscosity increase with time is a significant fact that can be interpreted in terms of partial cure of the polymer. Experiment III emphasizes the effect of acid concentration upon the viscosity. The graph in Figure III-A-3 shows a smaller amount of benzoic acid being formed, while the viscosity is considerably higher than that found in Experiment II. It is assumed that the mercurous oxide introduced into solution acts as benzoic acid acceptor, thus diminishing the depolymerizing

effect of acid concentration. After a certain length of time the viscosity curve drops suddenly in both cases II and III, and partially cured gum is found on the walls of the reaction vessel.

4. Conclusion.

The work thus far completed has shown the possibility of following the vulcanization of a silicone polymer in a solvent brought about by the decomposition of dibenzoyl peroxide. The analysis of the results obtained makes it possible to state that: (a) the neutralization of benzoic acid appearing as result of the decomposition of dibenzoyl peroxide will increase the extent of the vulcanization of silicone polymer; (b) most of the decomposition of the peroxide is due to heating and interaction with the solvent and (c) the mode of decomposition of dibenzoyl peroxide in solution in the presence of gum is complex, involving the free radical mechanism of benzoate and phenyl fragments.

A more complete analysis of the reaction mechanism should be possible by following the decomposition of chlorobenzoyl peroxide used to vulcanize hexamethyl siloxane. The latter is sufficiently fluid at ordinary temperature so that a homogeneous liquid phase polymerization can be effected without the use of solvent, which, as seen above, complicates the peroxidic decomposition reaction. The use of p-chlorobenzoyl peroxide would permit the determination of chlorobenzoate and chlorophenyl groups attached to the silicone polymer during the vulcanization reaction; this type of analysis has been employed by Bartlett and Cohen² and Price et al.⁹ with polystyrene. By a strong saponification

2) Bartlett and Cohen, J.A.C.S. 65, 543 (1943)

9) Price et al., J.A.C.S. 64, 1103 (1942)

and separation of the chlorobenzoate ester groups, it is possible to differentiate and determine individually the number of benzoate and phenyl groups which are attached to the siloxane chain. This analysis, along with free benzoic acid, carbon dioxide and benzene determinations should provide explanation of the complete reaction mechanism.

5. Summary and Recommendations.

An attempt has been made to establish the mechanism of vulcanization of silicone gum (General Electric SE-76) dissolved in an inert solvent by following the peroxide decomposition, the appearance of benzoic acid, the variation of the viscosity of the solution with time and by isolating the products of decomposition.

The products of peroxide decomposition quantitatively measured were benzoic acid and carbon dioxide. Benzene was also found among the decomposition products.

Vulcanization reached a maximum long before complete peroxide decomposition, indicating that depolymerization or devulcanization, possibly under the influence of benzoic acid, was occurring simultaneously. Eventually a sudden drop was shown by the viscosity curves, coinciding with the observed deposition of cured gum on the walls of the reaction vessel.

A program involving the use of simpler siloxanes and chlorobenzoyl peroxide is proposed. The former will permit easier following of the vulcanization reaction and the chloro group will allow identification of fragments from the peroxide if they attach themselves to the siloxanes.

B. Benzoic Acid in Silicone Rubber.

Benzoic acid is formed as a product of benzoyl peroxide decomposition during the vulcanization of silicone rubber. During long oven cures this material will bloom out of the compound if its concentration is sufficiently high.

It has been established that the presence of any acid is undesirable during curing. It appears to act as a depolymerizing agent counteracting the effect of the peroxide. For this reason, the most effective cures of silicone rubber are obtained with a minimum concentration of benzoyl peroxide. General Electric Compound No. 81223, for instance, contains 1.65 percent peroxide with Santocel C as a reinforcing pigment. Additional peroxide would be expected to provide a higher degree of cure, but the excess benzoic acid formed tends to minimize this and eventually lower the overall curing effect.

One of the chief deficiencies of a lower degree of cure is poor compression set performance. It has been found in the past that the addition of mercurous oxide to a peroxide-cured silicone rubber batch will improve the cure, especially with regard to compression set. It, therefore, seems likely that the Hg_2O acts in some way to counteract the benzoic acid, either by neutralization or compound formation.

The actual solubility of benzoic acid in SE-76 elastomer was not known, although it has been observed to bloom out at concentrations of peroxide as low as 2.0 percent. We, therefore, determined the solubility of benzoic acid in SE-76 by milling in various amounts, heating for

an hour at 300°F. (M.P. of ϕ COOH = 252°F.), and observing the mixture both visually and microscopically. No visible blooming occurred below 1.25 percent benzoic acid by weight but examination under a microscope showed minute crystals of the acid down to 0.40 percent by weight. It is concluded, therefore, that not more than about 0.4 percent of benzoic acid is compatible with SE-76 rubber at room temperature because of its low solubility. At higher temperatures below the sublimation point, benzoic acid is more soluble than this and exerts a depolymerizing action.

In some further experiments to ascertain the effect of Hg_2O on benzoic acid, varying amounts of these compounds were milled into SE-76 separately and together. The resulting mixtures were heated to 280°F. in a flask which was equipped with a cold finger to collect volatile material.

Benzoic acid alone (6 percent by weight) volatilized out forming crystals on the cooler surfaces in the flask and the condenser. Addition of 2 percent mercurous oxide decreased this sublimation noticeably, and an equimolar amount of Hg_2O (20.9 percent by weight) prevented any volatilization of benzoic acid at the same temperature (280°F.) that it had sublimed when present alone. It was apparent, therefore, that the mercurous oxide had reacted with benzoic acid in some manner to form a less volatile compound. We have not determined what this reaction is, although the formation of the salt seems a logical explanation. The action of mercurous oxide in low compression stocks is related to its scavanging action in cleaning up residual benzoic acid. Long high temperature cures have a similar effect since they cause sublimation

of benzoic acid.

Since mercury compounds are volatile and poisonous, a better way should be found of removing benzoic acid to improve compression set. The use of long high temperature cures is likewise objectionable for obvious reasons. Further study of methods of making low compression set silicone compounds is needed. In this connection it should be noted in Section I of this report that short press cures resulted in improved compression set. This result could be caused by the lower percentage of cross-links formed or by the lower percentage of benzoic acid formed. (See Section III A) A reduced percentage of cross-links should result in greater plastic flow under compression and higher compression set. It appears, therefore, that the idea of reduced concentration of benzoic acid, caused by short cures, and reduced amount of depolymerization and, consequently, reduced plastic flow is a probable explanation of the lower compression set obtained with short press cures.

Long oven cures, also favoring low compression set, probably function (1) by reducing benzoic acid concentration or (2) by volatilizing uncross-linked molecules or (3) by some other oxidation reaction which succeeds in cross-linking plastic components into the network. All three mechanisms are undoubtedly at work during long high temperature cures. A high molecular weight silicone fraction, cured without benzoic acid as a by-product might give reduced compression set. Such a polymer is not available at this time, but it is well known that General Electric 9979-G, which has a higher average molecular weight than the 81176 (SE-76) gum, gives much better compression set resistance.

C. Curing SE-76 Silicone Gum with Di-tert-Butyl-Di-Perphthalate Peroxide.

Dr. L. Scala, through earlier connections with Dr. Milas at The Massachusetts Institute of Technology, knew of a new peroxide and we investigated its effect as a vulcanizing agent for General Electric 81176 rubber. As shown in Table III-C-1, the curing activity at temperatures as high as 350°F. and with concentrations up to 10 percent was very slight so that no further work is indicated with this peroxide.

TABLE III-C-1

Curing Silicone Rubber with
Di-tert-Butyl-Di-Perphthalate Peroxide¹

<u>Compd. No.</u>	<u>Vol. Loading</u>	<u>Peroxide Wt. (%)</u>	<u>Press Cure</u>	<u>Remarks</u>
2045	40	2.0	15 min. @250°F.	Blistered cure.
2045	"	"	30 min. @350°F.	" "
2045-1	"	4.0	30 min. @300°F.	Slight cure.
2045-1	"	"	1 hr. @300°F.	No cure.
2045-2	"	8.0	1 hr. @300°F.	Slight cure.
2045-2	"	"	1 hr. @320°F.	Slight cure.
2045-3	"	10.0	1 hr. @320°F.	Slight cure.
2045-4	None	4.0	1½ hrs. @300°F.	Poor Cure.
2045-5	"	8.0	1½ hrs. @300°F.	Poor Cure.

¹ Stocks compounded with G.E. 81176 silicone gum, with 40.0 volumes of Titanox RANC (heated to 500°F.) and indicated amounts of peroxide.

IV. MOLECULAR WEIGHT AND SWELLING STUDIES ON SILICONE RUBBER

A. Introduction.

This phase of investigation has several basic practical as well as theoretical objectives. The general object is to study rigorously the magnitude and the mechanism of swelling of variously prepared samples of silicone elastomer in various organic solvents. Thus some of the molecular characteristics of the elastomeric polymer will be determined along with information about the compounding and curing conditions which affect the magnitude of swelling.

It is well known that most oils and fuels cause deterioration of rubber products. This degradation is due principally to the weakened nature of the vulcanized rubber network when it is saturated and consequently swelled by the solvent. The volume of natural rubber increases up to 500 percent when benzene is absorbed and its tensile strength decreases considerably even though its relative shape remains the same. After evaporation of the solvent, the rubber de-swells (retracts to its original size) and returns to nearly the same physical properties as it had before swelling. The synthetic elastomers, commonly referred to as rubbers, differ considerably in their behavior in different solvents: GR-S and Butyl swell about the same as natural rubber; Neoprene, Buna N and Thiokol are increasingly more fuel resistant because of the presence of polar groups

within the molecules. The swelling of silicone rubber varies considerably depending on the conditions of preparation and of vulcanization. Its strength when swollen is practically nil.

Swelling is a disadvantage in many applications where elastomers might be used. Fuel-line gaskets and hoses are among the most important examples. At operating temperatures between $-40^{\circ}\text{F}.$ and $250^{\circ}\text{F}.$ the aforementioned oil-resistant synthetics are quite acceptable. The upper temperature limit results from oxidation, excessive hardening or decomposition of these rubbers. The lower limit results from an appreciable loss of resilience and flexibility. (These rubbers can be plasticized for softness at lower temperatures but fuels extract the plasticizer.)

Silicone elastomers are capable of maintaining their physical properties over a much wider temperature range. Some compounds remain elastomeric from $-100^{\circ}\text{F}.$ to $500^{\circ}\text{F}.$ The deleterious effect of fuels, however, decreases slightly the usefulness of this unique elastomer. Fortunately, lubricating oils are less severe swelling agents than fuels; and reinforced silicone gaskets are being used for effective seals on hot-operating aircraft engines.

At the present time, no elastomer is commercially available which will withstand satisfactorily the action of fuels at extremely high or low temperatures.

The process of swelling of a rubber is essentially that

of liquid-liquid solvation; in the unvulcanized state the linear rubber molecules may be completely soluble. However, when the raw rubber is vulcanized in order to form a firm elastomeric network, solvation of each linear chain, previously unrestricted, is now inhibited by its cross-links to adjacent molecules.

Just as liquid-liquid solutions are treated thermodynamically, the swelling of elastomers in solvents is also well explained by theories involving the network configurational entropy and the heat and entropy of mixing of polymer and solvent. P. J. Flory, M. L. Huggins, G. Gee and others have made important contributions toward explaining the phenomenon of swelling and their equations provide a means of determining some of the important basic properties of polymer networks. A brief review of these equations and their use was included in the appendix of Progress Report No. 9.

Polymer properties that can be determined from swelling measurements are:

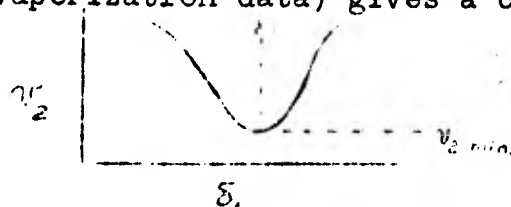
ϵ_2 = solubility parameter, also known as cohesive energy density (square root of the energy of vaporization per unit volume)

χ = polymer-solvent interaction coefficient

M_c = molecular weight of polymer chain between cross-links

The solubility parameter is determinable according to theories developed by Gee in which swell of a polymer is considered a function of the solvent cohesive energy density;

maximum swell is obtained in that solvent whose solubility parameter (δ_1) equals that of the polymer (δ_2). A plot of swell versus δ_1 , solvent cohesive energy density ($\sqrt{\frac{E_v}{V}}$ from energy of vaporization data) gives a curve,



whose equation at least approximates the Gaussian form

$$v_2 = v_2 \text{ min.} e^{\alpha V_1 (\delta_1 - \delta_2)^2} \quad \text{where:}$$

v_2 = volume fraction of polymer in the swollen network

$$= \frac{\text{volume of normal polymer}}{\text{volume of swollen polymer}}$$

$v_2 \text{ min.}$ = minimum v_2 obtainable with any solvent

α = constant

V_1 = molal volume of the solvent

It is apparent that $v_2 = v_2 \text{ min.}$ at $\delta_1 = \delta_2$.

The factor μ is essentially a heat of mixing term and, hence, is related to the energy of mixing of the polymer and solvent. The energy of mixing of two liquids is $\Delta E_1 = V_1 \chi_2^2 (\delta_1 - \delta_2)^2$. By considering polymer-solvent interaction to be analogous to liquid-liquid mixing, the heat of mixing is also a function of the same term, although the exact relationship is unknown at present. Scott and Magat have proposed the semi-empirical equation:

$$\mu = \mu_s + \frac{K V_1 (\delta_1 - \delta_2)^2}{RT}$$

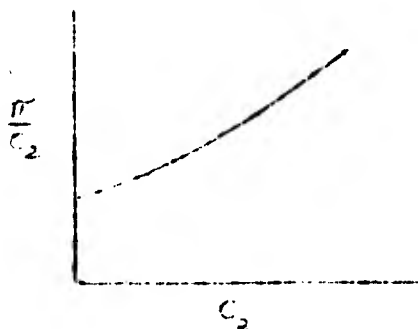
where: μ_s = constant about 0.3
 K = constant characteristic of the polymer = 1 for nonpolar rubber
 R = gas constant
 T = absolute temp.

This factor μ also appears in Huggins' equation for osmotic pressure of polymer solutions and μ can be determined from measurement of the osmotic pressure of polymer solutions of various concentrations.

$$\frac{\pi}{c_2} - \frac{RTd_1^2 c_2}{3M_1 d_2^3} = \frac{RT}{M_2} + \frac{RTd_1}{M_1 d_2^2} (1/2 - \mu) c_2$$

where: π = osmotic pressure
 c_2 = concentration of polymer in solution
 d_1 = density of the solvent
 d_2 = density of the polymer
 M_1 = molecular weight of the solvent
 M_2 = molecular weight of the polymer

This equation enables determination of the molecular weight of a soluble polymer since $\frac{\pi}{c_2} = \frac{RT}{M_2}$ at $c_2 = 0$ which is obtained by extrapolation of a $\frac{\pi}{c_2}$ vs. c_2 curve. From the slope of such a curve μ can be calculated.



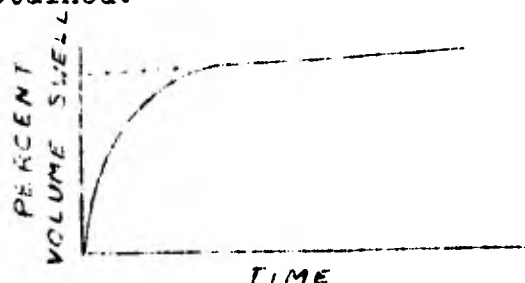
Flory's analysis of the configurational entropy of a cross-linked network makes possible a determination of the molecular weight between cross-links through swelling measurements.

$$M_c = \frac{-d_2V_1(v_2^{1/3} - \frac{v_2}{2})}{\ln(1-v_2) + v_2 + v_2^2\mu}$$

At small values of v_2 this can be reduced to the approximate equation $M_c = \frac{d_2V_1}{v_2^{5/3}(\frac{1}{2}-\mu)}$. This equation is graphed in figure IV-A-1, after page 75, as $\frac{M_c}{d_2V_1}$ vs. v_2 with μ as a parameter. This equation, derived by statistical mechanics and thermodynamics, involves an equilibrium value of v_2 .

Distinction of an equilibrium swell has been based upon a definition by Scott who presented one of the first classic treatments of the phenomenon of swelling of rubber. An initial rapid swell is observed, which then tapers off to a slow "incremental" swell which he attributed to oxidative breakdown of the rubber. As this incremental swell was found to be substantially linear with time, the breakdown effect could be subtracted by an extrapolation of the swelling curve to zero time. This extrapolated value of the swell has been considered the equilibrium value wherever incremental swelling is observed. Where percent volume swell is plotted against time, the following type

of curve is obtained:



As the present study is concerned with v_2 rather than the percent volume swell, a curve results which is the inverse of the above (see figure IV-C-6, after page 92). Relation between the two functions is: percent volume swell =

$$\left(\frac{1}{v_2} - 1 \right) 100.$$

Silicone elastomers are normally vulcanized with 1 to 10 parts of benzoyl peroxide per 100 parts of polymer; lesser concentrations cause low tensile strength and high elongation; higher concentrations lead to increased hardness and brittleness without materially improving tensile strength. The mechanism of vulcanization is not definitely known. After being compounded on a mill, silicone elastomers are press cured 10 to 20 minutes at 230 to 280°F. under 400/psi pressure. Following the press cure, an additional oven cure of 1 to 48 hours at 300 to 480°F. is used in order to complete the free-radical cross-linking reaction and to drive off benzoic acid (a by-product) and low molecular weight polymers. The effect on swelling characteristics of these curing and composition conditions is of practical interest and is being investigated in the first phase of this program.

This study was set up as a series of experiments which, though distinct as far as procedure is concerned, are considerably interrelated. Even though the sequence of tests has not been followed strictly, the original numeration is followed in this report. The program as outlined at present appears in Table IV-A-1. Only those tests marked with an asterisk are reported herein.

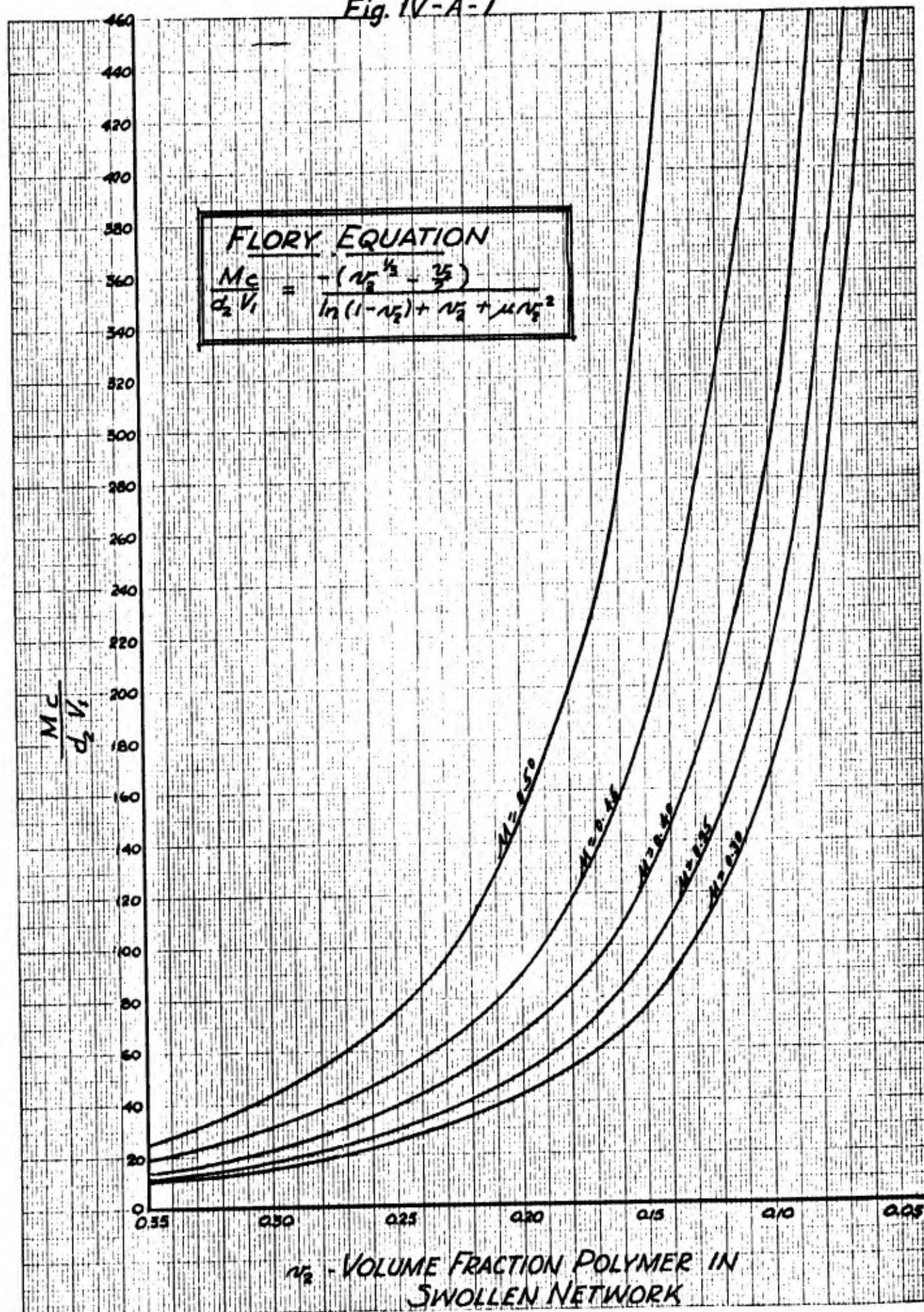
Further investigations will involve separation of the silicone polymer into various molecular weight fractions and determination of the linear molecular weight distribution and χ_1 by osmotic pressure measurements. Then, by vulcanizing various fractions, the dependence of M_c upon M (linear molecular weight previous to cross-linking) will be determined.

TABLE IV-A-1

Program of Swelling Study

<u>Test</u>	<u>Object</u>	<u>Conditions</u>
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.

Fig. IV-A-1



B. APPARATUS

Because of the large number of volume measurements to be made on individual samples of silicone rubber, a convenient and accurate method of volume determination was desired; such a method was not to involve the possibility of any de-swelling or solvent contamination during periodic volume measurement so that accurate rates of swell could be obtained.

Most swelling studies reported in the literature are based upon weight rather than volume measurements, and the swollen volume has been calculated from the weight and density of the solvent imbibed (absorbed) along with the original weight and density of the particular rubber sample. For a single determination this method is the most accurate; but it is not suitable where repeated determinations are necessary because the evaporation of solvent and consequent de-swelling of the sample during the time required for weighing introduce an incalculable error. The Jolly-balance method of weighing in air and then in water is conveniently used for fairly accurate laboratory swell determinations, but here again an appreciable de-swell is involved no matter how rapid the manipulation; and, for the lighter-than-water samples, an alcohol such as isopropanol is used rather than water. This causes contamination of the solvent when the sample is re-immersed.

Hence a new method of volume measurement was desired, and for the specific purposes of this project special immersion tubes were designed and constructed. The features

of convenience and easy repetition of measurements were paramount in design purpose and the instruments are unique in these respects.

Figure IV-B-1, following page 82 shows a cross-sectional view of the glass immersion tube, and its mode of operation is easily illustrated. Volume measurement is based upon displacement of a discernible volume of the solvent which is being used as the swelling medium. The lower portion of the tube is filled with solvent to a convenient level as is indicated by the level in the lower portion of the capillary side-arm. (Fig. IV-B-2). At any level of fluid in the main chamber (within the limits of measurement) there exists a corresponding level of fluid in the side arm; and, because the side arm is sloped approximately 5° from horizontal, a level change in the main tube causes a 12-fold (cosecant 5°) greater change of position in the side arm. Capillary rise in the side arm amounts to 1.5 to 2 inches, depending upon the solvent. The capillary rise in a given tube with a given solvent is assumed to remain constant. The removable cap and hook portion of the immersion tube performs a double function: suspension of the sample in the solvent; and sealing of the tube with a mercury well to prevent excessive vapor loss. The hook volume is negligible.

The immersion tube is clamped onto a mounting arm (Figure IV-B-3) which steadies it in position and which provides initial adjustment of slope to the optimum position. On the face

of this mounting arm was cemented a strip of millimeter graph which was shellacked for protection and numbered for calibration. Lines on this graph paper are easily visible through the capillary tube; hence the liquid level can be read on the scale in millimeters and, in fact, with the use of a jeweler's magnifying lens readings of 0.1 millimeters are possible. The upper return-half of the capillary side arm is calibrated in centimeters in order to help as a guide to the eye in making readings perpendicular to the face of the scale.

This scale is calibrated according to the actual volume of solvent in the main chamber. At the start of each swelling determination, the rubber sample is suspended on the hook and lowered into the solvent. To measure the sample volume at any time the liquid level is read on the side arm scale and the sample is lifted from the solvent sufficiently long for the level to equilibrate at a lower position on the scale. A second reading is then taken and the sample is re-immersed. The volume is determined from the difference of calibrated values corresponding to the two readings. No de-swelling is encountered during a measurement since the solvent can not evaporate into the saturated atmosphere during the 30-to 45-second operation. (This does not infer nor assume that equilibrium swell in a saturated vapor is the same as in a liquid.) A slight amount of vapor is lost during each measurement since the mercury seal is broken momentarily; however, this introduces no error.

Six immersion tubes are mounted radially about the central control unit of a constant temperature bath. The mounting plate is detailed in Figure IV-B-4, showing the holes through which the temperature control apparatus and the immersion tubes are placed. Only the lower portion of the immersion tube passes through the plate and is in contact with the constant temperature bath. Even though the sample and most of the solvent is in this chamber, a slight temperature differential is probably encountered in the upper part of the swelling fluid, and the liquid in the side-arm is undoubtedly at or near room temperature. The latter, however, is not so important as the swelling temperature of the sample. The small pins at the lower end of each mounting arm position the tubes, and the guide frame above the mounting plate prevents possible tipping of the tubes, yet permits easy removal when necessary. A small guide is clamped to the mounting plate at the outside end of each immersion tube in order to prevent any side-sway of the tube; this guide merely fits between the two slope-adjusting screws and is clamped to the plate with an ordinary laboratory hose pinch-clamp. The complete unit is illustrated in Figure IV-B-5; the tubes with dark fluid are being cleaned, the others are in operation and the liquid level can be seen in the side-arm of the tube at the left-front. The mounting plate is made of 1/8-inch steel and was coated with baked-on neoprene in order to prevent corrosion; the mounting arms are of 1/8-inch brass; the guide

frame (Figure IV-B-6) is of 3/4-inch plywood and it is held in place by three supports (Figure IV-B-7).

The constant temperature apparatus (schematic diagram, Figure IV-B-8) consists of a large glass jar filled with water (it also supports the mounting plate), stirrer, 250-watt knife heater, and Fenwall thermoregulator with relay. Temperature is controlled to $\pm 0.1^{\circ}\text{C}$ by this apparatus. The stirrer motor is mounted on a laboratory bench adjacent to the rest of the apparatus in order to prevent vibration interference.

After a few preliminary swelling tests, during which the slope of the side-arms was adjusted to learn the workable range of measurement for maximum accuracy, the adjustment screws were locked in place and glass leveling bulbs were cemented in proper position on the immersion tubes.

The tubes were then calibrated to relate volume within the immersion chamber to liquid level in the side-arm. Calibration involved the use of a small "gun" which dropped pellets of 0.0434 c.c. volume into the chamber containing the solvent. The "gun" was a simple tube and rod expelling device (Figure IV-B-9) made of a glass tube and rod and a medicine-dropper bulb into which "X"-slots were cut so that pellets could be expelled individually. The solvent level was initially adjusted to the apparent limit of capillarity, and as each pellet was dropped into the tube, the new level was read from the side-arm scale. The pellets were dropped at a constant rate and the time interval between dropping a pellet and reading the scale was also kept constant during

the calibration of each tube. These factors, however, varied slightly from tube to tube. Temperature was held constant at 25.0°C. during calibration and the pellets were warmed to that temperature before placement in the "gun".

Two or more calibration runs were made for each tube and the results were averaged. Calibration curves were plotted as unit volume (number of pellets) vs. scale reading along the capillary tube. In order to relate unit volume of the calibration curves to absolute volume in cubic centimeters, an additional calibration constant was employed. Ideally this constant should have been 0.0434 c.c. per unit volume for each of the immersion tubes; but because of the aforementioned time factors which varied for each tube, calibration constants were determined individually. This was accomplished by withdrawing in a calibrated pipette 1.04 c.c. of benzene from each immersion tube; scale readings were taken before and after withdrawal of the liquid, and by reference to the calibration curves the number of unit volumes equivalent to 1.04 c.c. was discerned. Calibration constants for the six tubes range from 0.0422 to 0.0443 c.c. per unit volume.

Initial volumes of the rubber samples are calculated in cubic centimeters from the initial weight and density; the latter is determined by pycnometer.

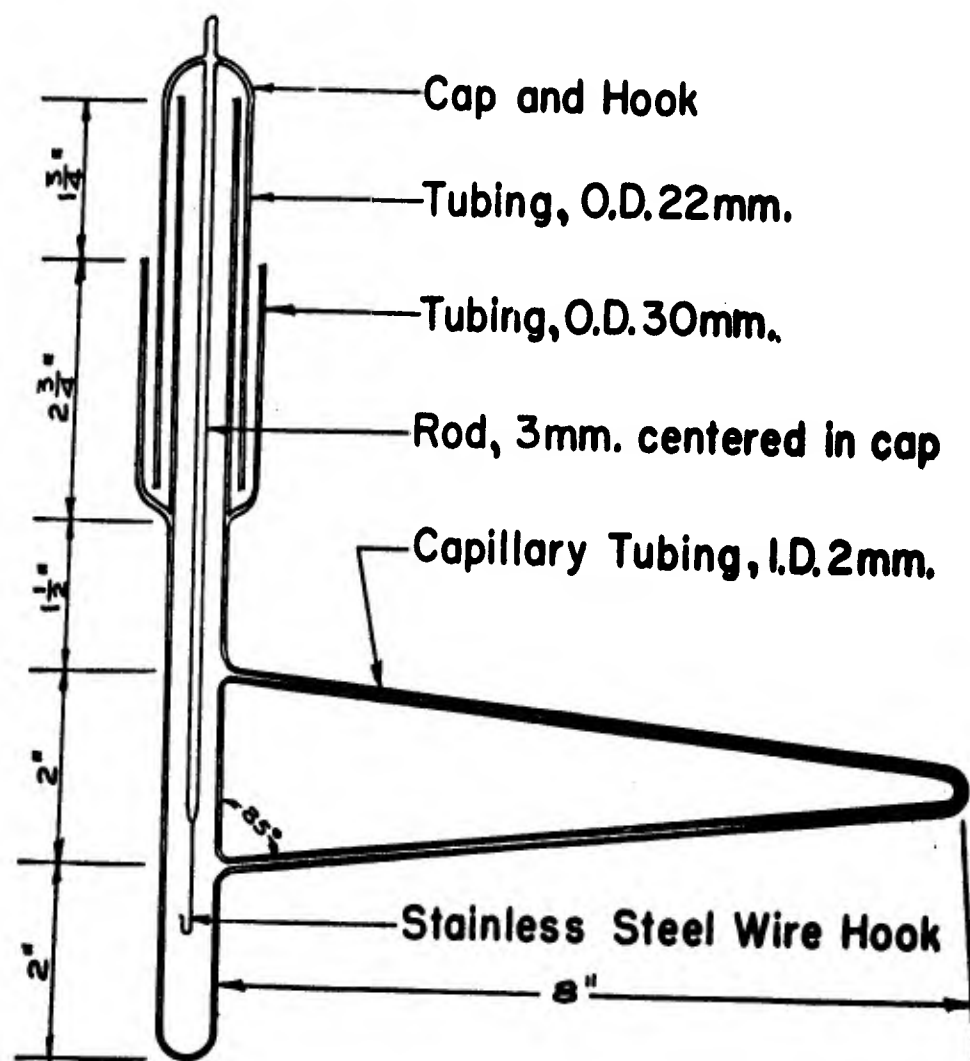
The precision of measurements of Test 1 averaged ± 2 percent and subsequent tests have shown even greater accuracy.

Sensitivity of the immersion tubes, defined as total range of scale reading divided by the corresponding total change in volume, is tabulated below:

<u>Tube</u>	<u>Sensitivity, cm. per cc.</u>
1	6.92
2	7.75
3	8.30
4	7.95
5	6.25
6	7.72

As the swollen volume of the samples is 1.0 - 1.5 c.c., the error involved in scale readings (to 0.1 mm.) is 0.1 to 0.14 per cent of the total scale variation; therefore the slight additional error is caused by other factors, probably surface tension and capillarity.

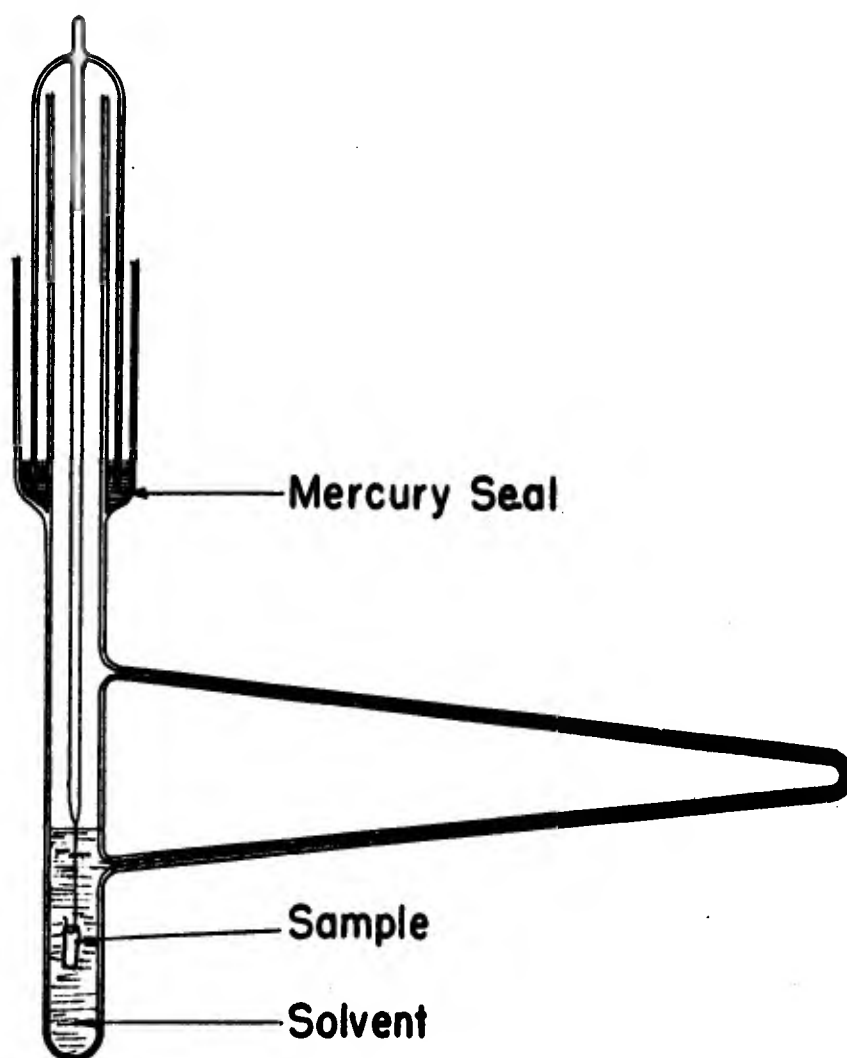
After each swelling test, the tubes are emptied of the solvent, and rinsed with acetone and then with water. A cleaning solution, consisting of concentrated $K_2Cr_2O_7$ - H_2SO_4 , is then placed within the tubes for at least an overnight period. The tubes are then drained of cleaning solution, rinsed with water, acetone and the swelling solvent, dried, and then filled with solvent for the next swelling test.



IMMERSION TUBE

Scale: $\frac{1}{2}$ Actual Size...

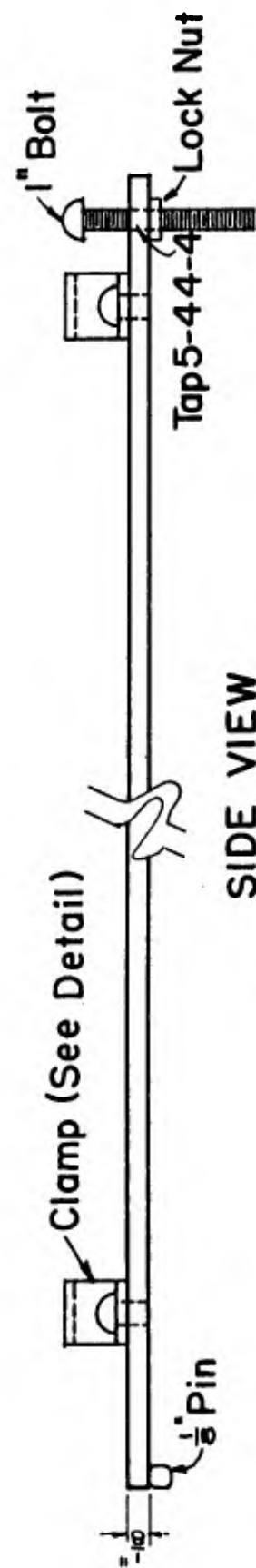
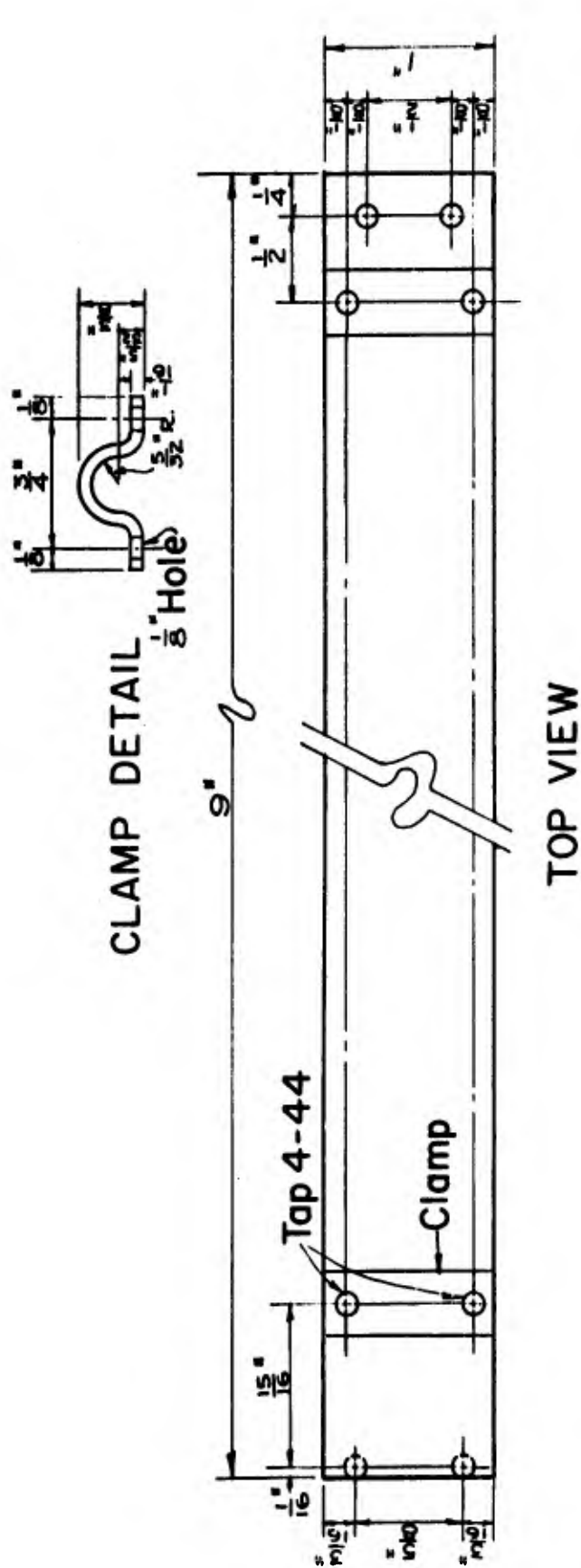
Fig. IV-B-1



IMMERSION TUBE

Scale: $\frac{1}{2}$ Actual Size

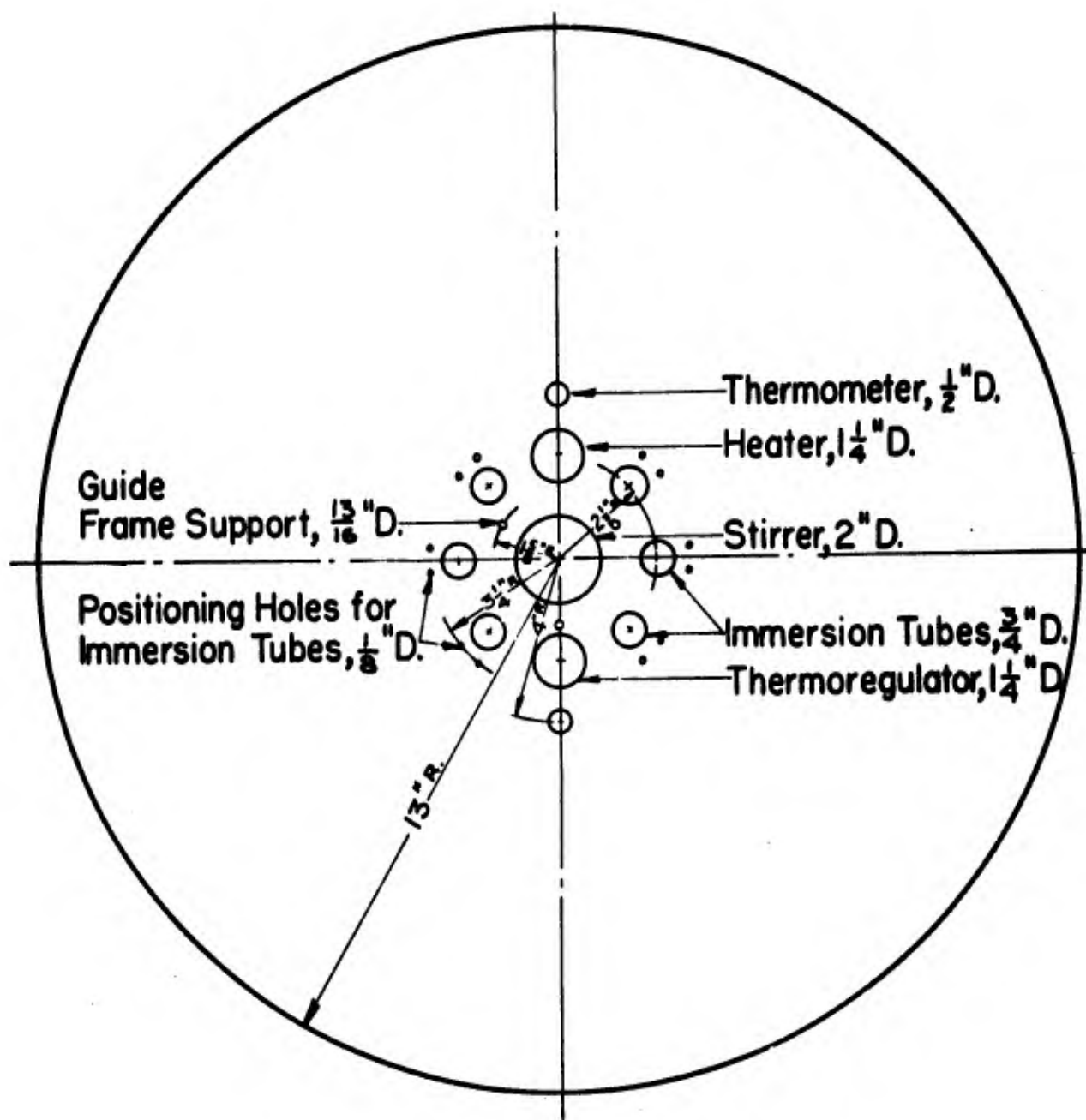
Fig. IV - B - 2



IMMERSION TUBE MOUNTING ARM

Scale: Actual Size

Fig. IV-B-3



MOUNTING PLATE

Scale: $\frac{1}{4}$ Actual Size

Fig. IV - B - 4

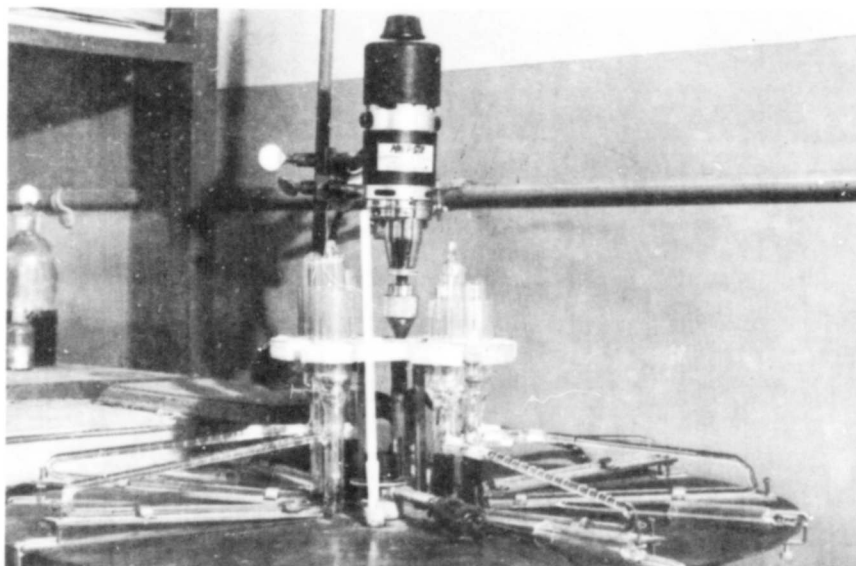
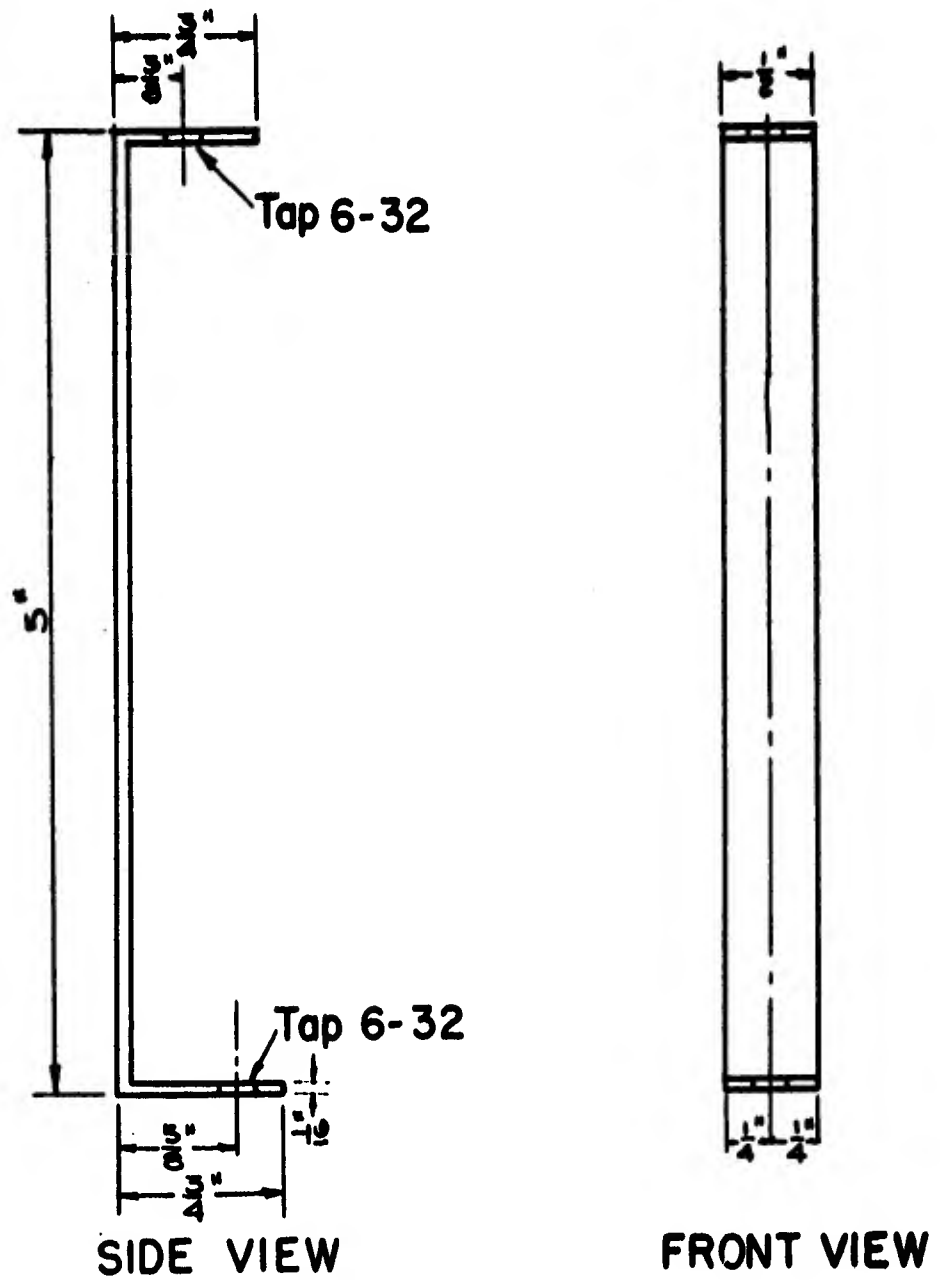


Figure IV-B-5

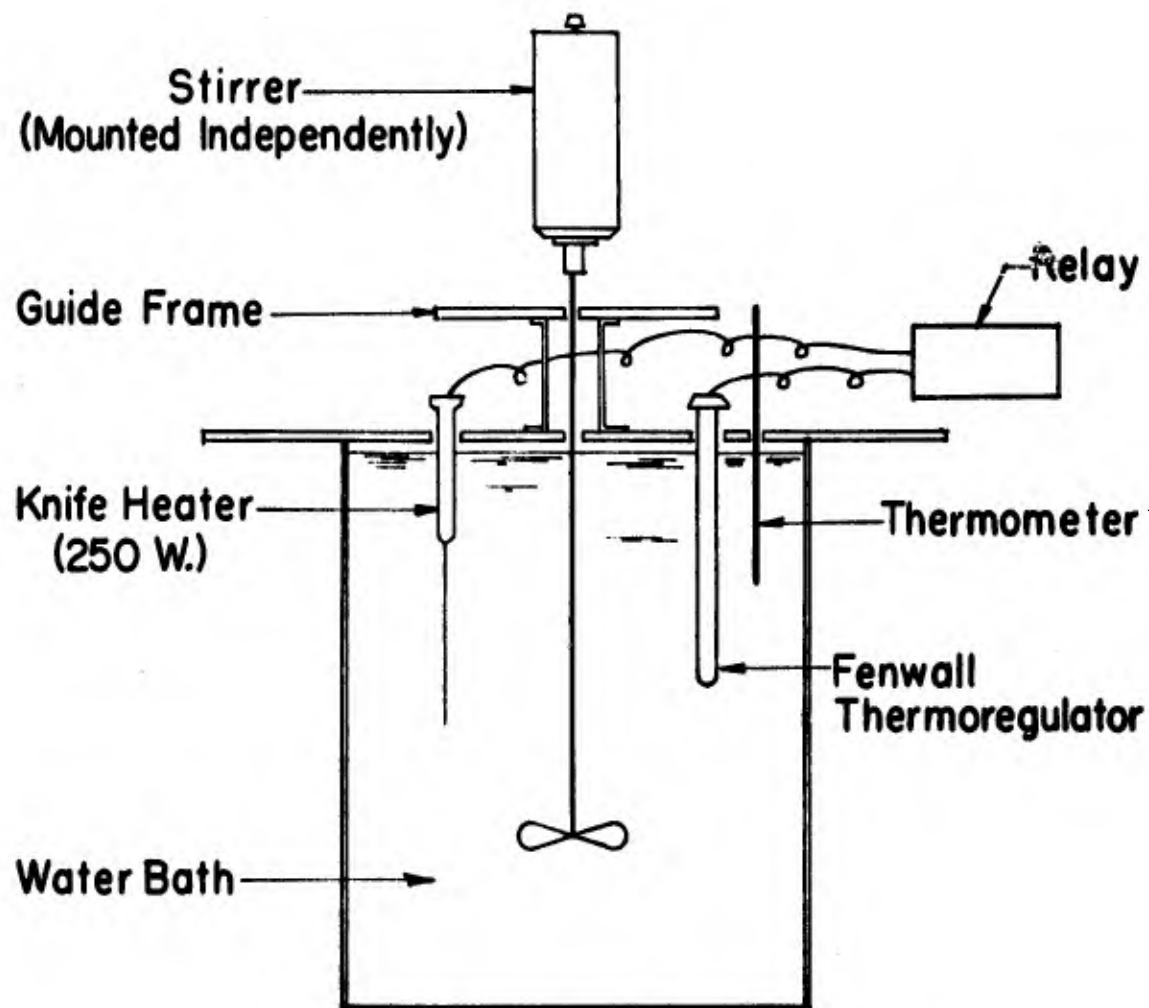
Photograph of the volume swell apparatus showing the mounting of the individual immersion tubes and the temperature control apparatus. The tubes whose caps are removed are being cleaned with H_2SO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$ solution, the others are in operation with samples immersed in the benzene. Liquid level in the side-arm of the tube at the left-front is visible.



GUIDE FRAME SUPPORT

Scale: Actual Size

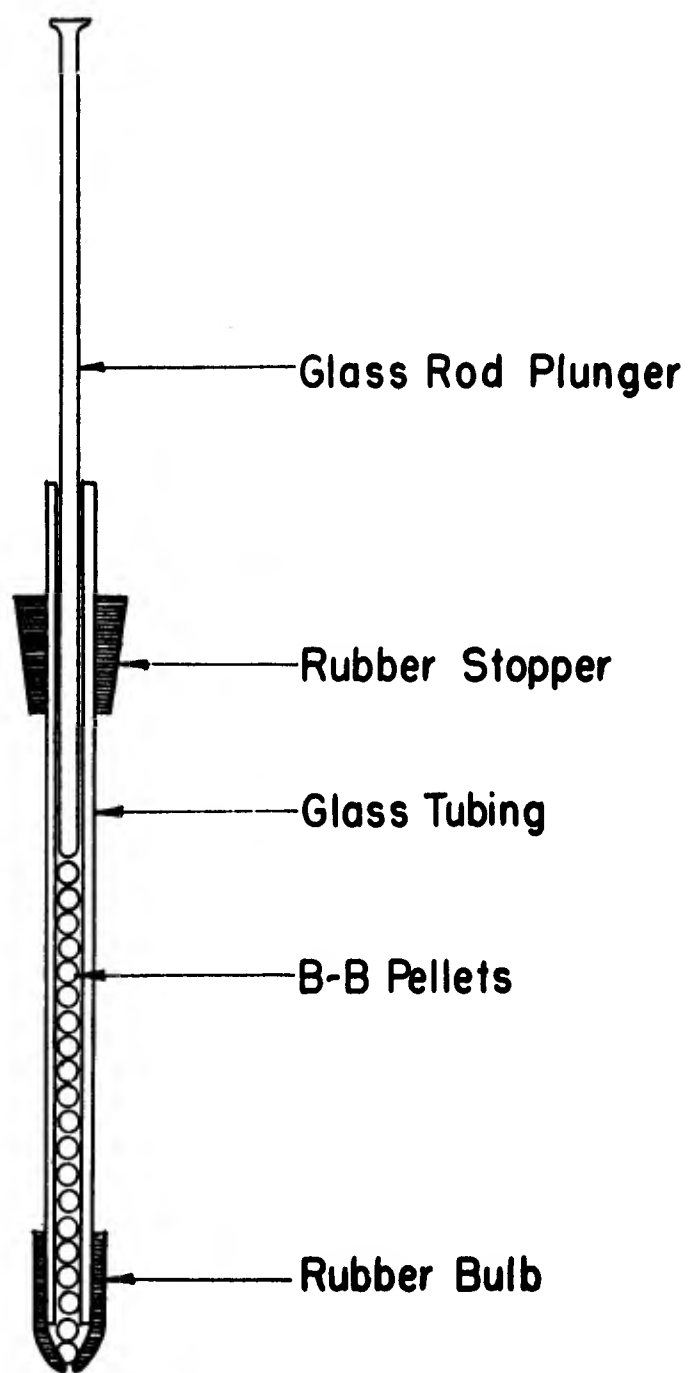
Fig. IV-B-7



MOUNTING UNIT

(Not to Scale)

Fig. IV-B-8



CALIBRATION GUN

(Not to Scale)

Fig. IV-B-9

C. Experimental.

Test 1 - Effect of Sample Size on the Accuracy of Measurement.

Object: The purpose of this test was to determine the precision of the immersion type measurements and to determine the effect of sample size on the rate of swell and on the accuracy of measurement.

Procedure: A test sample containing 30.0 grams of General Electric silicone polymer No. 81176 (Batch 7155) and 0.6 grams of Lucidol (purified) benzoyl peroxide was milled for 5 minutes and press cured in a 2" x 6" x .075" mold in an electrically heated and water-cooled press for 15 minutes at 250°F. and 550 pounds per square inch pressure. The press was then cooled to 100°F. and the sample removed. Further cure was effected with 24 hours at 300°F. in an air-circulating oven.

Samples were cut from along the 6" edge of the slab and small holes were drilled near the end of each sample. Dimensions and weights of the samples were:

<u>Sample</u>	<u>Dimensions</u>	<u>Weight, grams</u>
1a	3/8" x 1/4" x .071"	0.108
1b	3/8" x 1/4" x .070"	.108
1c	9/16" x 1/4" x .070"	.166
1d	9/16" x 1/4" x .070"	.164
1e	3/4" x 1/4" x .070"	.225
1f	3/4" x 1/4" x .069"	.212

Density of two samples of the same slab were determined by pycnometer weights, 0.965 and 0.955 gm./c.c. An average of 0.960 was thus assumed for the above samples and the

original volume, V_0 , of each was calculated therefrom.

The immersion tubes, previously cleaned with H_2SO_4 - $K_2Cr_2O_7$ solution, were rinsed with acetone and benzene and filled with distilled benzene to the desired level. After constant temperature of $25.0^\circ C$. was reached, the samples were immersed within the tubes and volume readings were taken at frequent intervals over a period of 238 hours. From the calibration curves and the calibration constants, volumes were calculated for the various samples. After swelling of the samples they were removed and dried to constant weight at room temperature. The benzene solvent was likewise dried to determine if it contained any solute. Density and volumes of samples 1a and 1b were determined by pycnometer after drying.

Results: Data are plotted as $\frac{V_0}{V_s}$ vs. time on the center curve of figure IV-C-1 (following page 87). Results from the six samples varied considerably during the early period of swelling but narrowed to a precision of ± 2 percent at 238 hours where $\frac{V_0}{V_s}$ equals 0.191. Average loss of weight was 6.1 percent due to extraction of low molecular weight polymer, as indicated by the oily residue from the evaporated solvent. Samples 1a and 1b showed no change of volume from the swell and de-swell, but density was reduced from 0.96 to 0.91 gm./c.c.

Log-log swelling curves of the individual samples are represented fairly well by two straight lines with change

of slope in the range of 2.5 to 4 hours. Thus the average line is represented similarly and it is based upon an average of the individual lines rather than upon a direct average of the data.

There was no definite trend of variation of data with original sample size, but precision of measurement was better with the larger sample..

Swelling of the samples appeared to be isotropic except for a slight curling of the larger samples.

Also in figure IV-C-1 are plotted extraction data from Test 8. Here the rate of extraction is represented as $\frac{V_p}{V_o}$, the fraction of polymer remaining within the network at any time. The product of the two curves, $\frac{V_p}{V_o} \times \frac{V_o}{V_s}$, gives v_2 , the volume fraction of polymer in the swollen network as a function of time. No reference has been found in the literature where rate of extraction is considered in conjunction with the rate of swell, even though network breakdown (and hence extraction) is known to exist.

In hydrocarbon rubbers the breakdown of primary bonds upon swelling is attributed to the effect of dissolved oxygen. In the natural state hydrocarbon rubbers are slowly decomposed by oxygen and breakdown by ozone is extremely rapid. On the other hand, silicone elastomers are so highly resistant to ozone that oxidative breakdown during swelling is unlikely.

Network breakdown can logically be pictured as fracture

of those chains receiving the greatest stress. This stress probably arises from the pull of other chains and from the high degree of molecular motion arising from polymer-solvent interaction. In the normal tightly coiled state of the molecule the methyl groups with their high degree of rotation protect the relatively weak Si-O bonds of the chain, but in the swollen state these bonds are exposed. There is probably some variation of chain length in any randomly cross-linked polymer. If the shortest chains receive the greatest stresses, which seems reasonable since there is less opportunity for self-relaxation of the stresses, these chains would break first and the average chain length would be continually increasing and likewise the sample volume would continue to swell. This is to be expected according to Flory's equation, for at small v_2 , $v_2 = \frac{K}{M_c^{3/5}}$. From a rate of swell determination M_c could also be calculated as a function of time from this equation.

As equilibrium swell and M_c assume the original network to be intact, v_2 is plotted against time in figure IV-C-6 (following page 92) and the linear portion is extrapolated to zero time and v_2 equaling 0.197.

Conclusions: The immersion tubes are capable of measuring volumes within a precision of ± 2 percent.

Size of the original sample (within the two-fold range employed) has no apparent effect on the rate of swell, and surface wetting of the sample during volume measurement does

not cause noticeable error. Subsequent measurements should use samples within the range of size of this test, preferably $3/4"$ x $.070"$ for greatest accuracy of measurement.

Rates of extraction must be considered in conjunction with rate of swell in order to determine v_2 as defined for Flory's equation for M_c .

Equilibrium v_2 for this silicone polymer compounded with 2 parts benzoyl peroxide per 100 parts of polymer and vulcanized by the above procedure is 0.197 for swelling in benzene at 25.0°C .

Breakdown of the silicone polymer network during swelling is probably caused by rupture of primary Si-O bonds rather than by depolymerization of the vulcanized cross-links.

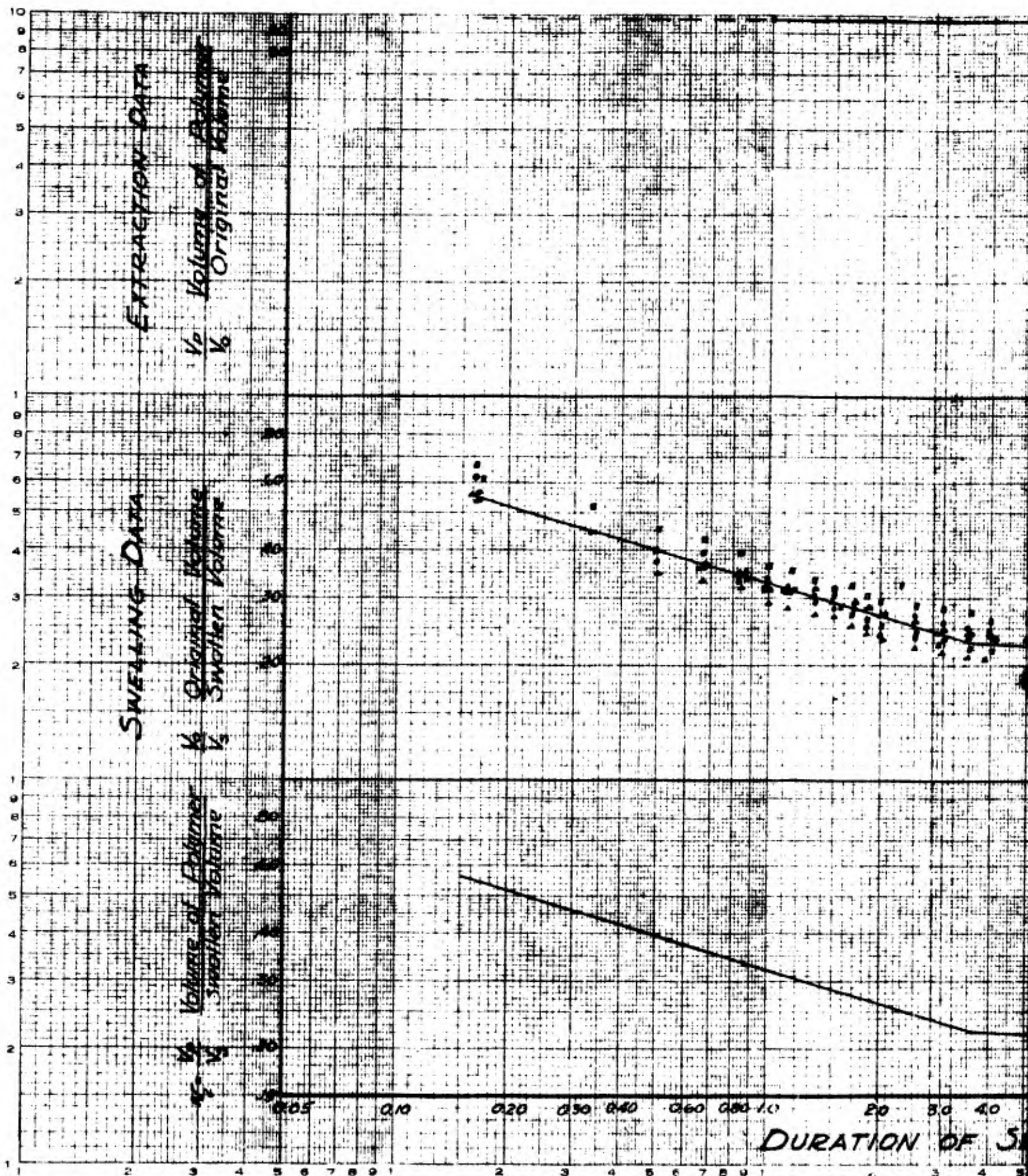


Fig. IV-C-1

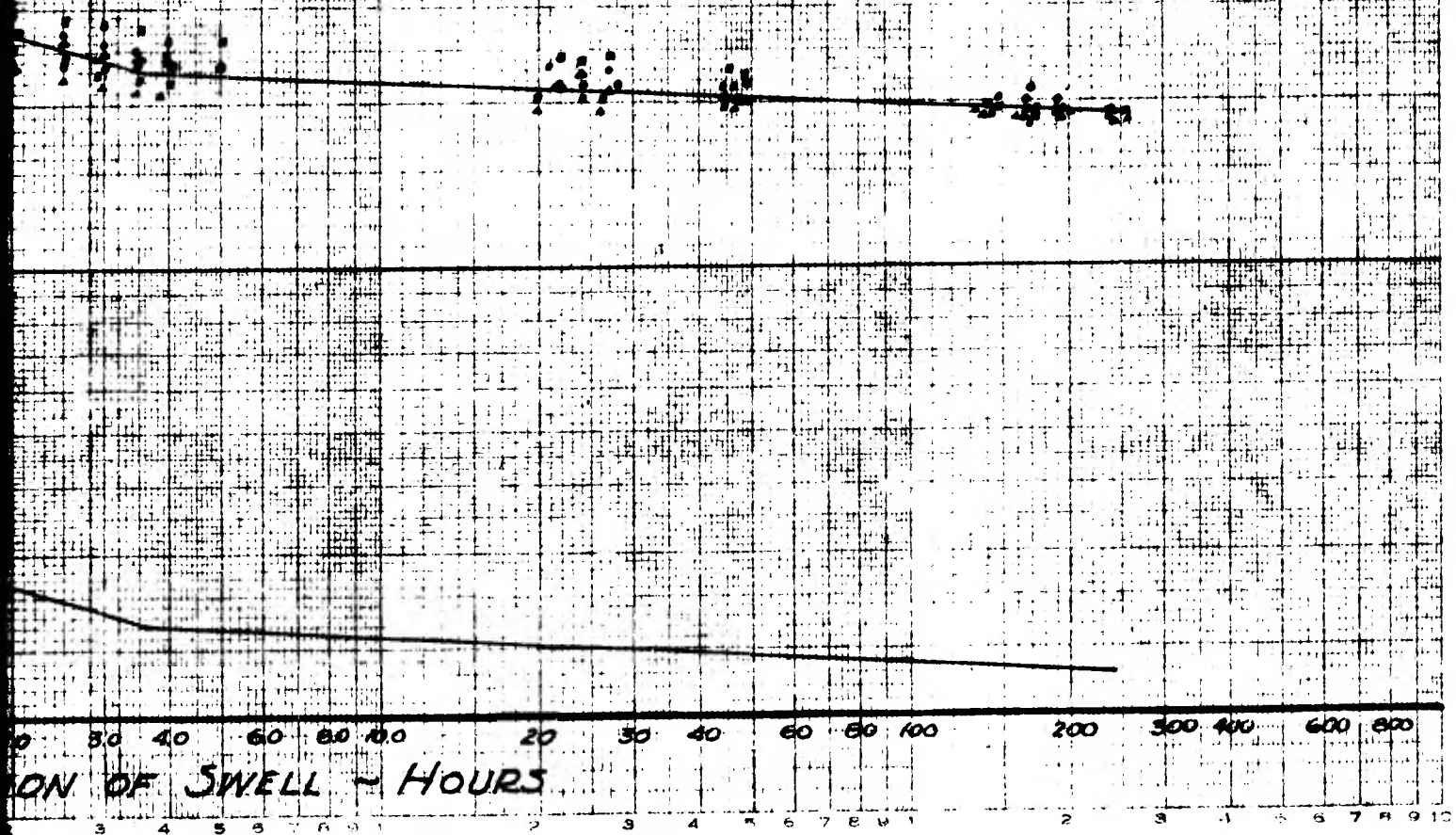
SWELL OF SILICONE RUBBER IN BENZENE

20 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER

PRESS CURE - 15 MINUTES - 250°F

OPEN CURE - 24 HOURS - 300°F

SAMPLE	SIZE
1a	$\frac{3}{8}$ " x $\frac{1}{4}$ " x 0.071"
1b	$\frac{3}{8}$ " x $\frac{1}{2}$ " x 0.070"
1c	$\frac{9}{16}$ " x $\frac{1}{4}$ " x 0.070"
1d	$\frac{9}{16}$ " x $\frac{1}{4}$ " x 0.070"
1e	$\frac{3}{4}$ " x $\frac{1}{4}$ " x 0.070"
1f	$\frac{3}{4}$ " x $\frac{1}{4}$ " x 0.069"



Test 2 - Secondary Swell of Silicone Elastomer.

Object: This test was conducted in order to determine the effect of previous swell and extraction on the rate of swell of silicone rubber and to determine, insofar as practicable, if a maximum swelling could be attained.

Procedure: Samples 1c, 1d, 1e and 1f, after having swelled for 238 hours in benzene and then de-swelled, were again placed in the immersion tubes in benzene at 25.0°C. for a determination of the secondary swelling characteristics. Original volumes of the samples, V_0 , were calculated from individual weights and from the density of samples 1a and 1b after swell and de-swell, 0.91 gm./c.c.

Volume measurements were taken over a period of 363 hours and then the samples with their solvent were placed in 2-ounce bottles which were sealed and placed in a constant temperature bath at 25.0°C. After a total immersion of 988 hours the samples were again placed in the immersion tubes and a small amount of solvent was added to each in order to replace that which had been lost by the transference. Several volume measurements were then made within the next 24 hours and the test was discontinued after a total immersion period of 1012 hours.

The samples were dried to constant weight in order to determine the extent of extraction during this test.

Results: Figure IV-C-2 (following page 89) presents rate of swell curves of this test and presents a comparison of

primary and secondary swelling curves. Primary swell presented two linear log-log relationships, but the rate of secondary swell is non-linear according to the average of the data (curves of two of the samples are linear, curves of the other two are not). However, there is fairly close comparison of trend of the two curves.

A more important correlation is shown on the graph of figure IV-C-3 where the time of secondary swell is added onto the 238 hours of primary swell. The secondary swelling curve corresponds closely to an extrapolation of the primary swelling curve up to the 1250-hour total.

Extraction of polymer during the 1012-hour period averaged 2.2 percent.

Conclusions: General Electric silicone polymer No. 81176 compounded with 2 parts benzoyl peroxide per 100 parts polymer and cured with 15 minutes at 250°F., high pressure, plus 24 hours at 300°F. will swell in benzene at 25.0°C. without attaining equilibrium in 1250 hours and the cross-linked network will partially break down permitting extraction of 8.3 percent of the polymer. It is very likely that swelling and breakdown of the polymer would proceed until complete solvation results in a period of possibly years.

Secondary swell proceeds at a rate differing slightly from primary swell.

After 1250 hours of swell in benzene at 25.0°C. for silicone polymer vulcanized as described in Test 1 v_2 is 0.169 $\pm$.003.

EXTRACTION DATA

$\frac{V_0}{V_s}$ VOLUME OF POLYMER / ORIGINAL VOLUME

SWELLING DATA

$\frac{V_0}{V_s}$ ORIGINAL VOLUME / SWOLLEN VOLUME

$\frac{V_0}{V_s}$ VOLUME OF POLYMER / SWOLLEN VOLUME

DURATION (t)

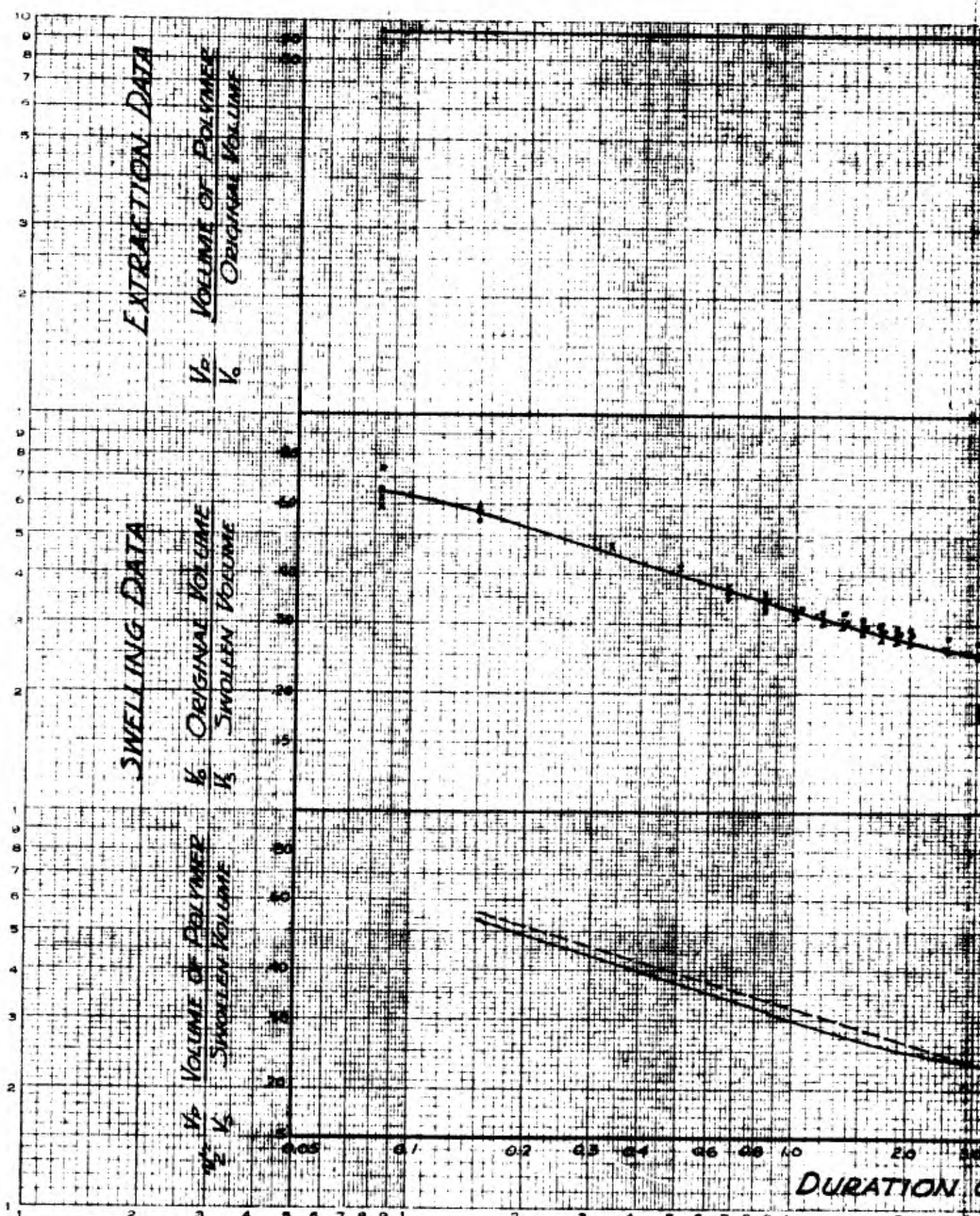


Fig. IV-C-2

SECONDARY SWELL OF SILICONE RUBBER IN BENZENE AT 25.0° C.

SAMPLE PREPARATION:

BENZOYL PEROXIDE - 2.0 PARTS

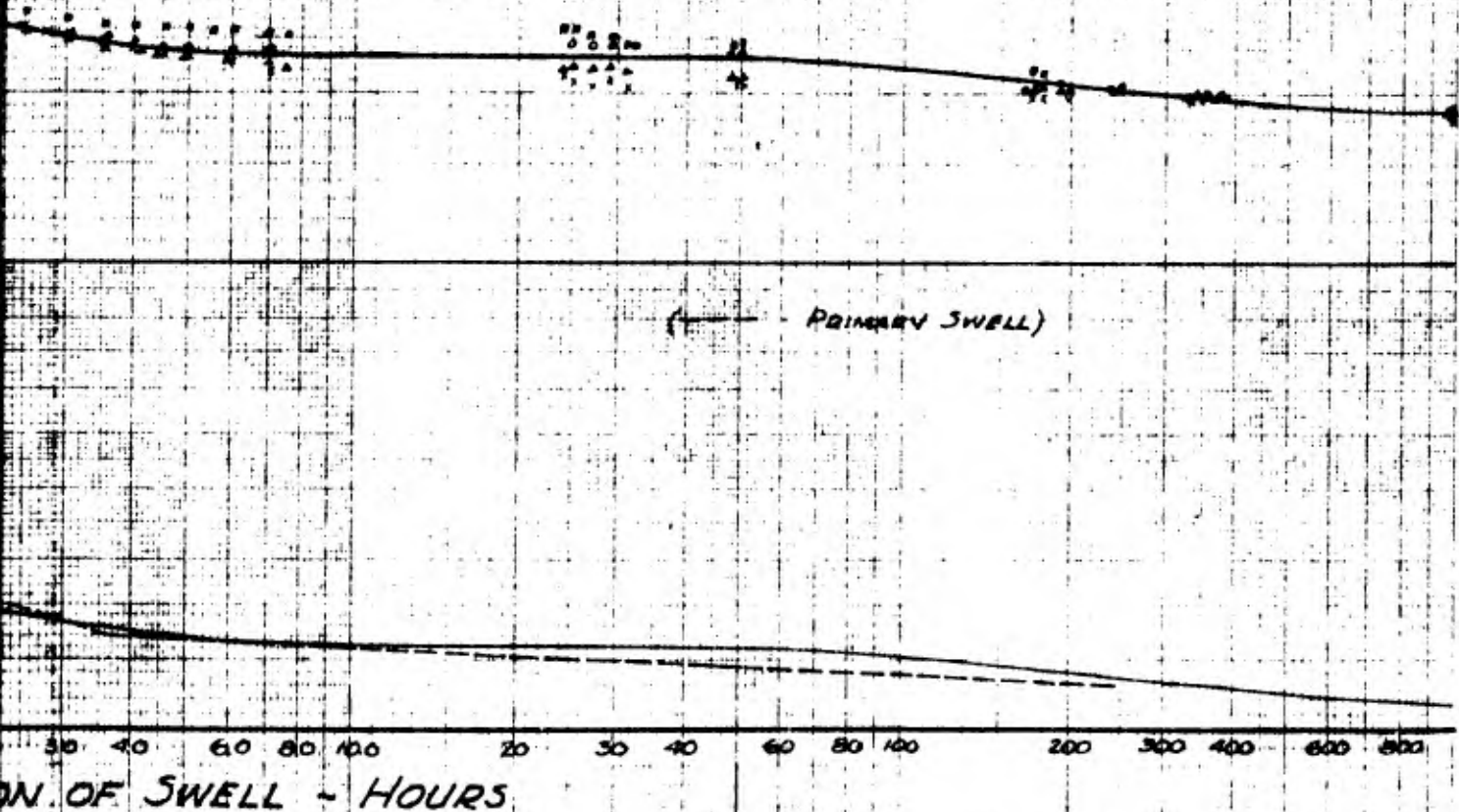
SILICONE POLYMER - 100 PARTS

PRESS CURE - 15 MINUTES - AT 250°F

OVEN CURE - 24 HOURS - AT 300°F

(PRIMARY SWELL - 238 HOURS. SAMPLE DRIED COMPLETELY
PRIOR TO SECONDARY SWELL.)

SAMPLE		SIZE
○	2a	3/16" x 1/4" x 0.070"
□	2b	3/16" x 1/4" x 0.070"
△	2c	3/4" x 1/4" x 0.070"
x	2d	3/4" x 1/4" x 0.069"



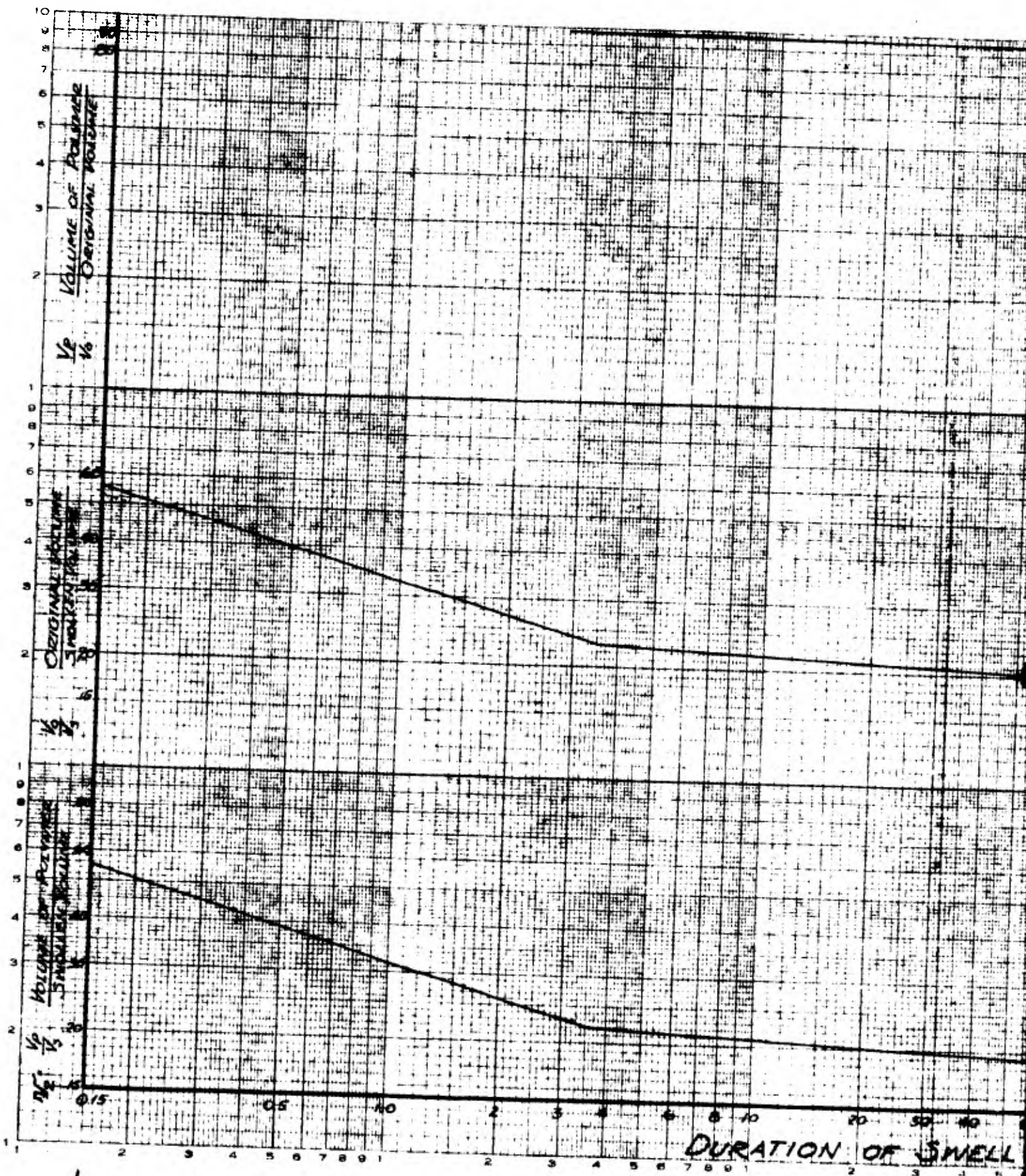


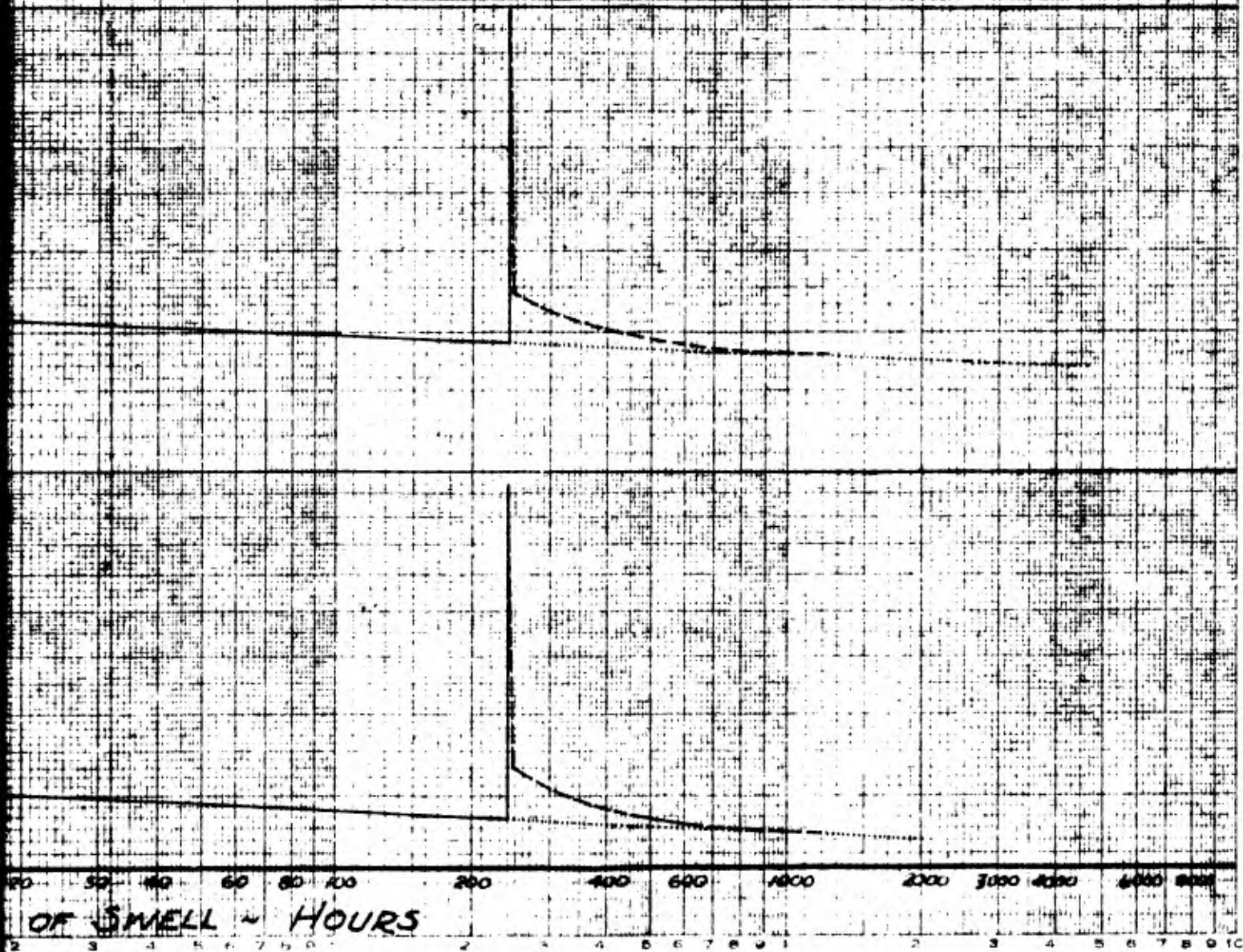
Fig. IV-C-3

CORRELATION OF PRIMARY AND SECONDARY SWELL OF SILICONE RUBBER IN BENZENE

SAMPLE
SILICON POLYMER - 100 PARTS
BENZOYL PEROXIDE - 2.0 PARTS
PRESS CURE - 15 MINUTES - 250°F
OVEN CURE - 24 HOURS - 300°F

COMPLETE DE-SWELL AFTER INITIAL 250 HOURS

— PRIMARY SWELL, AVERAGE OF SIX SAMPLES
..... EXTRAPOLATION OF PRIMARY SWELL CURVE
- - - SECONDARY SWELL, AVERAGE OF FOUR SAMPLES



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 two parts per 100 parts of polymer.

Procedure: Test samples 3a and 3i were prepared from slabs compounded with 0.5 and 8.0 parts of benzoyl peroxide per 100 parts of silicone polymer; milling and curing conditions were the same as in Test 1. For Test 3i, samples $3/4"$ x $1/4"$ x $.070"$ were used, but for samples of this size for Test 3a the swelling was so great that the sample size exceeded the dimensions of the immersion tubes; hence smaller samples were used as listed below:

3a₁ $1/2"$ x $1/4"$ x $.067"$
3a₂ $1/2"$ x $1/4"$ x $.067"$
3a₃ $1/2"$ x $3/16"$ x $.067"$
3a₄ $1/2"$ x $3/16"$ x $.067"$

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.

Results: Figures IV-C-4 and IV-C-5 following page 92 present log-log plots of the swelling data for samples 3a and 3i respectively.

In Test 3a the customary procedure of neglecting the effect of polymer extraction (considering $v_2 = V_0/V_s$ instead of V_p/V_s) would cause an anomaly of de-swell instead of continuing swell during the 20 to 175-hour period. The large amount of extraction in this case is an extreme, but it bears out the necessity of correlating the rate of extraction with the rate of swell in order to obtain v_2 accurately.

Distinct linear log-log relationships of v_2 with time were obtained as in Test 1, but the transition was not so abrupt. Comparison of Figures IV-C-4 and IV-C-5 reveals that the rate as well as the magnitude of swell varied considerably with benzoyl peroxide content.

Equilibrium swell as defined in Test 1 is determined in Figure IV-C-6 and the effect of benzoyl peroxide concentration is readily apparent. The results of Test 1, where 2 per cent of benzoyl peroxide was used, may be considered a portion of this test. Thus, the equilibrium values of v_2 for the three samples are:

Parts benzoyl peroxide per 100 parts polymer	v_2
0.5	0.085
2.0	0.198
8.0	0.231

Calculation of M_c values by Flory's equation will be possible after determination of the polymer-solvent interaction coefficients from other tests.

Conclusions: The swelling characteristics of silicone rubber are definitely a function of the amount of benzoyl peroxide used for vulcanization. However, proportionality of cross-linking with benzoyl peroxide concentration is unlikely considering the repetitive nature of the free-radical reaction; results of this test seem to indicate that direct proportionality does not occur, but proof awaits calculation of M_c .

LOGARITHMIC
3 CYCLE X 5 CYCLE

EXTRACTION DATA

$\frac{V_p}{V_0} = \frac{\text{VOLUME OF POLYMER}}{\text{ORIGINAL VOLUME}}$

0.88

0.8

0.75

0.7

0.65

0.6

0.55

0.5

0.45

0.4

0.35

0.3

0.25

0.2

0.15

0.1

0.05

0.02

0.01

0.005

0.002

0.001

0.05 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.0

20 30

DUR

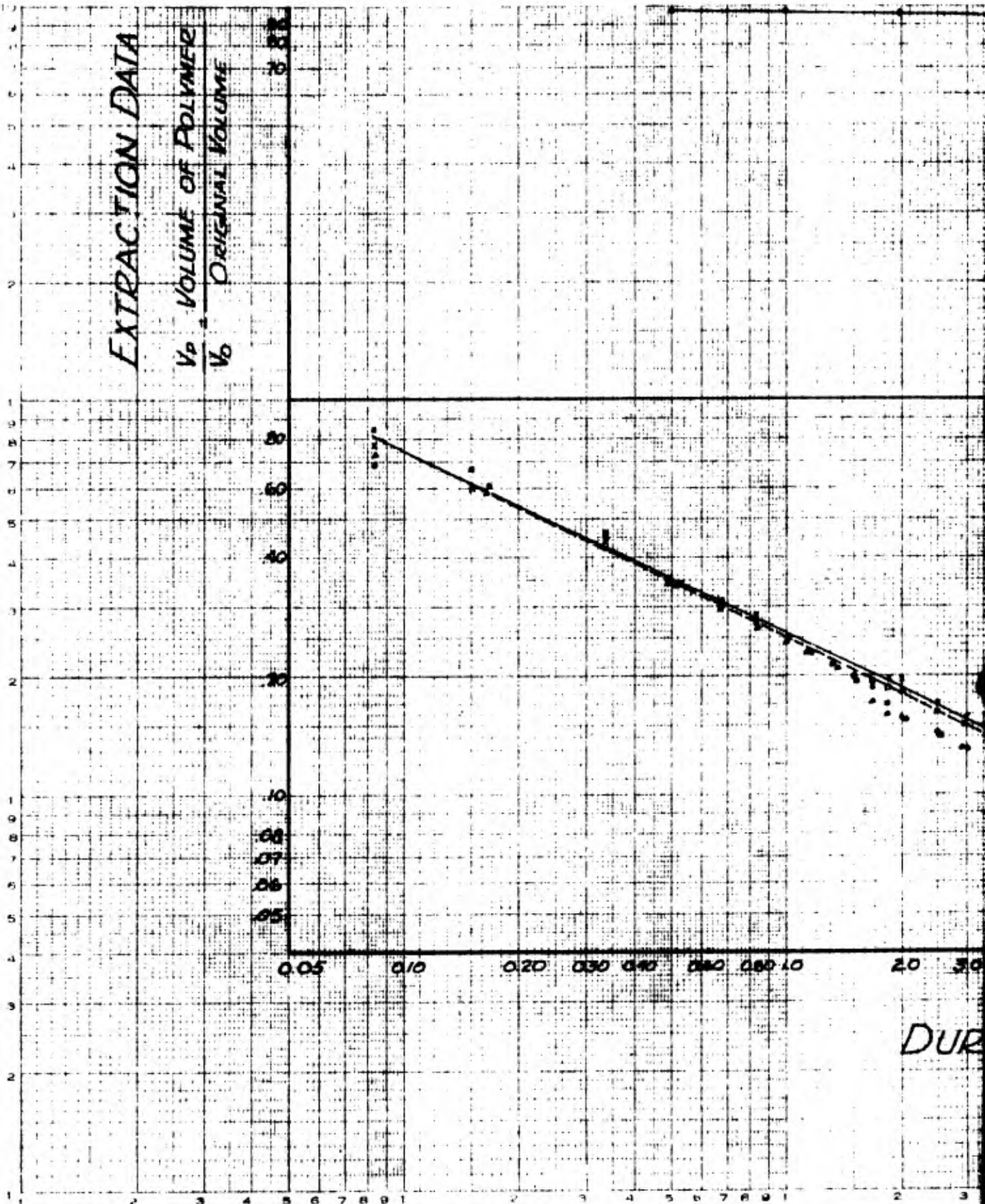
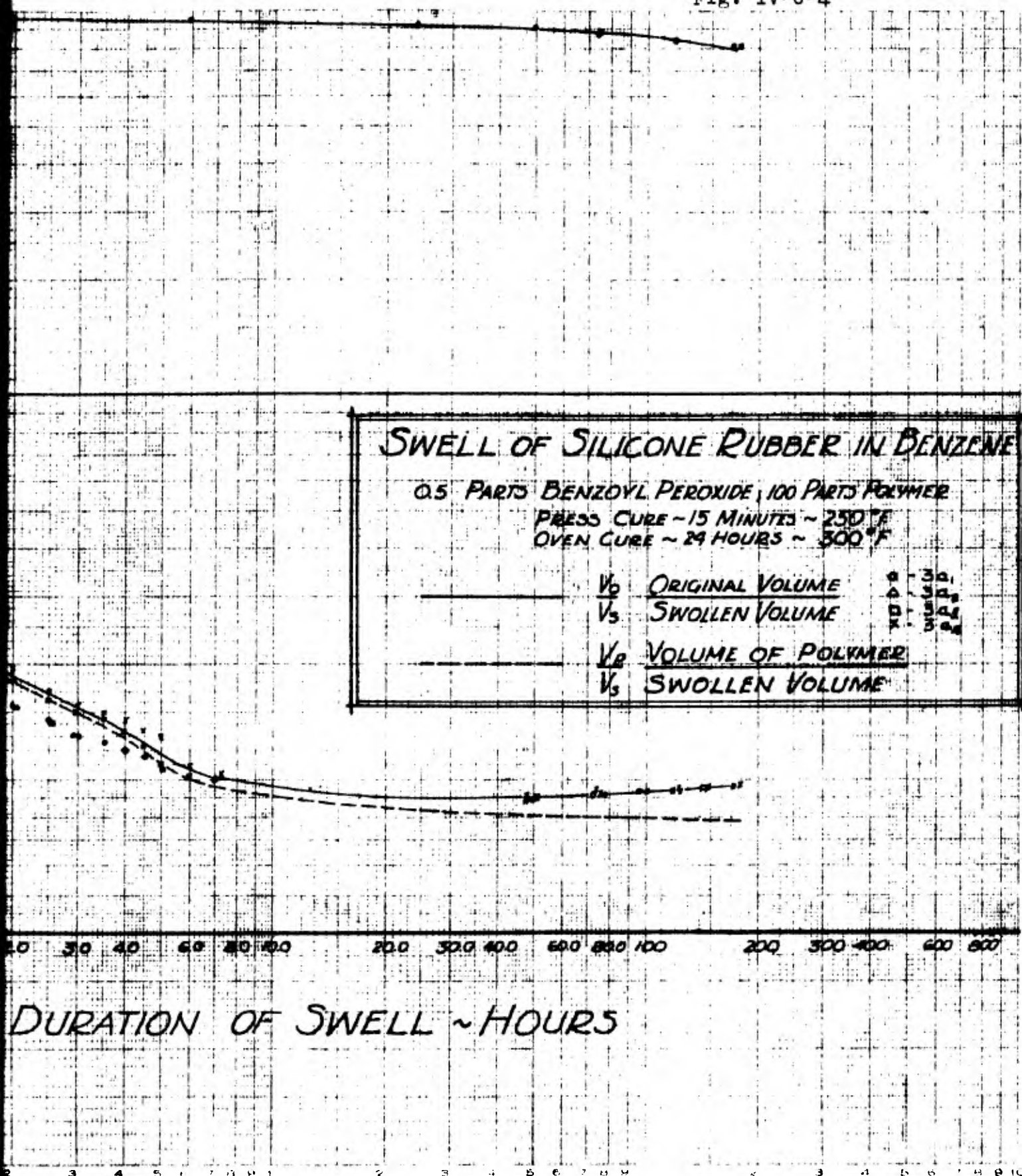


Fig. IV-C-4



EXTRACTION DATA

V_2 VOLUME OF POLYMER
 V_0 ORIGINAL VOLUME

SWELLING DATA

V_1 VOLUME OF POLYMER
 V_0 ORIGINAL VOLUME
 V_2 SWOLLEN VOLUME
 V_3 SWOLLEN VOLUME

V_1
 V_2

0.05

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1.0

1.1

1.2

1.3

1.4

1.5

1.6

1.7

1.8

1.9

2.0

2.1

2.2

2.3

2.4

2.5

2.6

2.7

2.8

2.9

3.0

3.1

3.2

3.3

3.4

3.5

3.6

3.7

3.8

3.9

4.0

4.1

4.2

4.3

4.4

4.5

4.6

4.7

4.8

4.9

5.0

5.1

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5.3

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5.5

5.6

5.7

5.8

5.9

6.0

6.1

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6.3

6.4

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6.6

6.7

6.8

6.9

7.0

7.1

7.2

7.3

7.4

7.5

7.6

7.7

7.8

7.9

8.0

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8.6

8.7

8.8

8.9

9.0

9.1

9.2

9.3

9.4

9.5

9.6

9.7

9.8

9.9

10.0

10.1

10.2

10.3

10.4

10.5

10.6

10.7

10.8

10.9

11.0

11.1

11.2

11.3

11.4

11.5

11.6

11.7

11.8

11.9

12.0

12.1

12.2

12.3

12.4

12.5

12.6

12.7

12.8

12.9

13.0

13.1

13.2

13.3

13.4

13.5

13.6

13.7

13.8

13.9

14.0

14.1

14.2

14.3

14.4

14.5

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14.8

14.9

15.0

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16.0

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17.0

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18.0

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18.7

18.8

18.9

19.0

19.1

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19.9

20.0

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20.9

21.0

21.1

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21.8

21.9

22.0

22.1

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23.0

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24.8

24.9

25.0

25.1

25.2

25.3

25.4

25.5

25.6

25.7

25.8

25.9

26.0

26.1

26.2

26.3

26.4

26.5

26.6

26.7

26.8

26.9

27.0

27.1

27.2

27.3

27.4

27.5

27.6

27.7

27.8

27.9

28.0

28.1

28.2

28.3

28.4

28.5

28.6

28.7

28.8

28.9

29.0

29.1

29.2

29.3

29.4

29.5

Fig. IV-C-5

SWELL OF SILICONE RUBBER IN BENZENE

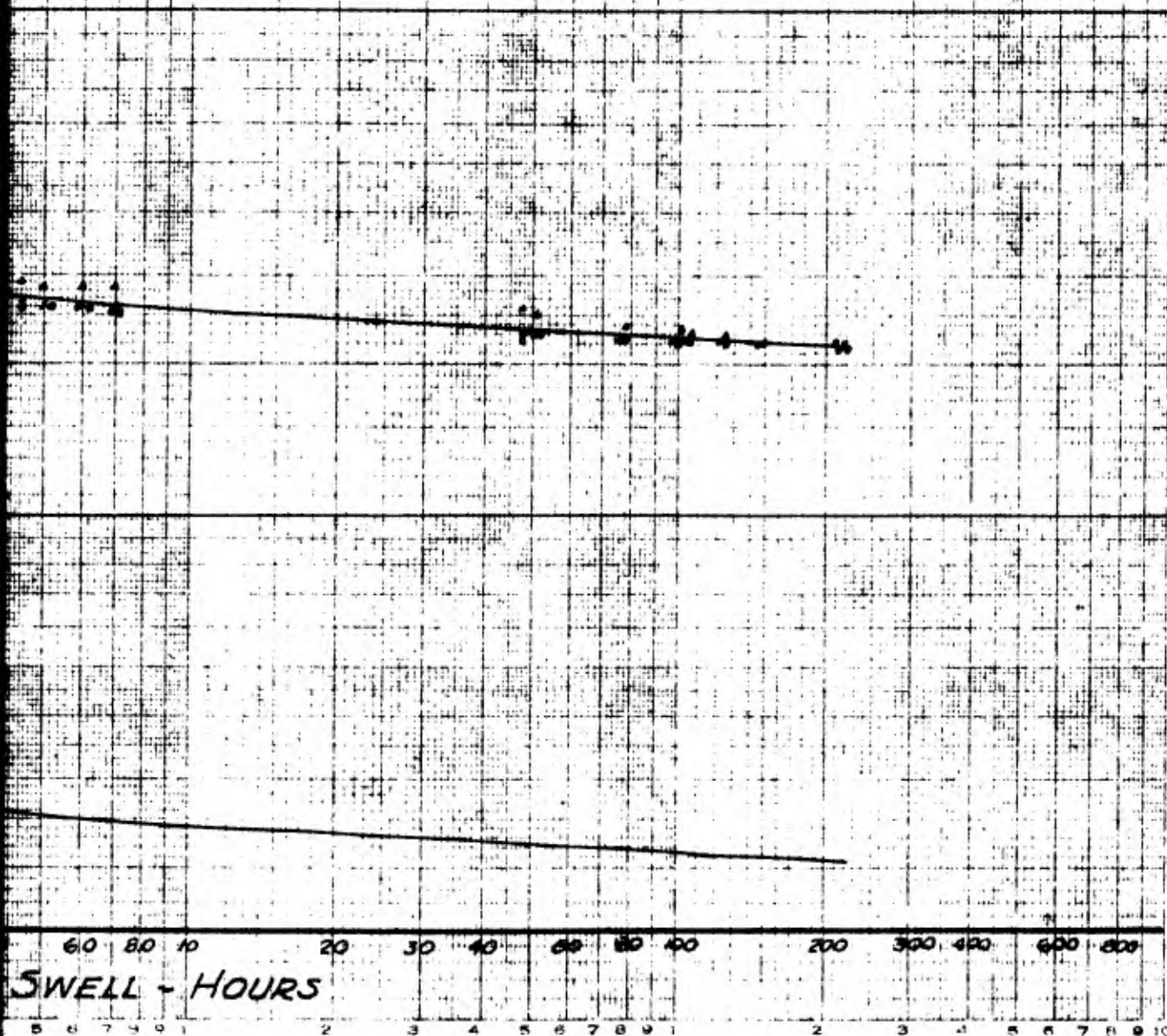
8.0 PARTS BENZOYL PEROXIDE, 100 PARTS POLYMER

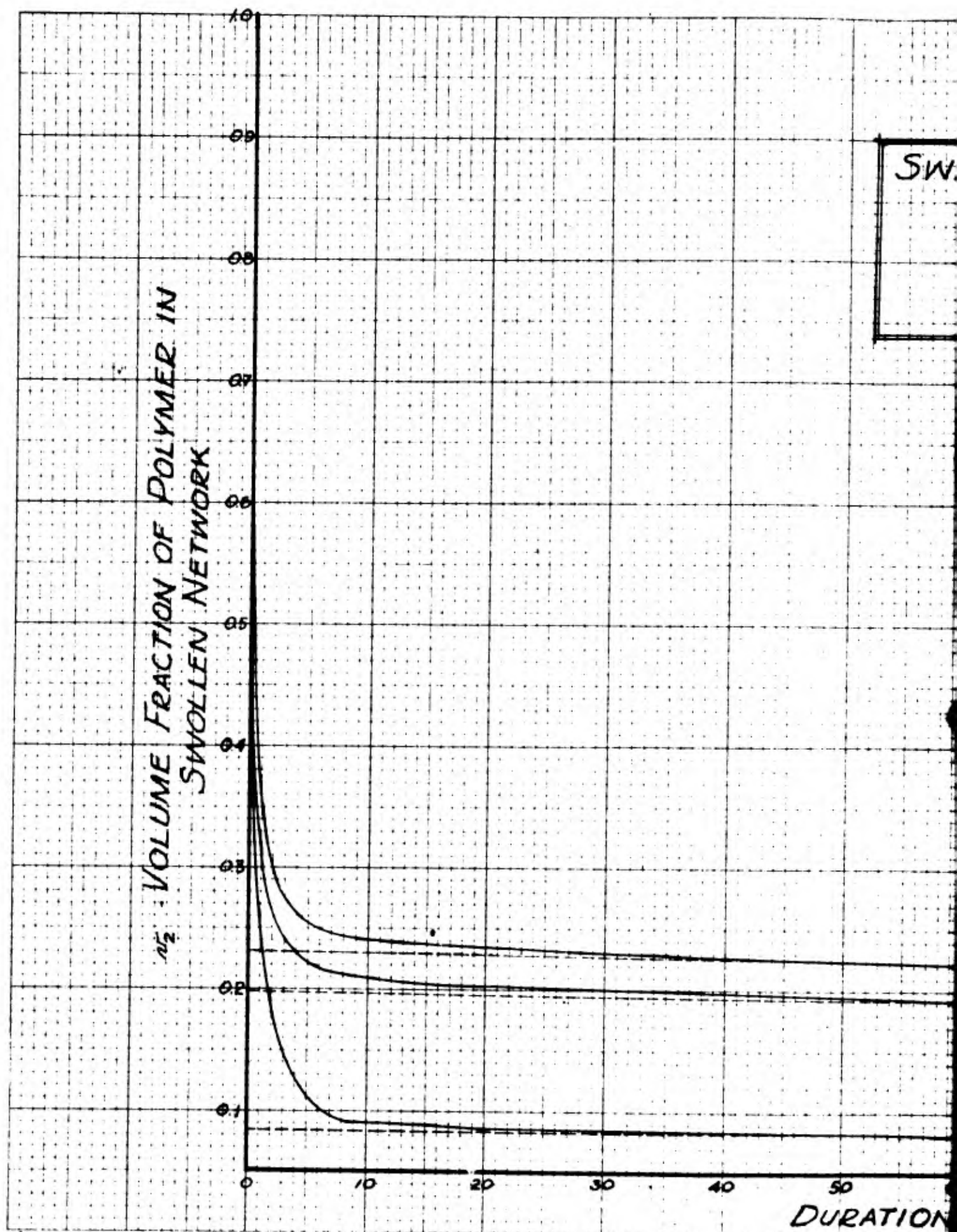
PRESS CURE - 15 MINUTES - 250°F

OVEN CURE - 24 HOURS - 300°F

SAMPLE

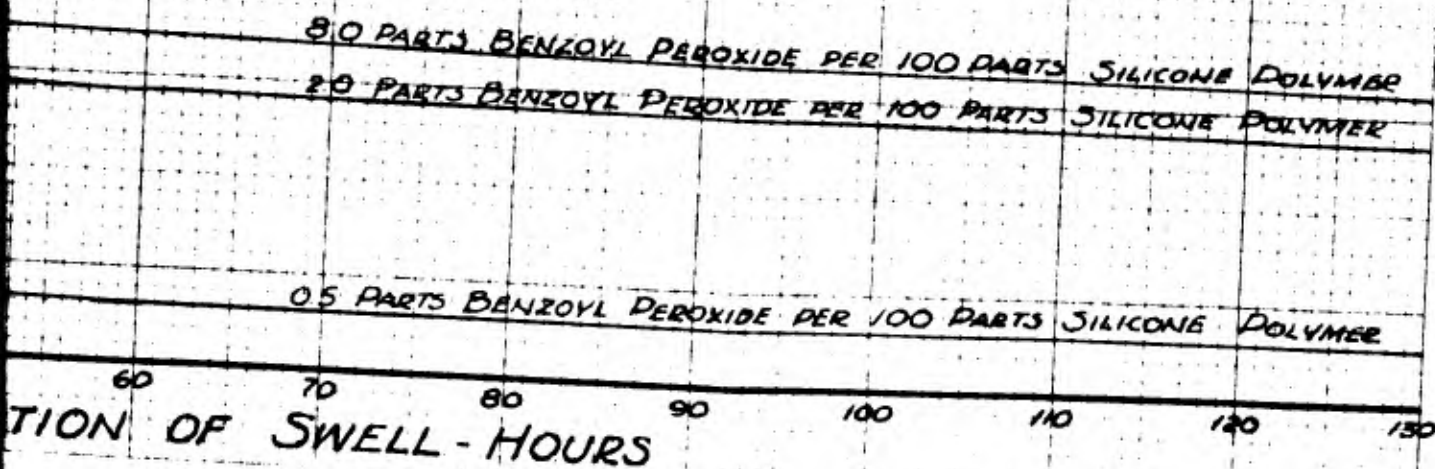
■ - 8m	▲ - 8r
● - 8n	□ - 8p 3 ₁
x - 8o	○ - 8q 3 ₂





SWELL OF SILICONE RUBBER IN BENZENE AT 25.0°C. VARIED BENZOYL PEROXIDE CONTENT

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



Test 8 - Rate of Extraction of Silicone Polymer from a
Vulcanized Network

Object: After it became apparent from Test 1 that extraction of polymer was indivisible from swelling determinations, this test was devised for the purpose of determining rates of extraction from various samples of silicone polymer.

Procedure: Samples of silicone elastomer $3/4"$ x $1/4"$ x $.070"$ compounded with 0.5, 2.0 and 8.0 parts of benzoyl peroxide per 100 parts of polymer were used for extraction measurements in benzene. The samples were cut from the same slabs that were swelled in Tests 1 and 3.

Samples were weighed and then placed within the immersion tubes with approximately 8 c.c. of benzene at 25.0°C . Volume measurements were made at frequent intervals to simulate the same agitation of solvent as occurred in the swelling tests. (Data for sample 31 obtained from these volume measurements was included in Figure IV-C-5.) Samples were removed after desired periods of immersion and dried to constant weight. Percent loss of weight was then calculated.

The solvent from Test 8 (sample 31 immersed in benzene for 125 hours) was analyzed by NaOH titration for the presence of benzoic acid which might have been present in the sample resulting from decomposition of the benzoyl peroxide curing agent.

Because of the small amount of solvent employed in these extractions and the finite concentration of polymer in solution (which retarded approach to equilibrium extraction), a

further investigation was undertaken using a Soxhlet extractor with about 200 c.c. of pure benzene. These extractions, most cycles consisting of 17.3 hours at 53°C. plus 32.7 hours at 20°C. are not directly comparable to the determinations using the immersion tubes. Nevertheless, this method of extraction would facilitate attainment of equilibrium, if possible, because of the large amount of solvent, constant recirculation, and higher temperature during part of the cycle. Results: Data for the immersion tube extractions is presented in Figure IV-C-7 following page 96 in the form of log-log plots of percent extraction vs. time, which are approximately linear in the range measured. These data were transferred to Figures IV-C-1, 2, 5, and 6 as V_p/V_o , the sample volume at any time divided by the original sample volume. Constant polymer density was assumed.

No detectable amount of benzoic acid was extracted from sample 8 during the 125 hours of immersion in benzene.

Results obtained from the Soxhlet extraction are presented in Table IV-C-1.

Conclusions: A comparison of extraction rates reveals a considerably greater difference between samples vulcanized with 0.5 and 2 per cent benzoyl peroxide than between 2.0 and 8.0 percent, indicating a decreased effectiveness of the cross-linking agent when used in high concentrations.

It is probable that some of the extraction is due to polymer that is not cross-linked into the network and is hence completely soluble. The remainder, however, may be attributed to breakdown of the cross-linked network in benzene, and breakdown may be a continuous process until complete solvation is reached.

Since no benzoic acid was present in a sample compounded with 8.0 parts of benzoyl peroxide per 100 parts of polymer, it may be concluded that there is no benzoic acid present in other samples prepared with smaller concentrations of benzoyl peroxide.

Soxhlet extractions using a large volume of pure solvent do not reach equilibrium even after 350 hours of immersion. It cannot be assumed, however, that repeated immersion periods, such as in this test, give the same effect as continuous immersion.

TABLE IV-C-1

Soxhlet Extraction of Silicone Polymer with Benzene

Period of Extraction	Duration of Extraction		Total Percent of Polymer Extracted			
	50°C.	Hours at 20°C.	Total Duration of Extraction Hours.			
			3a	3b	3c	3i
			Parts Benzoyl peroxide			
1	17.3	32.7	14.5	6.15	4.43	4.20
2	17.3	32.7	17.7	7.39	5.23	5.12
3	17.3	32.7	19.4	8.04	5.56	5.50
4	30.3	19.7	20.9	8.50	5.84	5.74
5	17.3	32.7	21.7	8.74	5.97	5.93
6	22.7	27.3	22.9	9.06	6.11	6.04
7	25.3	24.7	23.4	9.30	6.17	6.07

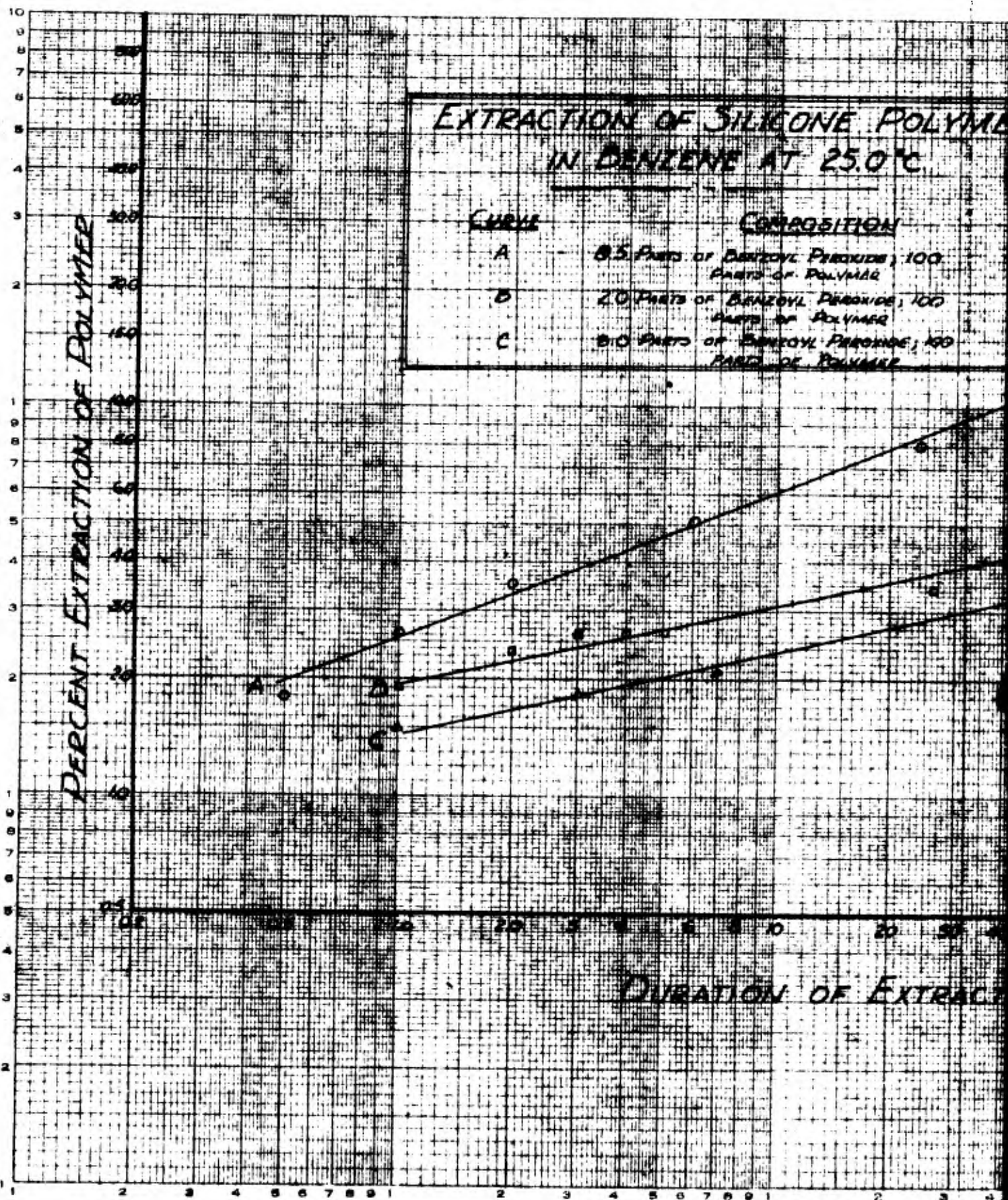
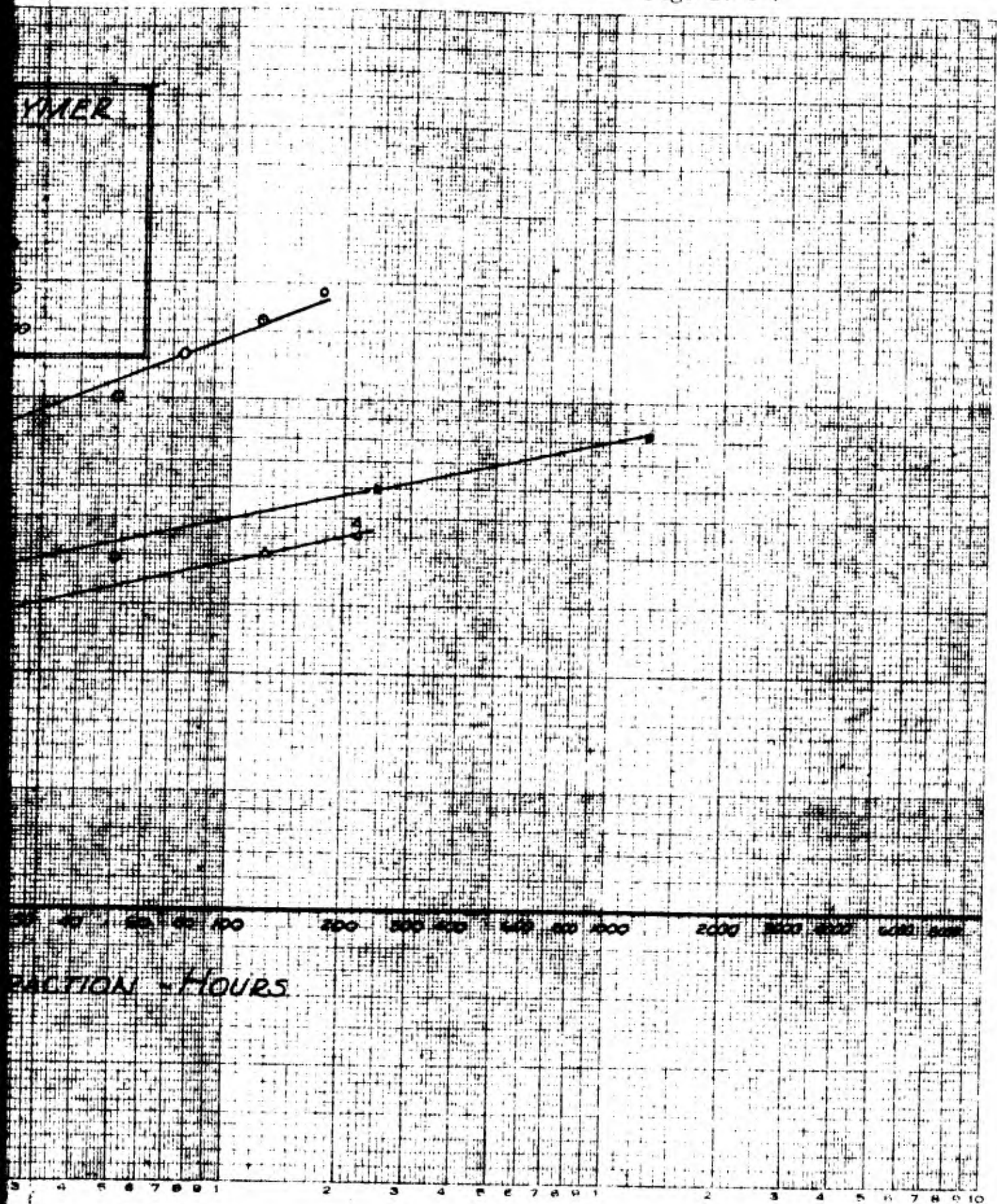


Fig. IV-C-7



V. STRUCTURE OF 81176 SILICONE RUBBER.

This section summarizes the findings of recent infrared analysis carried out on samples of depolymerized 81176 silicone gum (General Electric SE-76) and compares the results obtained by a new micro-analysis of the silicone gum with those obtained earlier.

A. Object.

The object of this work was (1) to investigate specifically the nature of the substitution on the silicon atom and (2) to determine whether the fundamental silicone backbone of the polymer in question contains periodic $\text{-}\overset{|}{\underset{|}{\text{Si}}}\text{-CH}_2\text{-}\overset{|}{\underset{|}{\text{Si}}}\text{-}$ groupings rather than continuous $\text{-}\overset{|}{\underset{|}{\text{Si}}}\text{-O-}\overset{|}{\underset{|}{\text{Si}}}\text{-}$ linkages.

B. Experimental.

The procedure followed by Dr. Harry H. Wasserman when conducting infrared analysis of the HCl depolymerized 81176 gum was the same as that employed earlier (see Progress Report No. 8), but the concentration of the samples examined was considerably lower (0.15 percent instead of 2 percent).

A sample of 81176 (General Electric SE-76, batch 7155) was sent to the Microchemical Laboratory of the Massachusetts Institute of Technology, Cambridge, Massachusetts, for carbon, hydrogen and silicon analysis.

C. Summary of Results.

Interpretation of the spectra obtained by conducting infrared analysis of the HCl depolymerized 81176 samples at low concentration (0.15 percent) in carbon tetrachloride showed (1) the principal type of

substitution on the silicon atom in the siloxane chain to be methyl and (2) there is no evidence of $-\overset{|}{\underset{|}{\text{Si}}}-\text{CH}_2-\overset{|}{\underset{|}{\text{Si}}}-$ groupings in the chain.

The results obtained from the recent microanalysis of the same polymer corroborated the above-mentioned interpretation of the structure of 81176.

TABLE V-C-1

Analysis of 81176

	$(\text{CH}_3)_2\text{SiO}-$	$[(\text{CH}_3)_2\text{SiO}(\text{CH}_3)_2\text{Si}-\text{CH}_2]$		
	<u>Calculated</u>	<u>Calculated</u>	<u>Found ¹</u>	<u>Found ²</u>
Carbon	32.39	41.01	32.41	40.27
Hydrogen	8.16	9.64	8.14	10.40
Silicon	37.85	38.42	37.62	38.48
Oxygen (by dif- ference)	<u>21.59</u>	<u>10.93</u>	<u>21.83</u>	<u>10.85</u>
	100.00	100.00	100.00	100.00

¹ Analysis done at the Massachusetts Institute of Technology.

² Previous analysis, reported in Progress Report No. 8.

D. Discussion.

The lowering of the concentration of the samples used for the infrared analysis did not change the results obtained from earlier similar work. This analysis showed no evidence of the presence of $-\text{CH}_2-$ groups in the polymer chain. Had they been present, they would have showed up at the low dilution of the solution used.

A substantial difference was present between the earlier micro-analysis and the more recent analysis done at the Massachusetts Institute of Technology. The latest values agree almost perfectly with the values calculated for the simple dimethylsiloxane, while the earlier results not only disagree with the calculated values for a methyl siloxane

chain but are in poor agreement also with the calculated values for a silicone chain containing alternate $-\overset{|}{\underset{|}{\text{Si}}}-\text{CH}_2-\overset{|}{\underset{|}{\text{Si}}}-$ groupings.

E. Conclusion.

From the evidence obtained by infrared and microchemical analysis, the General Electric SE-76 silicone polymer appears to be essentially a dimethylsiloxane polymer.

APPENDIX I *GS-199S in Elastomers.GS-199S in Natural Rubber:

Formulation:

Smoked Sheet	100 parts by weight
Stearic Acid	1 part by weight
Sulfur	3 parts by weight
Zinc Oxide	5 parts by weight
"Neozone A" Antioxidant	1 part by weight
GS-199S Silica	60 parts by weight
MBTS	2 parts by weight
Thiuram M.	0.1 parts by weight
Cured @ 287°F.	15 min.

Properties:

Tensile	5000 psi
Tear (crescent)	1005 #/in.
Modulus (300%)	825 psi
Elongation of Break	800%
Hardness (shore)	80

GS-199S in Standard GR-S Rubber:

Formulation:

GR-S Standard	100 parts by weight
"Neozone A" Antioxidant	1 part by weight
GS-199S	60 parts by weight
Zinc Oxide	5 parts by weight
Sulfur	3 parts by weight
MBTS	1.2 parts by weight
Thiuram M.	0.15 parts by weight
Cumar MH 2-1/2 Resin	10 parts by weight
Ethylene Glycol	3.5 parts by weight
Cure Time	20 min.

Properties:

Tensile	3390 psi
Tear (crescent)	330 #/in.
Modulus (300%)	610 psi
Elongation at Break	700%
Hardness (shore)	81

* Supplied by E. I. DuPont De Nemours & Co. in September 1951.

GS-199S in Cold GR-S Rubber:

Formulation:

GRS X-478	100 parts by weight
Neozone	1
GS-199S	40
Zinc Oxide	5
Sulfur	3
MBTS	0.3
Thionex	0.3
"Cumar MH" 2-1/2 Resin	10
Ethylene Glycol	3.5
Cure Time	10 min.

Properties:

Tensile	3260 psi
Tear (Crescent)	220 #/in.
Modulus (300%)	425 psi
Elongation at Break	680%
Hardness (shore)	70

GS-199S in Neoprene GN:

Formulation:

Neoprene GN	100	100	100	100
Magnesia	8	8	4	4
Zinc Oxide	2	2	5	5
Stearic Acid	0.5	2	0.5	0.5
GS-199	40	40	40	40
"Neozone" Antioxidant			2	2
"Circo" Light Oil				15

Properties:

Tensile	4350 psi	4350	4690	3650
Elongation at Break	810	820	260	1020
Hardness (shore)	86	85	82	70
Tear (crescent)	670#/in	600	595	447
Modulus (300%)	1170	1100	940	600

Yellow Test Piece

Formulation:

Neoprene W	100 parts by weight
TiO ₂	2.5
Yellow GD	1
Antioxidant 2246	2
Zinc Oxide	5
NA-22	1
MgO	4
Stearic acid	0.5
GS-199S Silica	40
Cure Time @ 287°F.	30 min.

Properties:

Tensile	4675 psi
Tear (crescent)	625 #/in.
Modulus (300%)	930 psi
Elongation at Break	1000%
Hardness (shore)	76

TESTS CONDUCTED BY:

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ChemistL. C. ScalaL. C. Scala
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SUPPLEMENTARY

INFORMATION

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1 February 1970

IDENTIFICATION	FORMER STATEMENT	NEW STATEMENT	AUTHORITY
AD-494 887 Connecticut Hard Rubber Co., New Haven. Progress rept. no. 10, 5 Sep-4 Dec 51. 8 May 52 Contract DA-44-109- QM-64	DDC users only.	No limitation	USAMC ltr, 19 Jun 69