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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

JUNE 5, 1950 to SEPTEMBER 4, 1950

[P. R. 5]

CONNECTICUT HARD RUBBER COMPANY
NEW HAVEN, CONNECTICUT

Copy 38

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for ALBERT E. HINDMARSH
Captain, USN
Deputy Director, Security

THE CONNECTICUT HARD RUBBER COMPANY   NEW HAVEN, CONNECTICUT

DEVELOPMENT OF SILICONE RUBBERS
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Progress Report for the Period
June 5, 1950 - September 4, 1950

[redacted]

December 11, 1950

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SUMMARY

The immediate objective of the investigations carried on under this contract has been the improvement of currently available silicone elastomers so that they can be used in preparing a rubber serviceable at extremely low temperatures. Our approach has been directed along two fundamental lines: we have, first of all, sought to secure the maximum reinforcement of the silicone gums now produced commercially, and secondly, have studied methods of modifying these elastomers chemically to obtain a base polymer with improved physical properties.

Pigment Studies

In previous reports we have outlined physical test results indicating the reinforcement obtainable by incorporating a series of pigments as received and after treatment. Other variables that were studied were loading conditions, mixtures of pigments and curing agents. All such previous results were based on stocks compounded on a conventional rubber mill. We are here reporting results obtainable by the use of the liquified silicone gum as the base polymer - reinforced by Celite 505. The essential features of this method of incorporating pigment involve the following steps:

1. Liquifaction (depolymerization) of shredded silicone gum by exposure to dry HCl (or other acids) for approximately 12 hours.

2. Dispersion of the pigment in sufficient solvent, (carbon tetrachloride) to permit an intimate mixing of pigment and liquified gum in a suitable mixing apparatus (Waring Blendor).

3. Addition of the required quantity of depolymerized gum with vigorous mixing (5 minutes).

4. Regeneration of the elastomer - pigment mixture, after solvent removal, by gentle heating.

Summarized below are physical test results of compounds prepared by the above technique and cured with benzoyl peroxide. These investigations have all been carried out using General Electric silicone gum 9979-G as the base polymer. This gum is the only currently and commercially available uncompounded silicone elastomer which shows promise as a starting material in preparing silicone rubber compounds. Hence, this is the only silicone polymer which has been subjected to our program of chemical modification. The physical properties of representative compounds follows:

Compound		Mill Compounding	Liquid Dispersion
75 parts Celite 505 per 100 parts gum	Tensile Strength psi	300	540
	Elongation, %	100	110
	Hardness, Shore A	55	65
58 parts (25 vol) Celite 505 per 100 parts gum	Tensile Strength,psi	220	425
	Elongation, %	120	155
	Hardness, Shore A	46	50

The above results indicate that the technique of incorporating the pigment into the gum has a marked effect on the physical properties of the resulting stocks. The same pigment when dispersed in the liquified gum gives compounds having twice the tensile strength of milled compounds.

Electron Microscope Studies

Electron micrographs have been taken of nearly all the pigments used in the compounding program in order to determine the role of particle size, particle shape and degree of agglomeration in silicone rubber reinforcement. Pictures of cured rubber specimens have been taken using the "vulcanization technique" and comparison studies with hydrocarbon rubber compounds have been made. From our work up to this point the following facts appear to be of significance:

1. On a microscopic scale the dispersion of pigment particles in the silicone rubber is by no means uniform.

2. Agglomeration of pigments is the rule rather than the exception.

An important line of attack on the reinforcement problem will be electron microscope studies of samples having improved physical properties due, very probably, to a better dispersion of the pigment when it is incorporated into the depolymerized gum.

Electrostatic Studies on Silicone Rubber

The study on the electrostatic properties of silicone rubber has been undertaken in collaboration with Dr. R. S. Havenhill of the St. Joseph Lead Company. Samples of a large number of silicone rubber stocks have been supplied for this work and Dr. Havenhill expects to have a detailed report of his findings for our next Progress Report.

Wetting or Dispersing Agents

A number of compounds have been incorporated into the depolymerized silicone gum or have been used in water solutions as the hydrolysis media for dimethyldichlorosilane to ascertain whether the reaction products might have useful properties as a wetting or dispersing agent in bonding pigment to the silicone matrix. In general these compounds should have a siloxane backbone with polar terminal groups.

The products of these reactions were tested by being compounded in standard stocks in concentrations of one to five percent of the weight of the silicone gum. Of the materials tested those containing glycerol appeared to give the most promising improvement in the physical properties of the cured stocks.

Chlorination of Silicone Gum

By passing dry chlorine into the depolymerized silicone gum in the presence of ultraviolet light, hydrogen atoms have been replaced by chlorine atoms. The degree of halogenation was controlled so as to vary the amount of chlorine introduced. After regeneration these stocks were compounded with Celite 505. The physical test results on these stocks show an increase in tensile strength, along with an increase in hardness. These increases are accompanied by corresponding decreases in elongation. Curing studies made on various stocks indicate that a much less severe oven cure is necessary to develop the optimum physical properties. The heat aging characteristics of these stocks probably suffer as a result of this faster curing.

The Action of Ammonia on Depolymerized Gum

The introduction of ammonia into depolymerized silicone gum with the subsequent removal of ammonium chloride results in an oily product which has properties differing appreciably from the liquified gum. This oil is quite stable compared to the depolymerized gum used as the starting material. The ammonia - stabilized liquid readily reverts to a gum in the presence of acidic reagents such as dry HCl, thionyl chloride and benzoyl chloride. The heating of this liquid under pressure yields a sticky gum with excellent adhesive properties.

Silicone - Polyvinyl Alcohol Mixtures

Tough films are formed from the hydrolysis of dimethyldichlorosilane in mixtures of polyvinyl-alcohol and water. The slurry from this hydrolysis yielded thin films on air drying. These films resist aromatic solvents and carbon tetrachloride. They char at 212°F and crack at -40°F.

INTRODUCTION

Some Considerations Bearing on the Low Tensile Strength of the Silicone Elastomers.

Silicone rubber is an elastomer composed of a backbone silicone polymer which, when compounded with a reinforcing filler and cured with a suitable cross-linking agent, yields stocks retaining their rubber-like properties at temperatures 200°F. higher and 30°F. lower than currently available hydrocarbon rubbers.

Recent studies by the Bureau of Standards (1) on the second order transition temperatures of various silicone rubbers has shown that whereas hydrocarbon rubbers are seldom useful below -70°F., all silicone rubber samples undergo second order transition at temperatures about -194°F. and are useful in the range -70°F. to -130° F. These studies showed that there was essentially no difference in second order transition temperatures among pure gum silicones, silicon-containing elastomers with filler and curing agent incorporated, and fully vulcanized stocks. In contrast to the behavior of natural rubber (2), fillers and vulcanization agents appear

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(1) Weir, C. E., Leser, W. H., and Wood, L. A., "Crystallization and Second-Order Transitions in Silicone Rubbers", Technical Report No. 3 to the Office of Naval Research, National Bureau of Standards, December 15, 1949.

(2) Boyer and Spencer, "Second-order Transition Effects in Rubber and Other High Polymers", Advances in Colloid Sciences, Vol. II, Chapter I, Monk, H., and Whitby, G. S., Interscience Publishers, Inc., New York (1946)

to have very little effect on the transition temperature below which the molecular motion responsible for the useful properties of silicone rubber ceases.

Because of their remarkable low temperature performance, the silicone rubbers, originally developed for high temperature applications, are potentially better for use under conditions of extreme cold than any other synthetic or natural rubber thus far studied. However, as ordinarily made, their usefulness as rubbers has been limited by their low tensile strength and low abrasion resistance.

In the early work on the silicones, the low tensile strength of the gums and rubbers had been ascribed to low molecular weight of the siloxane units. The process of forming the polymer usually involves a two-stage condensation in which cyclic intermediates are opened to form long chain siloxane networks. There is possible a wide distribution in molecular weight of the units thus formed (3). Two independent measurements of the average molecular weight in silicone rubber have shown, however, that very large molecules indeed are involved.

Scott (4) determined the molecular weight of a silicone elastomer by osmotic pressure measurements of a dilute ethyl

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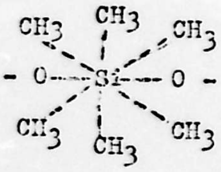
(3) A source of weakness in the silicone elastomer is probably due to the presence, in the gum, of a certain amount of low molecular weight oil carried along as an impurity in the polymerization process. A definite improvement in the existing commercial gums could be effected by cleaning out such impurities through methods such as solvent fractionation or distillation with superheated steam.

(4) Scott, D. W., Journal of American Chemical Society, <u>68</u>, 1877 (1946)

acetate solution containing the silicone sample. Rochow and Rochow (5) reported molecular weight findings on silicone rubber based on the techniques of resinography: fracturing a cooled silicone rubber specimen, preparing a replica of the surface, and then studying the size of the irregularities on the fractured surface by means of the electron microscope. The results of these investigations show that the average gram molecular weight of dimethylsiloxane rubber is over 300,000.

Rochow and Rochow conclude that the ease of molecular motion in the silicones (characterized by low tensile strength of the elastomer and low change in viscosity with temperature in silicone oils) is due not to low molecular weight, but rather to low intermolecular attraction between silicone molecules. This low intermolecular attraction between siloxane chains has been ascribed to the considerable freedom of motion of dimethylsiloxane units about the ionic -Si-O- bond which, according to Roth (6), results in zones of interference, lowering the van der Waals interaction between the molecules.



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(5) Rochow, T. G., and Rochow, E. G., Science, 111, [illegible] (1950)

(6) Roth, W. K., Journal of American Chemical Society, 69, 474 (1947)

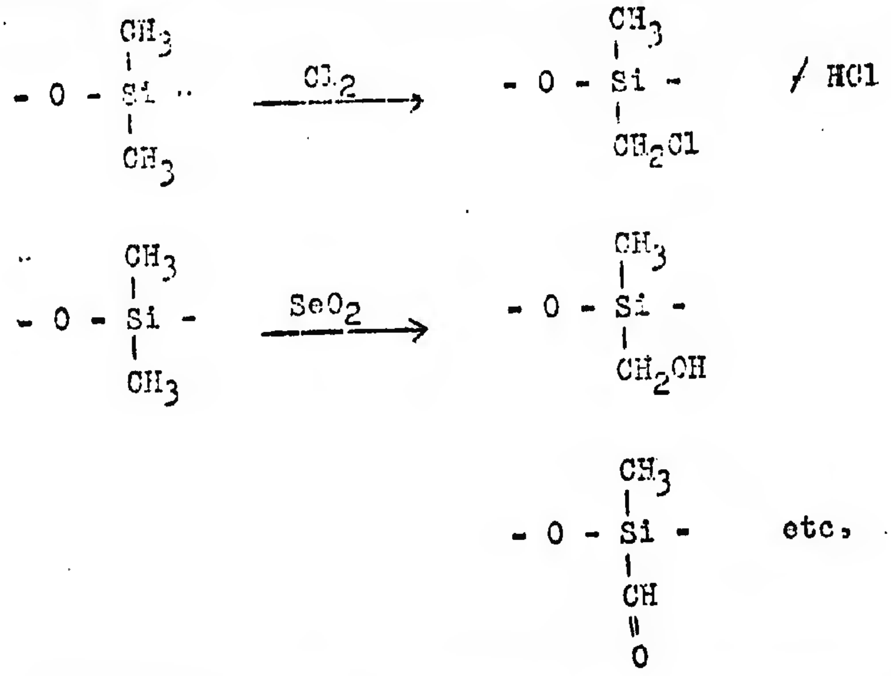
One of the most important approaches to the problem of improving the tensile strength of silicone rubber then, is to seek methods of increasing the intermolecular attraction of the siloxane units in the gum. With a stronger gum as a starting material, concomitant improvements in reinforcement and vulcanization might be expected to yield a much tougher cured stock.

Modifications of the Polarity of the Side Groups

Increasing the polarity of the elastomer chains by suitable modification of the groups attached to the silicone atoms in the elastomer would tend to increase the intermolecular attraction between siloxane units. Possible polar groups are halogen, hydroxyl, amino, and carboxyl. There is, of course, danger in too great polarity in the chains, since the low temperature properties of the silicones would suffer from factors which promote resinification or crystallization. Another factor to consider in the modification of the silicone chains is the enhanced tendency for carbon-silicon cleavage in systems with appropriately substituted polar groups. For example, although the system $-\overset{|}{\underset{|}{Si}}-CH_2-Cl$ is reasonably stable to hydrolysis, β-substituted halo-silanes $-\overset{|}{\underset{|}{Si}}-CH_2-CH_2-Cl$, cleave readily with hydrolytic agents to give the $-\overset{|}{\underset{|}{Si}}-OH$ intermediate and $CH_2=CH_2$. A silicon elastomer with any polar group so substituted would be extremely susceptible to hydrolysis.

The recent development by workers at the Connecticut Hard Rubber Company of a method for the liquifaction and repolymerization of the dimethylsiloxane gum has made possible the introduction of various polar reagents into the polymer backbone. Elsewhere in this report are described the techniques for depolymerization (or liquifaction) of the gum, the chemical reactions carried out on the gum in the transient liquid state and the reconversion of the reaction mixture to the gum state.

While in the liquid state, it is possible to side-chain-halogenate the gum and to incorporate oxidizing agents such as selenium dioxide and chromic oxide which could accomplish the desired substitution of polar groupings.



$$-O-\overset{CH_3}{\underset{CH_3}{Si}}- \xrightarrow{Cl_2} -O-\overset{CH_3}{\underset{CH_2Cl}{Si}}- \quad / \; HCl$$

$$-O-\overset{CH_3}{\underset{CH_3}{Si}}- \xrightarrow{SeO_2} -O-\overset{CH_3}{\underset{CH_2OH}{Si}}-$$

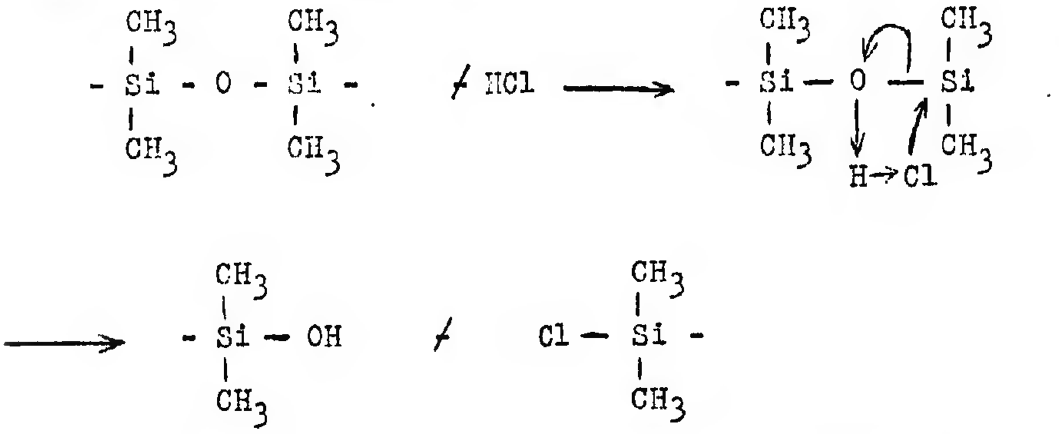
$$-O-\overset{CH_3}{\underset{\underset{O}{\overset{\|}{CH}}}{Si}}- \quad etc.,$$

The results of some of the photochemical halogenation work are described here, and more time will be devoted to this aspect of the problem in later months. The action of oxidizing agents other than selenium dioxide on the liquified gum has not as yet been studied. It is planned to work with chromic oxide, acid and alkaline permanganate, lead tetraacetate and other oxidizing agents.

Modification of the Siloxane Chains

In the depolymerized state, the chain character of the silicone gum is also subject to fundamental modification by the substitution, at intervals, of linkages other than oxygen.

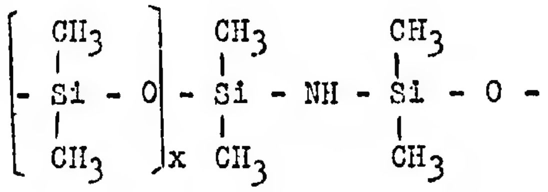
The mechanism for the break-down of siloxane chains is postulated as a simple ether-like cleavage promoted by dry HCl or other "Lewis" acids:



$$-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}- + HCl \longrightarrow -\underset{CH_3}{\overset{CH_3}{Si}}-\underset{H\rightarrow Cl}{O}-\underset{CH_3}{\overset{CH_3}{Si}}$$

$$\longrightarrow -\underset{CH_3}{\overset{CH_3}{Si}}-OH + Cl-\underset{CH_3}{\overset{CH_3}{Si}}-$$

The resulting silanol or halosilane functions are very reactive and could either interact to regenerate the gum, or condense with water, ammonia, active hydroxy, carboxy, or sulfhydryl compounds. Thus, after reaction with ammonia, the recombination of chain fragments could give rise to units of the type:



$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_x-\underset{CH_3}{\overset{CH_3}{Si}}-NH-\underset{CH_3}{\overset{CH_3}{Si}}-O-$$

After reaction with analogous sulfur-containing compounds, the $-\overset{|}{\underset{|}{Si}}-SH$ moiety could recombine with the reactive $-\overset{|}{\underset{|}{Si}}-OH$ or $-\overset{|}{\underset{|}{Si}}-Cl$ to form $-\overset{|}{\underset{|}{Si}}-S-\overset{|}{\underset{|}{Si}}$ units along the chain. The effects of introducing such periodic discontinuities along the siloxane chain are being studied. Some preliminary results on the ammonia treated gums are described in Section VI of this report.

Outline of Research Program for the Period Covered by this Report

The research program being carried out by the staff at the Connecticut Hard Rubber Company is outlined below.

I. Studies on the reinforcing action of various pigments with special emphasis on the incorporation of the pigment into the depolymerized silicone gum.

II. Electron microscope studies on pigments and their dispersion in silicone rubber.

III. Electrostatic studies on silicone rubber in collaboration with Dr. R. S. Havenhill of the St. Joseph Lead Company.

IV. Synthesis and testing of various silicone base wetting agents for the pigment-silicone gum system.

V. Chlorination of the silicone gum and curing studies on the resulting compounded stocks.

VI. The evaluation of products resulting from the treatment of depolymerized gum with ammonia.

VII. The preparation of silicone gums from the cohydrolysis of monomers and polyhydric alcohols.

I. STUDIES OF PIGMENTS

The evaluation of various pigments for reinforcing silicone gum continues to be an important phase of this project. Additional new pigments have been compounded at the 25-volume loading as received, for preliminary evaluation and at other loadings for further evaluation. One of the pigments previously studied had been coated with an organo-metallic salt in an attempt to improve its reinforcing properties. Mixtures of several pigments have been used with a single mixture of Alon II and Celite 505 being studied in the current period.

The compounding of the pigment in the gum while it is in the depolymerized liquid state has been carried out for a single pigment, Celite 505, over a wide range of loadings. The details of these studies follow:

A. Pigments As-received, 25-Volume Loading

Six new pigments (various types of calcium carbonates) have been studied during the period covered by this Progress Report. Samples of these pigments have been furnished by the New England Lime Company for our testing. The results of the physical tests on the compounds are given in Table 1 and Figure 1. None of these stocks are particularly outstanding at this loading. Several of the stocks (those compounded with Type 183 and Type 5950) show good values of ultimate elongation with low values of Shore hardness which would indicate that higher loadings might merit investigation. The results

NELCO PRECIPITATED CALCIUM CARBONATE

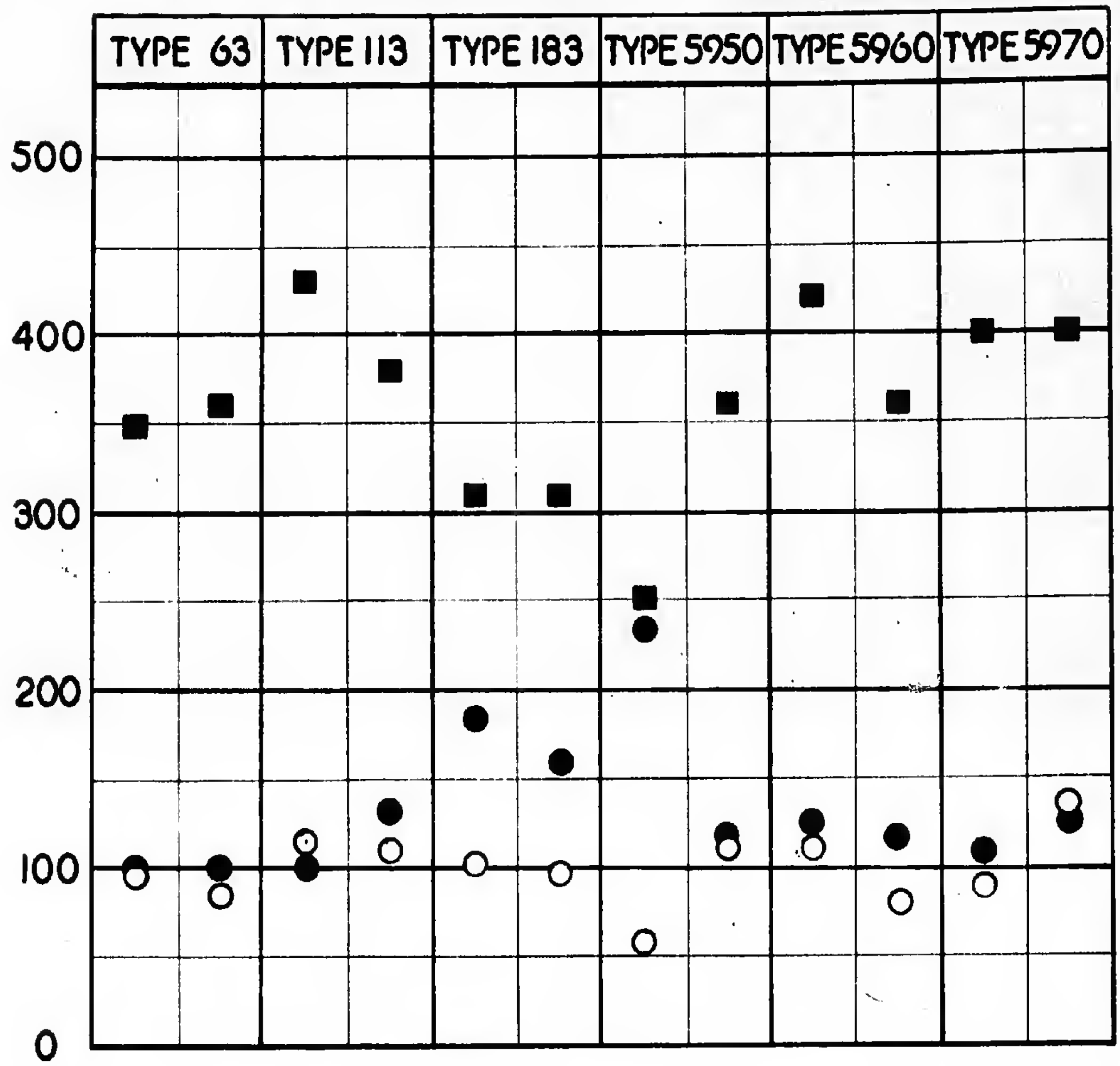


FIGURE-1 PIGMENTS AS RECEIVED
25 VOLUME LOADING

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○ = TENSILE - P.S.I.
● = ELONGATION - %
■ = HARDNESS × 10
SHORE A

of these variable loading studies are given in Part "C" of this section.

TABLE 1

Studies of As-received Pigments at 25-volume Loading.

Pigment	Compound No.	Parts pigment per 100 parts gum	Hardness Shore A	Tensile Strength psi	Elongation %
Precipitated Calcium Carbonate NELCO Type 63	1505	72	35 36	95 85	100 100
NELCO Type 113	1506	72	43 38	115 110	100 133
NELCO Type 183	1507	72	31 31	101 96	183 158
NELCO Type 5950	1508	72	25 36	57 110	233 117
NELCO Type 5960	1509	72	42 36	110 79	125 117
NELCO Type 5970	1510	72	40 40	88 136	108 125

B. <u>Pigments after Treatment with Aluminum Isopropoxide</u>

In order to ascertain the effect of an organo-metallic salt on the surface of a pigment, Celite 505 was coated with aluminum isopropoxide. The coating technique consisted of the following steps:

(1) The aluminum isopropoxide was dissolved in sufficient benzene to wet the quantity of pigment to be treated.

(2) The pigment and the benzene solution were stirred together until an intimate mixture was obtained and all of the pigment had been wet.

(3) The benzene was then removed by evaporation in an oven at 212°F. for 16 hours.

The pigments produced by this technique were compounded in the 25 volume loading with the gum and the usual 2.0 parts of benzoyl peroxide. The physical test results on these compounds are given in Table 2 along with those for compounds in which the same quantities of aluminum isopropoxide were added directly to the compound on the mill.

The results appear to be very inconsistent among themselves, some very high and some low values being obtained in each of the two highest concentrations of aluminum isopropoxide. The high values of tensile strength were obtained when the stocks were compounded very soon after the coated pigments were prepared, while the low values corresponded to those cases in which a long period of time (over one month) elapsed between the pigment preparation and its compounding. This change is probably due to the slow atmospheric hydrolysis of the aluminum salt. Considering only the results on the batches in which the coated pigment was freshly made, it may be seen that as the quantity of aluminum isopropoxide for a given quantity of pigment increases, the tensile strength increases up to 400 pounds per square inch for a compound containing 25 parts of aluminum isopropoxide to 100 parts of Celite 505, with no accompanying increase in hardness or decrease in elongation. The specific effect of this aluminum salt cannot readily be explained. Further study may give a logical answer as to why this extra reinforsing action takes place.

TABLE 2

Aluminum Isopropoxide in Silicone Rubber

Al i-P		Al i-P deposited on pigment				Al i-P compounded on mill			
Per 100 parts gum	Per 100 parts pigment	Cpd. No.	Hardness Shore A	Tensile strength psi	Elongation %	Cpd. No.	Hardness Shore A	Tensile strength psi	Elongation %
0	0	1599	43	167	150	1072	46	212	120
			42	167	150				
			57	252	117		46	260	150
0.75	1.25	1467	60	242	100	1590	47	261	142
			53	219	108		50	219	117
1.5	2.5	1468	56	253	125	1591	50	228	108
			54	229	100				
			53	230	100				
			35 *	179	142		56	293	100
3.0	5.0	1483	45 *	151	133	1592	55	294	100
			54	355	117				
			52	328	125				
			47 *	163	117		46	200	183
7.5	12.5	1486	45 *	155	117	1593	44	188	192
			45	411	144				
			45	406	142				
			46 †	204	125				
			53 *	279	125				
			52 *	268	125		45	318	167
15.0	25.0	1596	54 *	274	125	1594	40	326	192

† Poorly compounded

* Coated pigment was aged before compounded.

C. Variable Volume Loading

The six types of calcium carbonate studied at the 25-volume loading have been studied at loadings up to 60 volumes of pigment per 100 volumes of gum. Even at the higher loadings the maximum tensile strength of any of the compounds is approximately 200 pounds per square inch. The physical test results on all of the compounds are given in Table 3 and presented graphically in Figures 2 and 3. Tensile strengths equal to or better than the maximum obtained at any loading with these calcium carbonates have been obtained with other pigments at much lower loadings. None of this series of pigments can be called outstanding in its reinforcing properties.

D. Mixtures of Pigments

A mixture of two pigments which have shown promise as reinforcing agents alone has been tried at total volume loadings which should yield moderately high tensile strength values. The two pigments used were Celite 505 and Alon II at a total loading of 75 volumes. The physical properties of the resulting compounds are given in Table 4 and Figure 4. These properties are very nearly a linear function of the relative quantities of the two pigments as can be easily seen from Figure 4. It is also apparent that no great gains over using Celite 505 alone can be achieved by using any of the mixtures tested.

NELCO PRECIPITATED CALCIUM CARBONATE

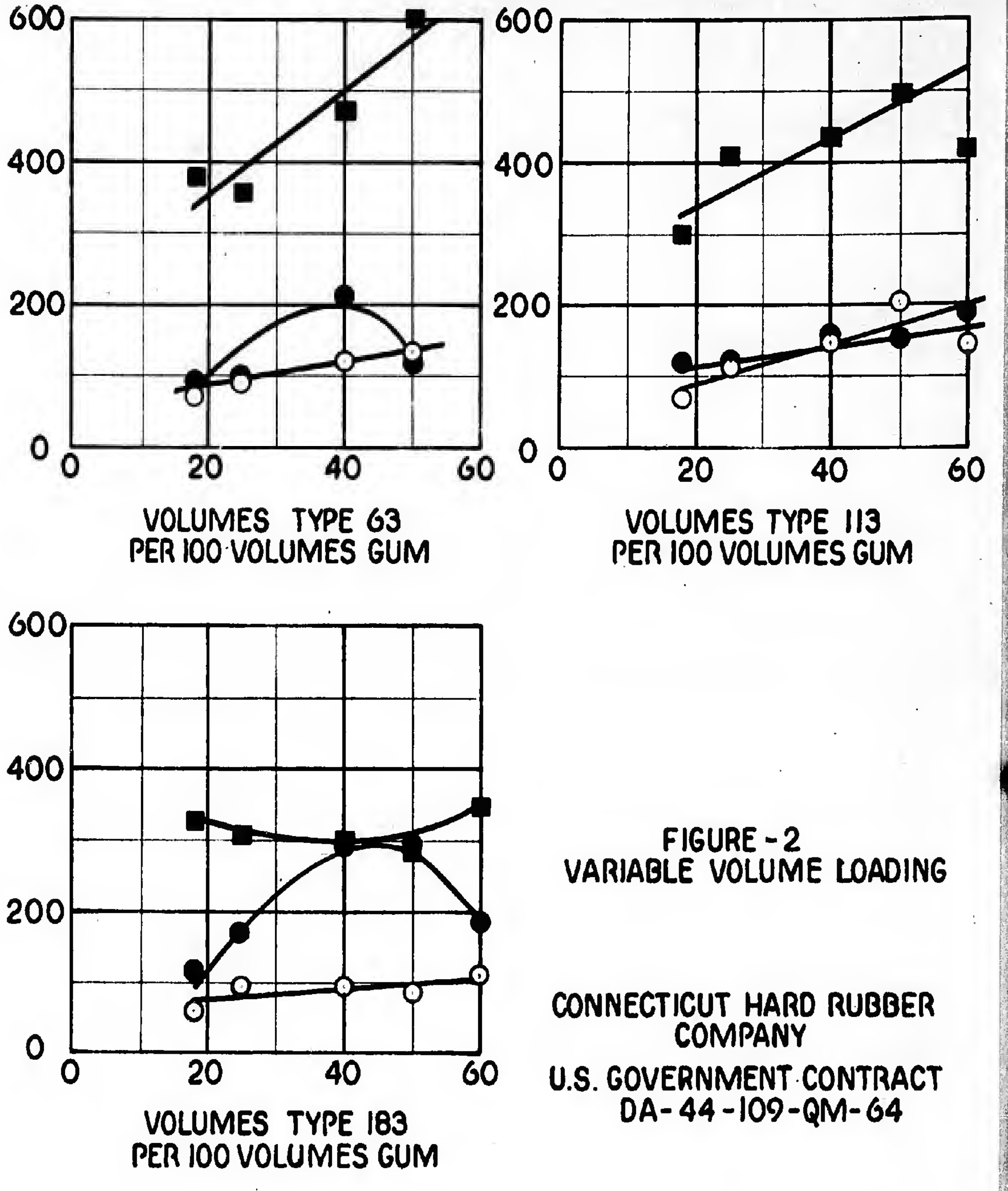

FIGURE - 2
VARIABLE VOLUME LOADING

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○ = TENSILE - P.S.I.
● = ELONGATION - %
■ = HARDNESS × 10
SHORE A

TABLE 3

Studies of Pigments at Variable Loading

Pigment	Compound No.	Volumes per 100 volumes gum	Parts per 100 parts gum	Hardness Shore A	Tensile strength psi	Elongation %
Precipitated Calcium Carbonate NELCO Type 63	1511	18	53	38	68	92
	1505	25	72	36	90	100
	1512	40	115	47	125	208
	1513	50	144	60	130	117
	1514	60	172	No Cure		
Precipitated Calcium Carbonate NELCO Type 113	1515	18	53	30	64	116
	1506	25	72	41	113	116
	1516	40	115	44	147	155
	1517	50	144	50	203	155
	1518	60	172	42	165	196
Precipitated Calcium Carbonate NELCO Type 183	1519	18	53	34	56	119
	1507	25	72	31	99	171
	1520	40	115	30	97	296
	1521	50	144	29	86	294
	1522	60	172	35	114	186
Precipitated Calcium Carbonate NELCO Type 5950	1523	18	53	42	85	113
	1508	25	72	31	84	175
	1524	40	115	42	146	183
	1525	50	144	47	149	121
	1526	60	172	60	180	100

TABLE 3 cont'd

Pigment	Compound No.	Volumes per 100 volumes gum	Parts per 100 parts gum	Hardness Shore A	Tensile strength psi	Elongation %
Precipitated	1527	18	53	46	77	94
Calcium Carbonate	1509	25	72	39	95	121
NELCO	1528	40	115	46	166	113
Type 5960	1529	50	144	44	167	196
	1530	60	172	46	203	177
Precipitated	1531	18	53	28	46	125
Calcium Carbonate	1510	25	72	40	112	117
NELCO	1532	40	115	47	156	134
Type 5970	1533	50	144	47	232	196
	1534	60	172	44	171	146

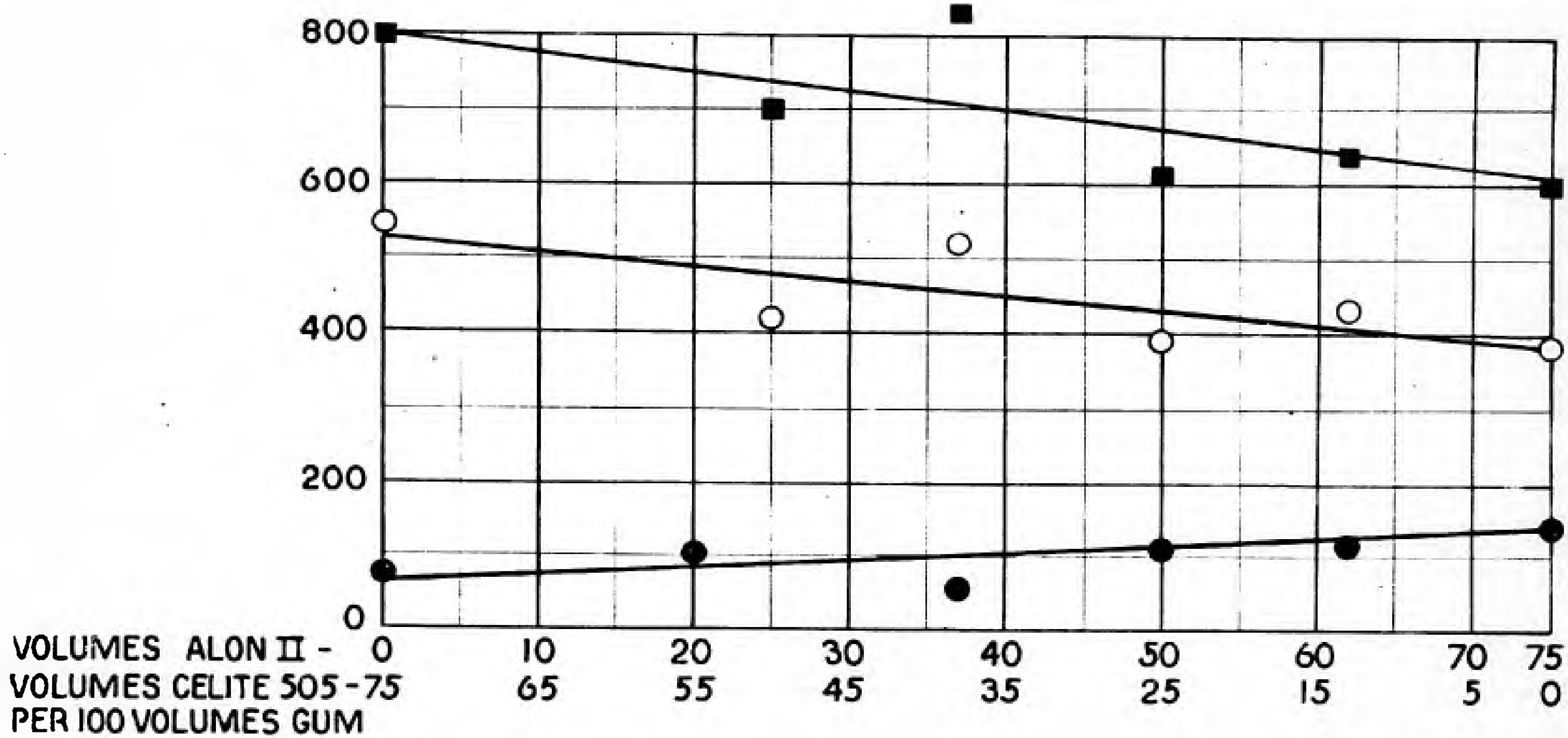

FIGURE -4 MIXTURES OF PIGMENTS

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

TABLE 4

Mixtures of Pigments

Celite 505		Alon II		Cpd. No.	Hardness Shore A	Tensile Strength psi	Elongation %
Parts	Volumes per 100 of gum	Parts	Volumes				
176	75	0	0	1555	81	544	75
					80	555	75
117	50	98	25	1554	70	427	100
					70	407	100
88	38	147	37	1553	82	504	50
					84	532	58
59	25	196	50	1552	61	368	100
					62	407	117
29	13	245	62	1551	64	452	125
					65	409	100
0	0	294	75	1484	60	363	125
					60	399	142

E. Incorporation of Pigments

To give a better pigment dispersion and intimate mixing of the silicone polymer and the pigment, Celite 505 has been compounded with the HCl depolymerized silicone gum utilizing a Waring Blendor (a small high-speed laboratory mixer) to do the mixing. It was hoped that more intimate mixing might be obtained than can be done in conventional compounding on a 2-roll rubber mill. The technique used in the laboratory follows:

(1) The pigment was placed in the Waring Blendor with sufficient carbon tetrachloride to form a thick paste. This paste was mixed for five minutes after which the depolymerized gum was added and the entire mixture was mixed for five more minutes. This resulted in a thin paste of very uniform consistency.

(2) This paste was heated on a hot plate to remove the bulk of the carbon tetrachloride with the last traces being removed in an air circulating oven at 212°F.

(3) The compound was then milled, with the benzoyl peroxide being added at this stage.

Compounds containing a wide range of loadings of Celite 505 have been prepared and the physical test results on these compounds are given in Table 5 along with those obtained with the same loadings using conventional mill compounding. The same comparison is presented graphically in Figure 5.

At the standard 25-volume loading the tensile strength has been doubled with a small increase in elongation and approximately a 5 point increase in the hardness. At all loadings the tensile strength obtained on compounds made in the Waring Blendor is well above that obtained by mill compounding. The spread between the hardness curves appears to increase as the loading increases. The values of elongation at the higher loadings are substantially the same by both compounding techniques.

A partial explanation of the increase in tensile strength can be found in improved dispersion of the filler in the gum while it is in the liquid state. The electron microscope should be a very valuable tool in determining the quality of the dispersion in this phase of the investigation. Another contributing factor may be a better wetting of the pigment by the liquid depolymerized gum than can be obtained with the standard gum.

Investigations are in progress on the compounding of other pigments with the depolymerized gum in the Waring Blendor which should furnish more evidence on the nature of the compounds obtained by this intimate mixing of the pigment and the polymer. As mentioned above, it is planned to use the electron microscope extensively in this investigation to assist in the analysis of some of the results obtained.

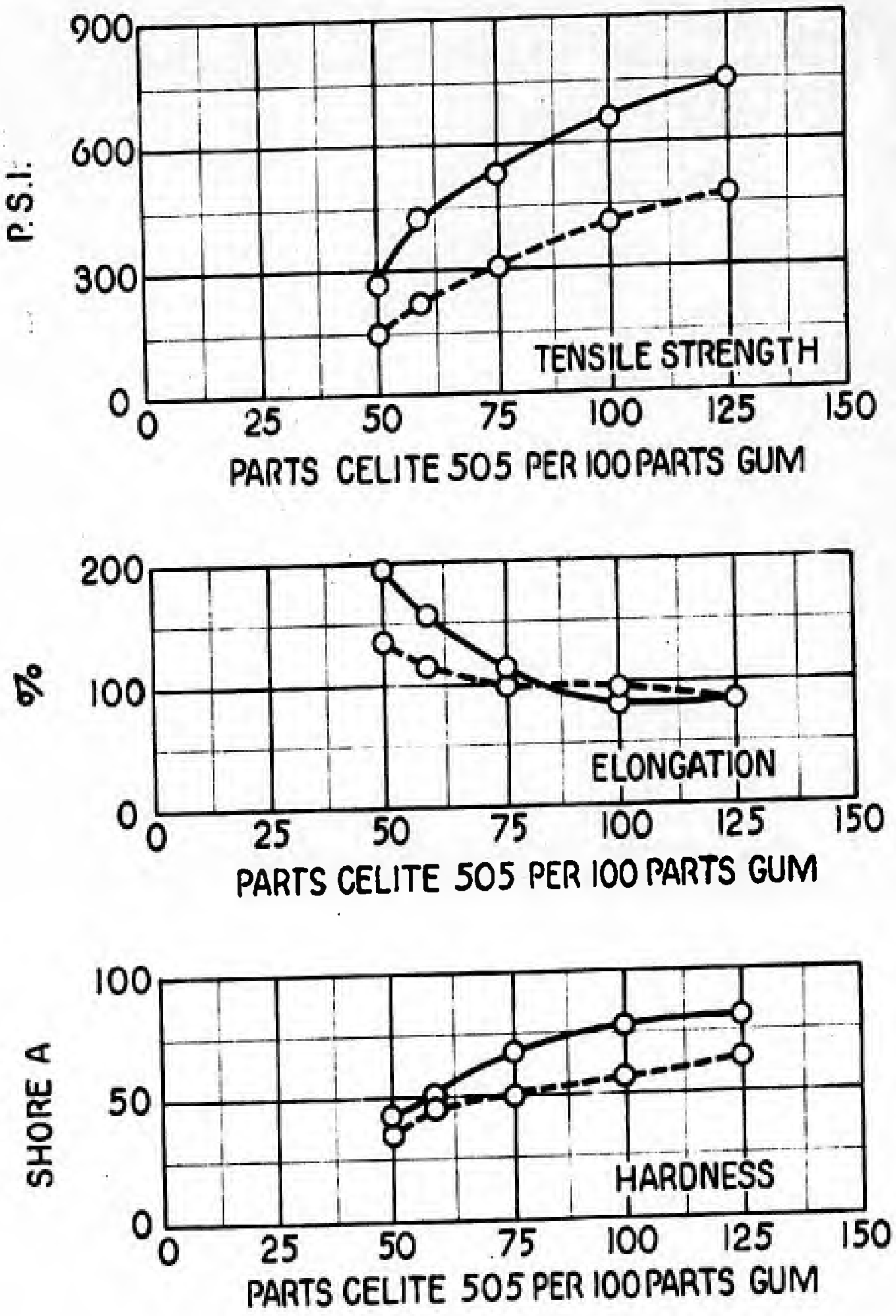

FIGURE - 5 EFFECT OF PIGMENT INCORPORATION TECHNIQUES ON PHYSICAL PROPERTIES —

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DA-44-109-QM-64

WARING BLENDOR COMPOUNDING	———
MILL COMPOUNDING	- - - - -

TABLE 5

Comparison of Conventional Mill

Compounding and Waring Blendor

Compounding of Depolymerized Silicone Gum

Pigment	Parts pigment per 100 of gum	Mill Compounding			Waring Blendor Compounding		
		Hardness Shore A	Tensile strength psi	Elongation %	Hardness Shore A	Tensile strength psi	Elongation %
Celite 505	50	35	130	135	38	253	197
" (25 volumes)	58	46	220	120	50	431	155
Celite 505	73	55	300	100	66	536	110
" "	100	63	400	95	75	660	85
" "	125	70	470	85	80	750	85
Hi-Sil	53	62	215	110	68	540	90
	75	Cannot be compounded			82	540	50
Celite Super Floss	63	45	180	125	60	490	125

(2

II. ELECTRON MICROSCOPE STUDIES

Electron microscope studies of pigments and cured rubber specimens have been continued as outlined in previous reports (see particularly Progress Report, Dec. 5, 1949 to March 4, 1950). The general purpose of this work has been to provide some additional clues as to the fundamental nature of pigment reinforcement in silicone rubbers and to aid in the interpretation of the results of other parts of the program. The electron micrographs taken fall into two groups:

(1) Pictures have been taken of nearly all of the pigments used in the compounding program in order to gain a better knowledge of their size, shape and degree of agglomeration as received. The latter may be important inasmuch as it appears that in many cases these agglomerates are not broken up in the milling process with a resultant detrimental effect on the reinforcing properties of the pigment.

(2) Pictures of very thin sections of cured rubber specimens have been taken using the "vulcanization technique" previously described. In this method an extremely thin specimen of rubber is prepared by press curing small disk samples in special molds under pressures of the order of 100,000 pounds per square inch. A large number of electron micrographs of silicone rubbers have now been taken and some representative samples are reproduced in Plates 2-5. Plate 1, a picture of carbon black in hydrocarbon rubber, is for comparison purposes. We intend making further comparison studies of hydrocarbon rubbers in the hope that some clues as to reasons for the much higher quality of

hydrocarbon rubbers over their silicone counterparts can be found.

In the pictures taken so far, certain interesting facts emerge. On a microscopic scale the dispersion of the pigment particles in the silicone rubbers is by no means uniform. Agglomeration is the rule rather than the exception. This is true to a varying degree of all the compounds so far observed. To make accurate quantitative comparison of the degree of dispersion in different samples many more pictures are necessary in order that the results may have statistical reliability. We hope to be able to say more on this matter at a later date when a much larger number of pictures will have been taken.

This agglomeration gives encouragement to efforts toward improving the dispersion of the pigment in the rubber matrix. It might well be possible, for example, to obtain a substantial improvement in the quality of a Hi-Sil silicone rubber by suitably dispersing this very fine pigment in the rubber. Two approaches that have considerable promise are now being made to this dispersion problem. (1) By depolymerizing the gum with dry HCl it is put into a liquid state, which allows a thorough dispersion of the pigment in the liquid gum by use of a Waring Blendor. This approach is described in Section I and has shown remarkable promise, giving an improvement in tensile strength by a factor of two in the case of Celite 505 compounds.

Reliable electron microscope checks on the change in dispersion of the pigment in the rubber as a result of this dispersion technique are not yet available. This is being checked and the results will help determine whether this or some other hypothesis accounts for the success of this compounding process.

(2) The second approach involves treatment of the pigment before compounding. Earlier it was mentioned that a considerable degree of agglomeration exists in the pigments as received. This agglomeration presumably occurs during the process of formation of the pigment and could perhaps be reduced considerably by coating of the pigment with a suitable substance during the manufacturing process before the pigment has settled. Dr. Havenhill of the St. Joseph Lead Company is now attempting to prepare some silicone coated zinc oxide pigment for use in our testing of this hypothesis. This coating is being applied at the Monaca, Pennsylvania, plant by spraying the finely divided zinc oxide dust with silicone oil as it is formed in the oxidation process.

Plate 1

Electron Micrograph of P-33 Carbon Black in Cured G.R.S.

Magnification 53,000 X

Composition

G.R.S.	100.00
P-33	50.00
Zinc Oxide	5.00
Bardol	4.50
Pine Tar	3.00
Sulfur	1.80
Santocure	1.00

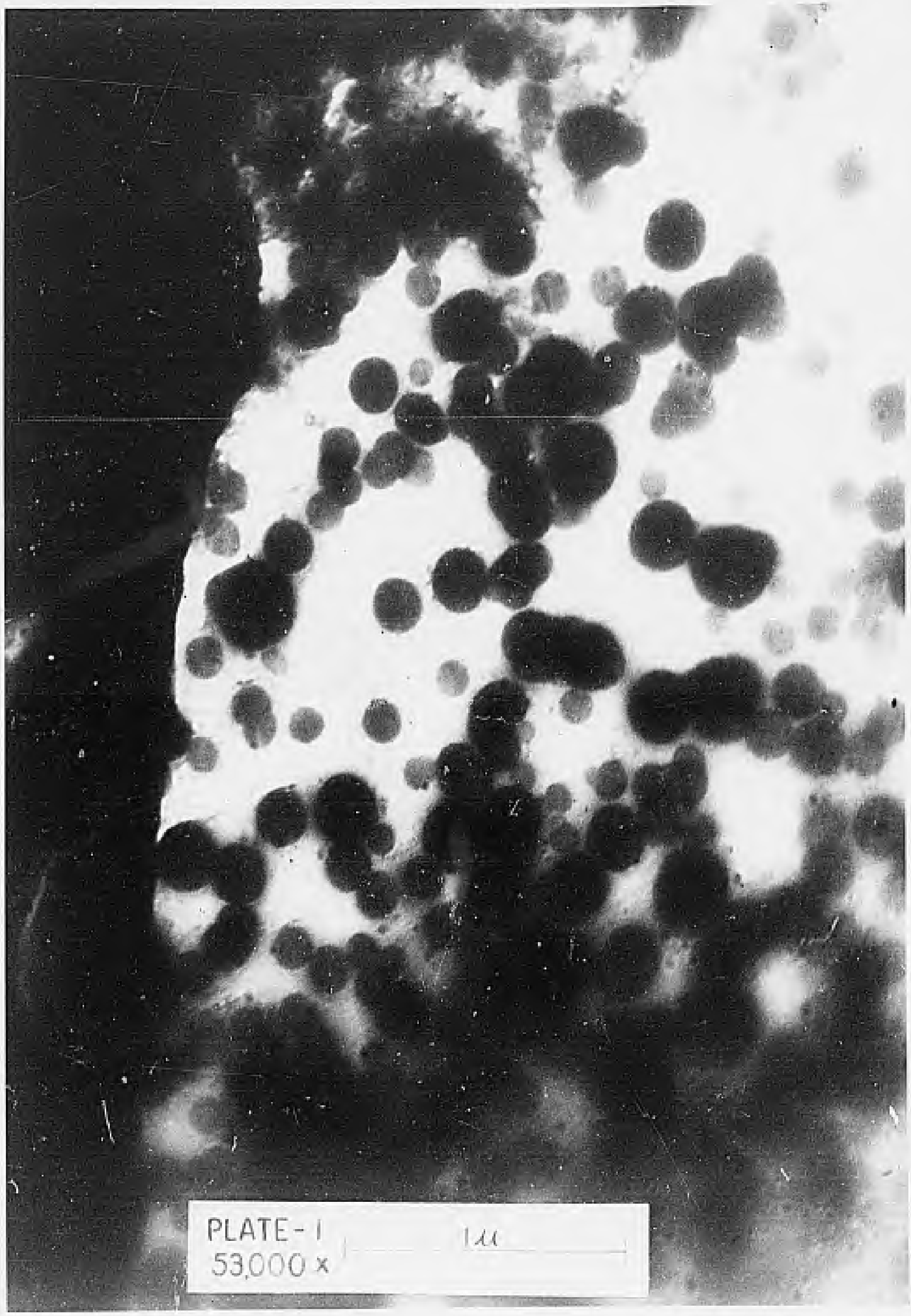

PLATE - I
53,000 ×

Plate 2

Electron Micrograph of Titanium Dioxide and Celite 505 in Silicone Rubber.

Magnification 66,000 X

Compound No. 1066

Composition

Silicone Gum 9979-G	100.00
Celite 505	100.00
DuPont R510 TiO_2	75.00
Benzoyl Peroxide	2.00

Compounding

Standard milling technique.

PLATE-2
66,000x

Plate 3

Electron Micrograph of Zinc Oxide in Silicone Rubber.

Magnification 80,000 X

Compound No. 1479

Composition

Depolymerized Silicone Gum	100.00
AZO-ZZZ-66 Zinc Oxide	152.00
Benzoyl Peroxide	7.80

Compounding

The HCl depolymerized silicone gum was diluted in CCl_4 and mixed with the pigment in a Waring Blendor. After repolymerizing the mixture by heating, the benzoyl peroxide was added on the mill.

PLATE - 3
80,000 x

Plate 4

Electron Micrograph of Alon
in Silicone Rubber.

Magnification 80,000 X

Compound No. 1477

Composition

Depolymerized Silicone Gum	100.00
Alon	98.00
Benzoyl Peroxide	2.00

Compounding

The HCl depolymerized silicone gum was mixed with the pigment in a Waring Blendor. After repolymerizing the mixture the benzoyl peroxide was added on the mill.

PLATE - 4
80,000 x

Plate 5

Electron Micrograph of Hi-Sil
in Silicone Rubber.

Magnification 23,000 X

Compound No. 1476

Composition

Depolymerized Silicone Gum	100.00
Hi-Sil	53.50
Benzoyl Peroxide	2.20

Compounding

The HCl depolymerized silicone gum was mixed with the pigment in a Waring Blendor. After repolymerizing the mixture the benzoyl peroxide was added on the mill.

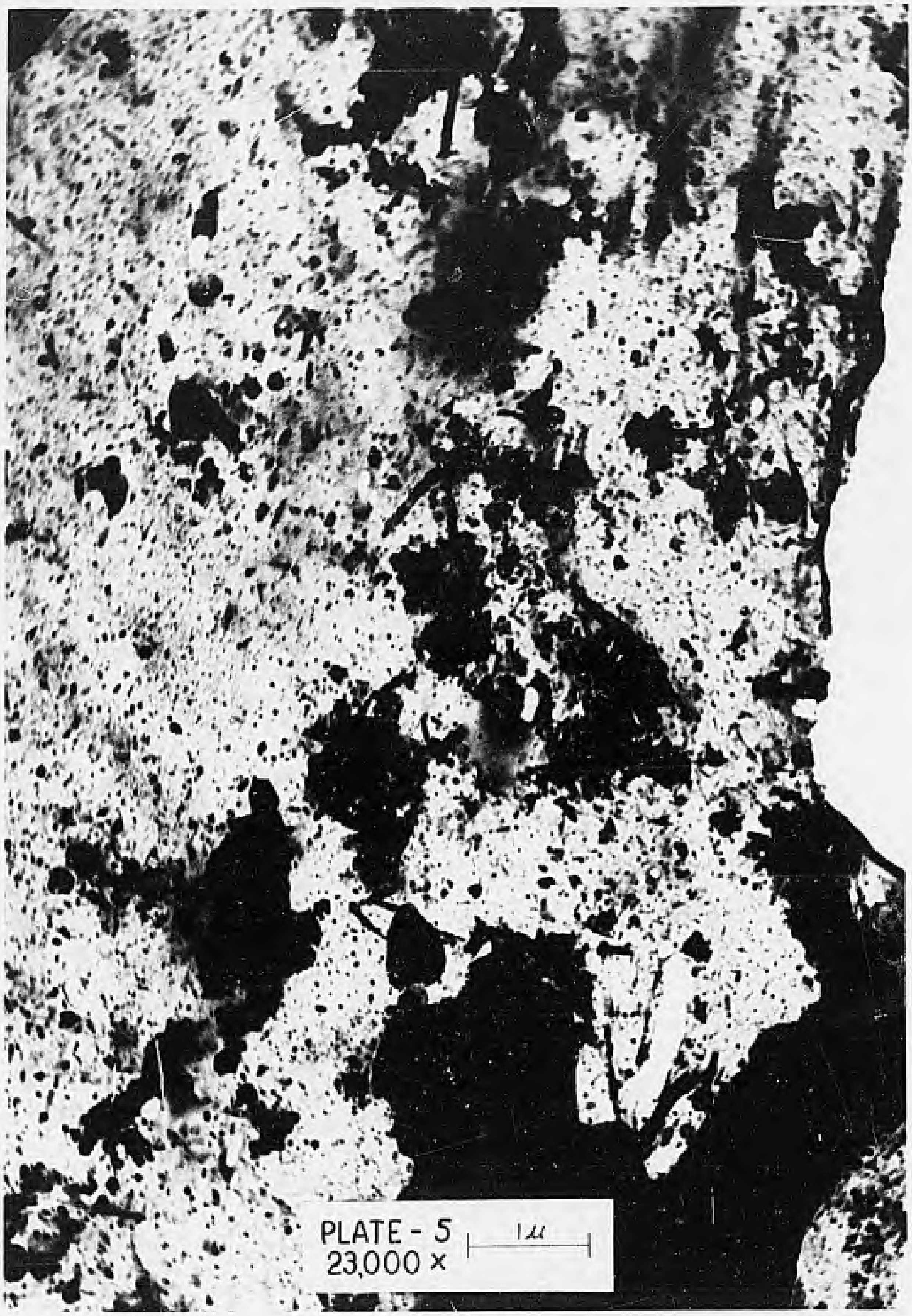

PLATE - 5
23,000 ×

III. ELECTROSTATIC STUDIES ON SILICONE RUBBER

A study of certain electrostatic properties of silicone elastomers is being undertaken in collaboration with Dr. R. S. Havenhill and his associates at the St. Joseph Lead Company. Havenhill, et al., (7, 8, 9) have proposed a general theory of electrostatic reinforcement of rubber and at the suggestion of Dr. C. C. Vogt the application of these ideas to the problem of silicone rubber reinforcement is being explored.

The electrostatic measurements are being made by Havenhill at the St. Joseph Lead Company with the silicone rubber samples supplied by The Connecticut Hard Rubber Company. A detailed report on this work will be included in the next Progress Report.

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(7) Havenhill, R. S., O'Brien, H. C., and Rankin, J. J., Journal of Applied Physics, 15, 731 (1944)

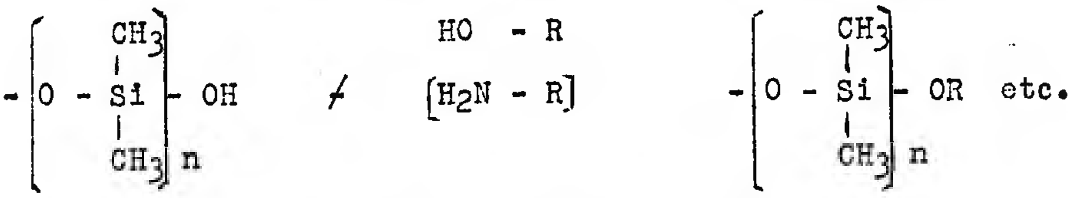
(8) Havenhill, R. S., O'Brien, H. C., and Rankin, J. J., Journal of Applied Physics, 17, 338, (1946)

(9) Havenhill, R. S., Carlson, L. E., and Rankin, J. J., Rubber Chemistry and Technology, 22, 477 (1949)

IV. WETTING OR DISPERSING AGENTS

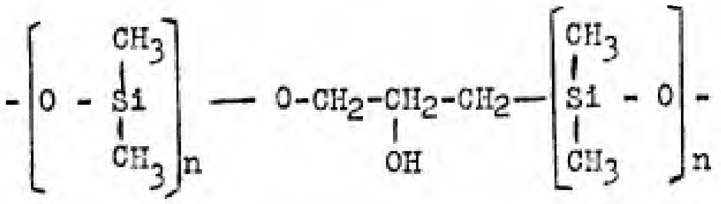
A number of compounds have been incorporated into the depolymerized silicone gum or have been used in water solutions as the hydrolysis media for dimethyldichlorosilane, to ascertain whether the reaction products might have useful properties as a wetting or dispersing agent in bonding pigment to the silicone matrix.

In general, the molecules which were incorporated possessed hydroxyl or amino functions (to condense with the active -OH or -Cl present in the liquified gum) and other functional groups such as carboxyl, cyano, amino, etc., to impart polarity to the condensation product. The composition of the resulting oil, gum or solid would then be:



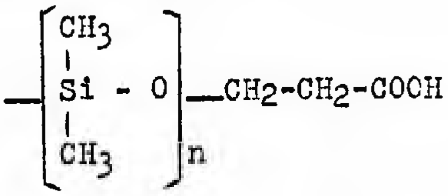
$$-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-OH \quad + \quad \begin{matrix}HO - R\\ [H_2N - R]\end{matrix} \qquad -\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-OR \quad \text{etc.}$$

Incorporation of glycerol could, for example, produce a polymer of the following structure as well as cross linked reaction products involving the third hydroxyl.



$$-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n - O-CH_2-\underset{OH}{CH_2}-CH_2-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-$$

Reaction with ethylene cyanohydrin $HO-CH_2-CH_2-C\equiv N$, followed by hydrolysis, could result in a polymer having a siloxane backbone with carboxyl groups as terminals.



$$-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-CH_2-CH_2-COOH$$

Four substances have been incorporated with the liquified gum and five have been used with water as hydrolysis media. The following tabulation indicates the reaction combinations that have been used:

Reacted with depolymerized gum	Used with water for hydrolysis of $(CH_3)_2SiCl_2$
Glycolic acid	Glycolic acid
Ethylene cyanohydrin	Ethylene cyanohydrin
Decanol	Ammonia
Glycerol	Glycerol
	Triethanolamine

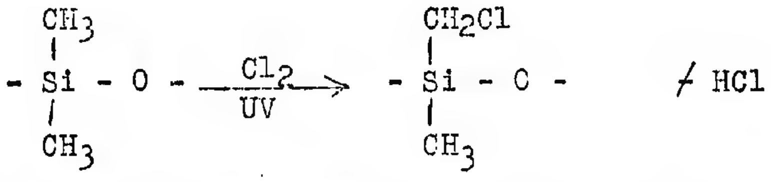
The products resulting from these various reactions were tested as wetting agents in the following manner. One to five parts of the substance to be tested (oil, gum or solid) per 100 parts of gum were added on the mill to a compound containing 25 volumes of Celite 505 as a filler and cured using benzoyl peroxide. The physical properties of the resulting cured compounds were compared with those of control batches containing no wetting agent.

Of the materials tested, those containing glycerol showed most promise in improving the physical properties. These results are being subjected to further confirmation and the full details of this experimental program will be presented in the next Progress Report.

V. CHLORINATION OF SILICONE GUM

The possibility of introducing polar halogen groups into the siloxane side groups has been investigated further.

By bubbling dry chlorine into the liquid depolymerized silicone gum under the catalysis of strong ultraviolet light, hydrogen atoms have been replaced by chlorine atoms. The halogenation has been controlled so as to vary substitution by chlorine according to this scheme:



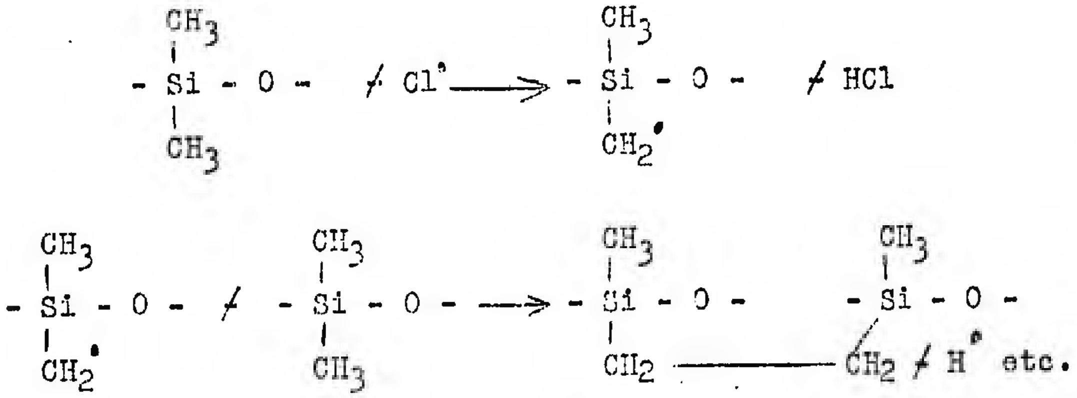
$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O- \xrightarrow[UV]{Cl_2} -\overset{\displaystyle CH_2Cl}{\underset{\displaystyle CH_3}{Si}}-O- \quad + HCl$$

In the work described here, the ratio of chlorine to silicon has been varied, with the maximum ratio being 0.25.

After halogenation was completed, the liquified gum was reconverted to the elastomeric state by gentle warming. Physical tests have been run on cured compounded stocks containing a 25-volume loading of Celite 505 and 2.0 parts of benzoyl peroxide as curing agent. The testing results show a definite increase in tensile strength with increasing chlorine content (Figure 6). The tensile strength increased from an average value of 220 pounds per square inch with no chlorine incorporated to values of 400-500 pounds per square inch when the Cl:Si ratio was 0.25.

On the other hand, the hardness on the Shore A scale rose from a value of 45 to values in the range of 80-90 with corresponding decrease in the values of the ultimate elongation from 120% to 30%.

It is possible that the increase in hardness of the halogenated stocks may in part be due to an additional curing action taking place during the chlorination. The chlorine radicals produced during the UV-initiated decomposition of chlorine gas could promote cross linking reactions in a manner analogous to the action of benzoyl peroxide (see Section A in the Appendix).



$$-\overset{CH_3}{\underset{CH_3}{Si}}-O- + Cl^{\cdot} \longrightarrow -\overset{CH_3}{\underset{CH_2^{\cdot}}{Si}}-O- + HCl$$

$$-\overset{CH_3}{\underset{CH_2^{\cdot}}{Si}}-O- + -\overset{CH_3}{\underset{CH_3}{Si}}-O- \longrightarrow -\overset{CH_3}{\underset{CH_2}{Si}}-O- \quad -\overset{CH_3}{\underset{CH_2}{Si}}-O- + H^{\cdot} \text{ etc.}$$

The above cross linking reaction could, if carried on to any degree, increase the hardness, as well as the tensile strength of the product.

In order to cut down on the total amount of cure to which these chlorinated gums are being subjected (assuming cross linking during the halogenation as well as during the regular peroxide catalyzed cure), the time and temperature of the final oven cure was gradually decreased and the effect of the less severe curing conditions on tensile, elongation and hardness determined. The sample chosen had an approximate Cl:Si ratio of 1:8. The results of this study are summarized in Table 6. It appears that the tensile strength of the stock has not varied appreciably over the wide range of curing conditions, but as the cure becomes less severe, the values of the elongation have increased and the hardness decreased.

The above results indicate that the chlorinated silicone polymers require a much less severe cure to develop the optimum tensile strength. Under these faster, milder conditions of cure, however, the heat aging characteristics of the rubber may suffer. We shall report further on the results of these studies,

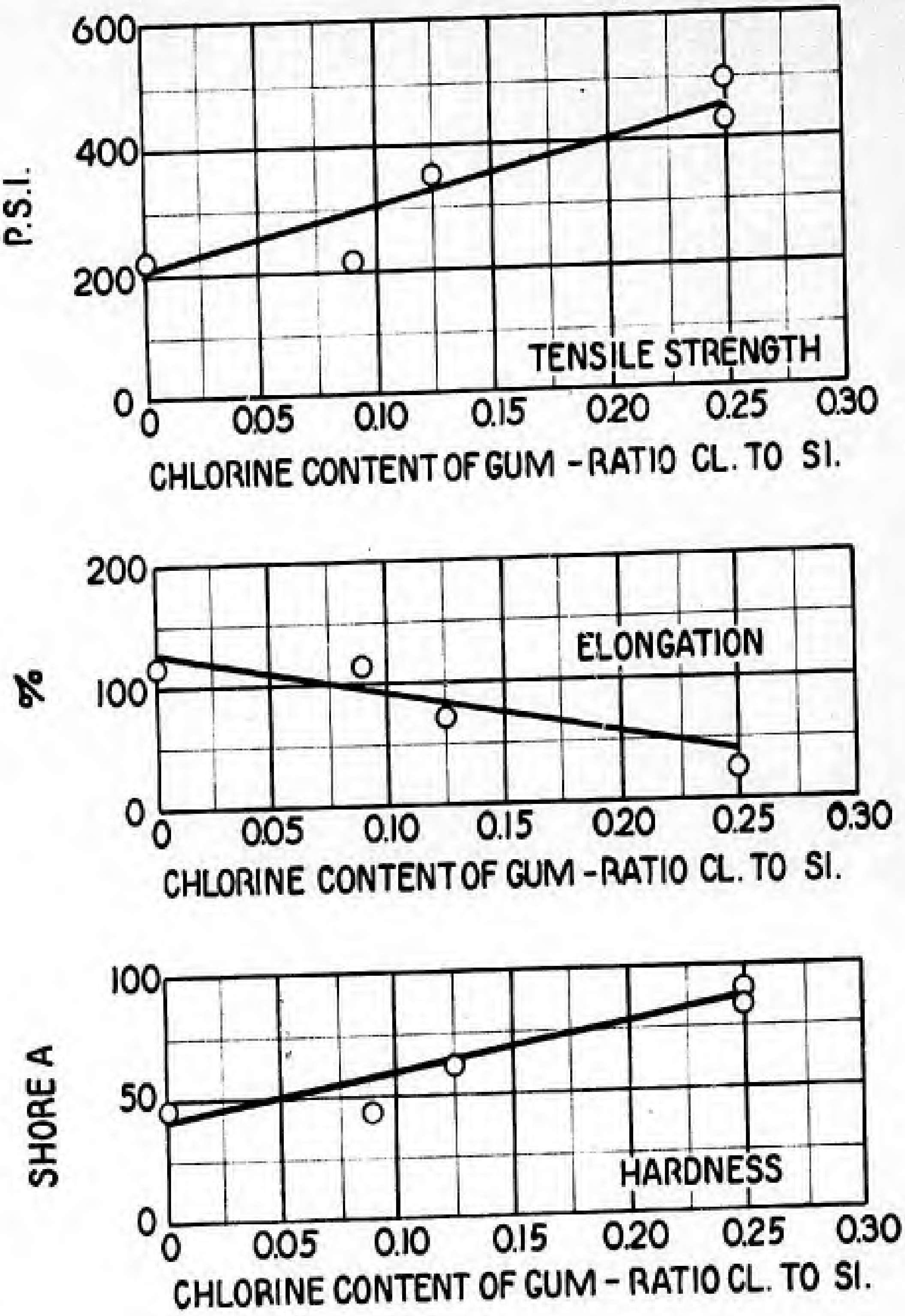


FIGURE - 6 EFFECT OF CHLORINE CONTENT OF GUMS ON PHYSICAL PROPERTIES OF COMPOUNDS (25 VOLUME LOADING CELITE 505)

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Table 6

Curing Studies on Compounds Containing Chlorinated Gum

Cure	Hardness Shore A	Tensile Strength p.s.i.	Elongation %
Basic Cure Only	43	257	158
Basic Cure plus 16 Hrs. @ 300°F.	47	204	113
Basic Cure plus 16 Hrs. @ 350°F.	46	215	125
Basic Cure plus 16 Hrs. @ 400°F.	50	262	125
Basic Cure plus 16 Hrs. @ 450°F.	66	250	63
Normal Cure Cycle	62	355	75

*The Cl:Si ratio of the gum was 1:8.

Normal Cure Cycle

Time, hours	Temperature, °F.
0	70
4	200
6	225
10	235
16	250
18	270
20	300
22	325
24	350
26	390
28	420
30	440
32	460
34-42	480

Basic Cure

8 hours @ 225°F.

4 hours @ 300°F.

VI. THE ACTION OF AMMONIA ON DEPOLYMERIZED GUM

Introduction of ammonia into the HCl depolymerized gum and subsequent removal of the by-product ammonium chloride by washing with water, results in a residual oily product which has properties differing from the original liquid polymer. The product is stable to air and can be maintained in the liquid state for long periods of time. This ammonia-stabilized liquid gum appears to be a mixture of silazine and siloxane chains, the -Si-NH-Si- linkage being formed during the ammonolysis.

If the process of depolymerization, as pictured, results in labile -Si-OH and -Si-Cl groupings distributed throughout the siloxane matrix, then reaction of the active chloro functions with ammonia would yield periodic $-Si-NH_2$ groupings, which could then condense with -Si-OH units to eliminate ammonia, thus forming siloxene links or water to form silazine links. During the removal of ammonium chloride by washing with water, hydrolysis of -Si-NH-Si- groupings could take place to regenerate the siloxane type of link.

The following observations on the ammonia-stabilized liquid are significant:

(1) In contrast to the original starting gum (9979 G) which is depolymerized by the action of HCl, the ammonia-treated liquid forms a gum readily on treatment with HCl. It has also been possible to obtain gums from ammonia-treated liquids by the action of acidic reagents such as thionyl chloride and benzoyl chloride.

(2) Caustic fusion of the purified ammonia-stabilized liquid has yielded ammonia gas - indicative of the presence of -NH- linkages in the polymer chain.

(3) Heating the ammonia-stabilized gum in an autoclave at 300°C. yields a sticky gum which has excellent adhesive properties.

Experimental Procedures

In a typical preparation, 200 grams of HCl depolymerized gum was dissolved in an equal volume of carbon tetrachloride. A slurry of Celite 505 (approximately 15 grams) in CCl_4 was added to the gum and stirred until a homogeneous mixture was obtained. The mixture was filtered through glass wool on a Buchner funnel until a clear, slightly yellow solution was obtained.

Gaseous ammonia was bubbled into the solution until it turned an opaque white. The reaction mixture was washed several times with water to remove ammonium chloride and then placed over calcium chloride to dry. After drying, the carbon tetrachloride was evaporated from solution, care being taken to avoid excessive heating. The resultant product is a slightly cloudy gray oil.

It has been possible to obtain gums with excellent adhesive properties through a repolymerization, under heat and pressure, of the ammonia-stabilized liquid.

A sample of stabilized gum (90 grams) was placed in an electrically heated autoclave. The vessel was heated to 300°C. and maintained at this temperature for one hour.

After cooling, the pressure was released and a dark, sticky gum was obtained. This gum, after compounding with TiO_2 (DuPont R510) and benzoyl peroxide, is an extremely effective bonding agent for cured silicone stocks.

In more recent experiments, it was possible to obtain a gum by heating at atmospheric pressure. Samples of the stabilized gum were heated until a slight darkening (decomposition) occurred. These samples repolymerized on standing for short periods. The gum is similar to that obtained from the autoclave but the method of preparation involves a high loss of product through evaporation.

Other gums have been formed by treating the ammonia-stabilized gum with acidic reagents. A sample of stabilized gum was treated with dry HCl gas. An immediate increase in viscosity was noted and in approximately 5 minutes the sample was a solid white gum.

Samples of the stabilized gum have been treated with thionyl chloride and benzoyl chloride. These reagents were added in a ratio of 10% by weight to the stabilized gum. As in the reaction with dry HCl gas, there was an immediate increase in viscosity, followed by gum formation.

As mentioned previously, it is likely that the washing of the stabilized gum to remove ammonium chloride brings about a hydrolysis of silazine bonds. A sample of highly purified stabilized gum was fused with sodium hydroxide to determine whether the hydrolysis was complete.

The odor of ammonia was detected during fusion and the presence of the basic gas verified with litmus. Apparently the hydrolysis of silazines is not as complete in the higher molecular weight compounds as it is in the lower members of the series (10).

The available physical test data on the compounded gums prepared are tabulated below:

Gum	Tensile Strength p.s.i.	Elongation %	Hardness Shore A
Stabilized gum heated in autoclave	227	100	52
Stabilized gum treated with dry HCl	364	142	51
Stabilized gum heated at atmospheric pressure	398 386	100 142	61 56

All compounds contain 25 volumes Celite 505 and 2.0 parts of benzoyl peroxide.

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(10) Sauer, R. O., Journal of the American Chemical Society, 68, 241 (1946)

VII. THE REACTION OF DIMETHYLDICHLOROSILANE WITH POLYVINYL ALCOHOL - WATER MIXTURES

The possibility of forming condensation products which could combine the useful properties of both polyvinyl alcohol films and silicone polymers was investigated in a cohydrolysis study.

The reactants used were: Dimethyldichlorosilane, designated as component (S), DuPont "Elvanol" polyvinyl alcohol grade 72-51, designated as component (P), and water, (W).

Tough films are formed by exposing various hydrolysis mixtures to air. The best and most rapidly forming film resulted from a S 10 grams, P 5 grams, W 50 grams hydrolysis. It resists aromatic solvents and carbon tetrachloride, but becomes brittle when heated with anhydrous pyridine and acetone, probably because of the greater affinity for water possessed by these solvents. On re-exposure to air after being heated with solvents, the film regains its original properties. It is stable to dry HCl but breaks down almost completely in concentrated HCl. It is sensitive to sharp humidity changes—water softens and swells it. The film is tough, but not very elastic; it cracks at -40°F. and chars at 212°F.

Experimental Procedures

Polyvinyl alcohol (PVA) was dispersed in cold water, warmed on a hot plate, any lumps being broken up, and cooled to room temperature. Overheating causes darkening with the formation of a hard film. Dimethyldichlorosilane was added dropwise (1 gram/minute) from a dropping funnel accompanied by vigorous mechanical stirring. HCl gas was evolved and allowed to escape, and the hot reaction mixture was cooled in a water bath or in an ice bath when necessary. Stirring was continued for 20 minutes after the reactants were mixed, in order to remove as much HCl as possible--a problem to be solved is that of removing completely the HCl, which together with the heat of reaction breaks down the mixture. A portion of the resulting slurry was spread out to dry in air on a watch glass.

The results of a series of experiments are appended in Table 7. In general, with varying proportions of S, P, and W, either

(1) a film formed, while ether extraction of the slurry yielded a small amount of light oil; or

(2) two layers separated on standing, an oily layer which did not cure well when heated with ferric chloride and a viscous layer which formed no film and could not be cured, though ether extraction of this second layer removed a small amount of gummy material which became a horny solid in air. The results do not indicate the relation between the nature of the film and the SPW ratio, beyond establishing that the most efficient ratio is S 10 grams, P 5 grams, and W 50 grams.

A comparative study was made of the effect of combining 100 grams of water and 10 grams of PVA with each of the following:

(1) 20 grams Silicone Oil GE81119

(2) 20 grams Silicone Oil GE9981-LT-4

(3) 20 grams oil obtained by hydrolyzing dimethyldichlorosilane

(4) 20 grams dimethyldichlorosilane

In cases (1), (2) and (3), no reaction appeared to occur; no heat was evolved and in each case the resulting white slurry, when spread out, formed a brittle film similar to a PVA film, and an oil separated out. The slurry obtained from the reaction of case (4) was neutralized with ammonium hydroxide; half of the neutral portion was dried over the hot plate and left to settle into a rubbery mass which was broken up on the mill, washed repeatedly with water to remove ammonium chloride and dried with carbon tetrachloride and a stream of air. The resulting fragments were found to shrivel in the oven, and no compounding was possible. The other portion was extracted with ether; the extract yielded a small amount of oil, and the remaining portion was warmed on the hot plate and allowed to stand. A rubbery mass formed, from which a few drops of water oozed slowly over a period of days. Again, a sample piece soon became shrivelled in the oven and no compounding was possible.

Since the resulting film or gum formed during the cohydrolysis is to some extent elastic, it is likely that a compound is formed, rather than a mixture such as results from the oils (mixtures (1), (2) and (3)), and that this polymeric compound incorporates water during the hydrolysis stage.

Further experiments are being performed to investigate the quantitative nature of the water present as plasticizer, under varying conditions of exposure and temperature and the effect of using a plasticizer such as distearin with the cohydrolysis product.

As a modification of the procedures described, DuPont 'Ludox' colloidal silica suspension was substituted for water as the solvent for PVA. S 10 grams, P 2.5 grams, Ludox 25 milliliters, gave an almost solid mixture which was of no apparent value. Reducing the amount of Ludox to 5 milliliters in 45 milliliters of water gave a rubber film, although the colloidal suspension was apparently broken, and air bubbles decreased the strength of the film. This modification deserves further study.

In a second modification, 8.7 grams of fibrous asbestos was stirred into a batch of S 10 grams, P 5 grams, W 50 grams, in an attempt to prepare a suitable gasket material. This proved to be far too much asbestos, and the film had no rubbery properties at all.

TABLE 7

Summary, Silicone - PVA Mixtures

REACTANTS	% PVA (approx)	S:PVA soln.	TREATMENT	RESULTS	REMARKS
S 5g, P 0.5g, W 50g	1	1:10	Exposed to air Extracted w/ether	Forms film slowly same	Light oil in extract
S 5g, P 2.5g, W 50g	5	1:10	same	same	same
S 5g, P 5g, W 50g	10	1:10	Extracted w/ether Freeze dried	Forms film same	same Water remained
S 10g, P 10g W 100g	10	1:10	none	same	
S 10g, P 5g, W 50g	10	1:5	Heated in oven @ 60°C	Forms film quickly	Poor film - air bubbles
same	10	1:5	Exposed to air	Forms film	Best film *
S 15g, P 5g, W 50g	10	1:33	same	Two weeks - film part formed	Slurry shrinks-oil formed
S 20g, P 5g, W 50g	10	1:25	same	Two weeks - no film	More shrinkage - more oil
S 50g, P 2.5g W 25g	10	2:1	Washed w/water	Oil separates	Viscous layer - water solution

TABLE 7 cont'd

REACTANTS	% PVA (approx)	S: PVA soln.	TREATMENT	RESULTS	REMARKS
S 50g, P 2.5g, W 25g	10	2:1	Oil decanted - viscous layer exposed to air	Viscous layer- no film	Oil gums w/$FeCl_3$ and heat
same	10	2:1	Separate layers - extract both w/ether	Viscous layer - gummy solid	same
same	10	2:1	Separate layers - viscous layer washed w/N_2	Viscous layer - no film	same

S= $(CH_3)_2 Si Cl_2$ P= Polyvinyl Alcohol (PVA) W= Water

* Cracks @ -40°F

Chars @ 212°F

APPENDIX

A. The Role of Benzoyl Peroxide in Silicone Rubber Curing

The best picture of the mechanism by which dibenzoyl peroxide effects the curing of rubber seems to be that proposed by Farmer and collaborators (11, 12).

To study the behavior of benzoyl peroxide in this process, Farmer examined the action of the peroxide on a typical olefin, cyclohexene (analogous to the unit, $-CH_2\cdot CH{:}CH\cdot$ in rubber) and found that:

(1) The peroxide decomposes thermally to give free radicals by either fashion (a) or (b).

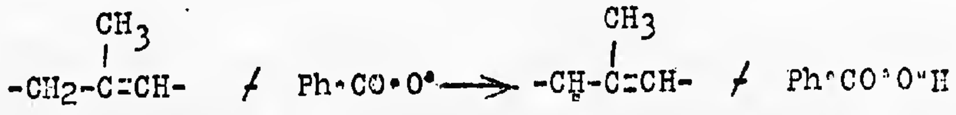
(a) $Ph\cdot CO\cdot O\cdot O\cdot CO\cdot Ph \longrightarrow Ph\cdot CO\cdot O\cdot + CO_2 + Ph\cdot$

(b) $Ph\cdot CO\cdot O\cdot O\cdot CO\cdot Ph \longrightarrow 2\ Ph\cdot CO\cdot O\cdot$

(2) These radicals as shown below, lead to the linking of olefin molecules and the formation of (benzoyl) derivatives of both the simple and polymeric olefins.

(3) The attack on the olefin molecules seems to be directed principally at the α-methylene groups.

Farmer proposes that cross-linking or vulcanization taking place during the curing of rubber seems to be due to a similar α-methylene attack by the peroxide fragments, where the radicals initially formed serve to continue the process in a chain type reaction as follows:



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH- + Ph\cdot CO\cdot O\cdot \longrightarrow -C\underset{\cdot}{H}-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH- + Ph\cdot CO\cdot O\cdot H$$

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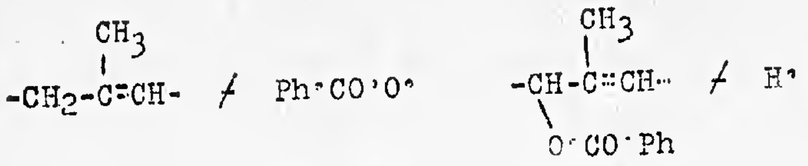
(11) Farmer, et al., Transactions of the Faraday Society, 38, 340, 348, 356 (1942)

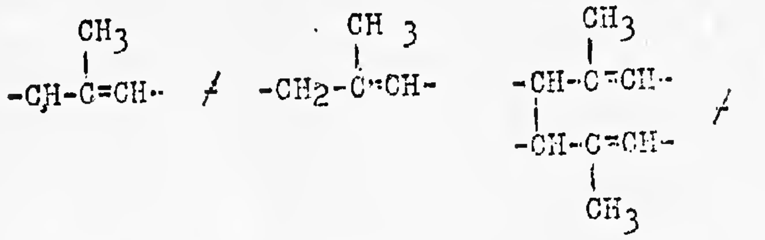
(12) Farmer and Michael, Journal of the Chemical Society, 144, 513 (1942)

or



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH- + Ph\cdot CO\cdot O\cdot \qquad -\underset{\diagdown O\cdot CO\cdot Ph}{CH}-\overset{CH_3}{\overset{|}{C}}=CH- + H\cdot$$

Substitution



$$-\dot{C}H-\overset{CH_3}{\overset{|}{C}}=CH- + -CH_2-\overset{CH_3}{\overset{|}{C}}=CH- \qquad \begin{matrix} -CH-\overset{CH_3}{\overset{|}{C}}=CH- \\ | \\ -CH-\underset{CH_3}{\underset{|}{C}}=CH- \end{matrix} + H\cdot$$

Cross Linking

It was pointed out by Farmer (13) that in order to avoid intercombination of any free radicals initially formed, the ratio of uncured rubber to peroxide (or other vulcanizing agent) must be large (thus, radicals would be more likely to attack the "parent molecule" and continue the chain, rather than attack another free radical).

The mechanism of α-methylene attack established for hydrocarbon rubber and supported by other evidence (14), can be applied to the peroxide initiated cross-linking of silicone chains if it is assumed that there is sufficient activation of the α-CH_3 group of the unit $-Si(CH_3)_2-O-$ to permit a similar attack by free radicals, with subsequent formation of $-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{Si}}-$ bridges as by the following reaction scheme (15):

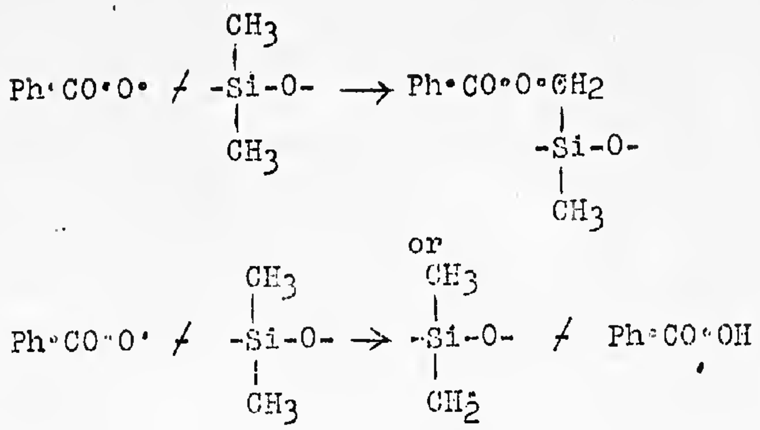
---

(13) Farmer, et al., loc. cit.

(14) Bell Telephone Company Patent, Chemical Abstracts, 42, 5714 (1948)

(15) Farmer and Michael, loc. cit.

1.

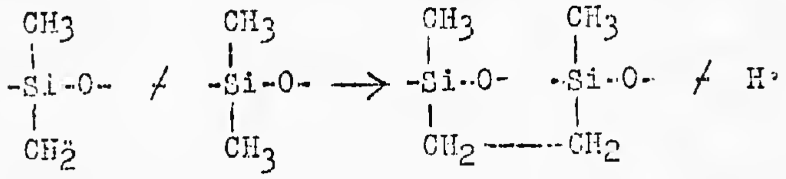


$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{-\overset{CH_3}{\underset{CH_3}{Si}}-O-} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH_2-\underset{CH_3}{Si}-O-}$$

or

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{-\overset{CH_3}{\underset{CH_3}{Si}}-O-} \rightarrow \mathrm{-\overset{CH_3}{\underset{CH_2^{\cdot}}{Si}}-O-} + \mathrm{Ph{\cdot}CO{\cdot}OH}$$

2.



$$\mathrm{-\overset{CH_3}{\underset{CH_2^{\cdot}}{Si}}-O-} + \mathrm{-\overset{CH_3}{\underset{CH_3}{Si}}-O-} \longrightarrow \mathrm{-\overset{CH_3}{\underset{CH_2}{Si}}-O-} \quad \mathrm{-\overset{CH_3}{\underset{CH_2}{Si}}-O-} + \mathrm{H^{\cdot}}$$

This picture of the cross linking would anticipate that (as in the case of hydrocarbon rubber) other compounds which break down spontaneously, or on heating, to give free radicals would have a curing action on silicone chains analogous to that promoted by dibenzoyl peroxide. Thus, diazocompounds of the type, $R{-}N{=}N{-}\overset{H}{N}{-}R$, such as diazoaminobenzene might serve as active vulcanizing agents by breaking up into free radicals, viz:

$$\mathrm{Ph - N = N - NH - Ph \qquad Ph^{\cdot} + N_2 + PhNH^{\cdot}}$$

This type of curing agent is reported (16) to give transparent vulcanizates which age well, but which are sometimes porous due to evolved nitrogen.

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(16) Stiehler and Wakelin, Industrial and Engineering Chemistry, 39, 1647 (1947)

B. Personnel employed on U. S. Government Contract DA-44-109-qm-64

During the period of June 5 - September 4, 1950

		Fraction of time spent on Contract
H. H. Wasserman, Ph.D.	Project Director	one-half
B. J. Humphrey, Ph.D.	Consultant Chemist	one-fifth
H. A. Fairbank, Ph.D.	Consultant Physicist	one-fifth
C. A. Walker, D.Eng.	Consultant Chemical Engineer	one-fifth
A. Pfenninger, B.E.	Chemical Engineer	one-fifth
N. A. Duke, M.E.	Rubber Technologist	full
T. S. Moroney, M.S.	Chemist	full
D. Wayman, B.S.	Chemist	full
R. Conca, B.S.	Chemist	full
H. Zimmerman, B.S.	Chemist	full
A. Glime, B.S.	Laboratory Technician	full
L. Corbo	Laboratory Technician	full
F. Taragowski	Laboratory Technician	full
P. Blanchard	Stenographer	one-third

C. Bibliography

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Weir, C. E., Lesser, W. H. and Wood, L. A., "Crystallization and Second Order Transitions in Silicone Rubbers", Technical Report No. 3 to the Office of Naval Research, National Bureau of Standards, December 15, 1949.

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A. Pfenninger Jr.
A. Pfenninger
Staff Chemical Engineer

Approved by:

C. M. Doede
C. M. Doede
Vice President

SUPPLEMENTARY

INFORMATION

TAB No. 70-3

1 February 1970

IDENTIFICATION	FORMER STATEMENT	NEW STATEMENT	AUTHORITY
AD-494 886 Connecticut Hard Rubber Co., New Haven. Progress rept. 5 Jun-4 Sep 50. 11 Dec 50 Contract DA-44-109-QM-64	DDC users only.	No limitation	USAMC ltr, 19 Jun 69