N 70 34148
NASA CR 108568

FINAL REPORT

DEVELOPMENT OF
A FLAME-RESISTANT SILICONE RUBBER

to

NATIONAL AERONAUTICS & SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER
HOUSTON, TEXAS 77058

CONTRACT NO. NAS 9-9510

ADL REFERENCE 71549

DATE: JULY, 1970

Arthur D. Little, Inc.

NASA CR 108568

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1 June 1969 to 1 June 1970

A FLAME RESISTANT SILICONE RUBBER

by

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TO: National Aeronautics & Space Administration
Manned Spacecraft Center
Houston, Texas 77058

Contract: NAS 9-9510
ADL Reference: 71549
Date: June 25, 1970

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ABSTRACT

To improve the flame resistance of silicone rubbers, we have compounded them with selected flame retardants. For the base stock in this investigation, we used the reinforced gum stock from General Electric, SE-517. This stock produces rubbers with good strength properties and very low temperature flexibility.

Because the silicone gum is cured at an elevated temperature in the presence of peroxides, the selection of the flame retardant was restricted to those additives that are stable under these conditions. Although the polymeric backbone of silicone rubbers is stable at elevated temperatures for an extended period, silicone rubbers are affected by the presence of slightly acidic or basic materials. Accordingly, in our screening of flame retardants, we were careful to select additives with a neutral pH that did not degrade to give residues that were either acidic or basic. After the initial screening, we found two types of additives that were effective as flame retardants for silicone rubber: aluminum silicates and aromatic bromides.

Natural kaolins or aluminum silicates can be incorporated in the rubber at levels up to 100 parts per 100 parts of the base gum stock to give a flame-resistant rubber with reasonably good physical properties. The high concentration of aluminum silicate in the rubber tends to reduce the resilience of the rubber and generally tends to make it stiff. For this application, the aluminum silicates must have a neutral pH. Although the silicates are effective flame retardants, apparently they only improve the flame resistance of the silicone rubber when the specimens are burned at the top. The oxygen-index measurements in our laboratories and the flammability tests at NASA-Houston confirmed this result.

To improve the flame resistance of these rubbers when they were burned at the bottom, halogen-containing additives were found to be the most effective and, in particular, the aromatic bromides. Aromatic bromides are sufficiently stable to easily withstand the elevated temperature of the cure, and their volatility is low enough so that the flame-resistant product loses essentially no weight at 10^{-7} torr. after 72 hours.

Aromatic bromides containing hydrogen atoms were shown to be deleterious. Apparently HBr can evolve during the cure and degrade the silicone rubber. Thus, we have found that the best flame retardant for silicone rubber is decabromodiphenyl. This product has low volatility and easily withstands the cure temperatures without degrading the elastomer.

The decabromodiphenyl used as a flame retardant must be very pure and also must be added to the gum as a very fine powder. Particle dimensions equal to or less than 3 microns are preferred. We have found that the best compromise in terms of flame resistance and physical properties can be achieved by incorporating 75 parts of decabromodiphenyl per 100 parts of the gum stock. This formulation has an oxygen index as measured by

the bottom-burning test of 40 and is self-extinguishing at 10 psia in atmospheres containing from 40 to 50% oxygen. This formulation has a tensile strength of approximately 750 psi.

Where additional strength is required, a small amount of the highly reinforcing silica, Cab-O-Sil HS-5, can be added (5 to 8 parts). The additional silica added to the mill after the gum has been compounded with the flame retardant yields an elastomer with a tensile strength of approximately 850 psi. However, the addition of this silica reduces the resilience of the rubber and reduces its low-temperature flexibility.

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INTRODUCTION

In space exploration, extravehicular activity (EVA) both in the earth orbit and on the lunar surface is essential. Furthermore, with the advent of the space station and the shuttle, additional elastomeric materials for fabrication of garments, EVA equipment, and components of the space station and shuttle will be needed. These materials will have to withstand environmental extremes, from -250°F to 250°F. Moreover, because much of this equipment will be exposed to oxygen-rich atmospheres both during launch and during orbit, safety requires that the elastomeric materials be nonflammable in this environment.

Characteristically, materials become harder and more brittle at low temperatures. To be useful, they must retain both flexibility and compressibility at low temperatures. In addition, they must have useful properties at or above room temperatures. The silicone elastomers with their unique polymeric backbone have good flexibility at low temperatures and retain their superior properties at elevated temperatures for extended periods. Unfortunately, these elastomers fail to meet the nonflammable criterion.

To improve the flame resistance of these silicone rubbers, we have compounded them with selected flame retardants. Additives have been selected on the basis of their low volatility, good low-temperature characteristics, and their ability to minimize any undesirable effect on the properties of the elastomer. Realizing that the peroxide curing system required to vulcanize the silicone gum can be inhibited by certain additives, we have attempted to screen out these additives during the initial phase of the work. Our approach was to first select the best flame retardant system, disregarding the strength properties of the compounded elastomer, and then optimize the physical properties of the resulting flame-resistant silicone rubber.

EXPERIMENTAL

MATERIALS

Base Polymers.-- The silicone base polymer, whether gum or reinforced gum, is the most important ingredient in any silicone rubber compound. It dictates the shrinkage characteristics of the compound, the surface temperature range, the processing characteristics, and to some extent the profile of physical properties. In working with the pure gum, we have used General Electric's SE-54. This is a low-temperature stock with low shrinkage. It has a specific gravity of 0.98 and contains both phenyl and vinyl groups.

In most of this investigation, we used the reinforced silicone rubber gum, SE-517 (General Electric). This reinforced gum uses essentially the same gum stock, but it contains approximately 22% of a highly reinforcing silica filler, and a proprietary low-molecular-weight silicone compound that promotes the wetting action of the silica. Generally, SE-517 is characterized by an ability to accept additional reinforcing fillers and produce high-strength, resilient stocks ranging in hardness from 30-80 durometer. It has a specific gravity of 1.13.

Reinforcing Silica Fillers. -- Fumed silicas having narrow pH ranges with surface areas between 200 and 300 m^2/g. are preferred for compounding with silicone gums. In formulating compositions starting with pure gum stock, we have used Cab-O-Sil MS-7. This has a surface area of 250 m^2/g. The acid number is approximately 0.4 and the OH concentration is approximately 2%. In our formulations with the reinforced gum, we have used Cab-O-Sil HS-5. This has a surface area of 325 m^2/g. and an hydroxyl concentration of 8%.

Peroxide Curing Agent. -- In most instances, we have used the peroxide 2,4-dichlorobenzoyl peroxide. This was used as the commercial product, Luperco CST (Lucidol). This peroxide has a half life of 1.4 hours at 158°F and 0.25 hours at 185°F. The peroxide is used as a 50% active material with silicone oil as the diluent.

Flame Retardants. -- We have compounded with decabromodiphenyl (D.B.D.P.) from two sources, Great Lakes Chemical and Michigan Chemical. The product from Great Lakes was recrystallized from the reagent-grade trichlorobenzene as follows: a 5% solution of the bromo derivative was heated to 230°F to attain solution, and the decabromodiphenyl was recovered as fine crystals from the solution after it was cooled to room temperature. This product could also be purified merely by washing it first with distilled water and then with isopropyl alcohol. It was dried in a vacuum oven at 100°C.

The preferred technique for purifying decabromodiphenyl from Michigan Chemical was to recrystallize it in the following manner. It was first dissolved in trichlorobenzene using a ratio of 6 parts solvent to 1 part of the bromo derivative (on a weight basis) at a temperature of approximately 180°C. To remove extraneous insoluble material, the hot solution was filtered and then added rapidly to a large volume of isopropyl alcohol. Usually a ratio of 2 parts of alcohol to 1 part of the chlorinated solvent (on a volume basis) was used. The purified decabromodiphenyl in a finely divided form was then filtered and washed a few times with isopropyl alcohol to remove the trichlorobenzene. Finally, the bromide was dried in a vacuum oven for 4 hours at 400°F.

Other additives were used without further purification. In some instances they were dried in a special manner. Special treatment is described in the section on Results.

PROCESSING CONDITIONS

The silicone rubber compositions were compounded on a conventional 12-inch, two-roll mill. Typically, batch sizes were approximately 150 grams, but larger master batches were occasionally prepared. The mixing was carried out on a cool mill, and we found that it was best to use a scraper blade to simplify the removal of the gum.

In a typical procedure, the gum was added to the mill, allowed to band, and filler addition was started immediately. The filler, which could be additional silica or the flame retardant, was mixed with the gum for approximately 15 minutes. Finally the peroxide was added and mixed for an additional 5 minutes.

After milling, the usual practice was to immediately cure the sample in a mold at 50,000 psi. The primary objective was to impart dimensional stability. Samples were cured at temperatures varying from as low as 250°F up to 287°F. The mold thickness was 0.035". Occasionally a 0.075" mold was employed. The best procedure for molding was to maintain a constant temperature. In some instances, however, we did start with a cold mold. Molding time was varied from 5 to 20 minutes.

Because our objective was to prepare a flame-resistant elastomer containing a very low concentration of volatiles, oven curing or post curing was normally carried out in a vacuum oven at <1 torr. at 400°F for 4 hours. Alternately, we pre-dried the silicone gum rubber at 400°F/ <1 torr. for 4 hours and then carried out the oven cure in the forced-draft oven at 400°F for 4 hours.

The reinforced gum SE-517 had a weight loss of 5% if it was pre-dried for 4 hours, and if the gum (as received) was cured in the vacuum oven,a similar weight loss was obtained. If the pre-dried gum was used to formulate the flame-resistant rubber,the rubber lost ca. 1.5-1.6% weight in the forced-draft oven during the 4-hour cure. Extending this cure to 16 hours increased the weight loss to a total of ca. 2.0%. On the other hand, if the gum (as received) was used in the formulation containing 75 parts of the flame retardant, the flame-resistant rubber lost 3.5-3.6% weight in the vacuum oven during the 4-hour cure. After 16 hours the total weight loss was ca. 3.9%.

TESTING PROCEDURES

Oxygen Index. -- Flammability of the cured samples was tested by the oxygen-index method (tentative ASTM method, May 14, 1969). In this test, the oxygen index N of a material is the percentage concentration of oxygen in a mixture of oxygen and nitrogen at atmospheric pressure that will maintain equilibrium burning conditions. Physically, this is the lowest concentration of oxygen that will support sustained combustion of the material and is computed according to the formula

$$N = \frac{100\,[O_2]}{[O_2] + [N_2]},$$

where $[O_2]$ is the oxygen concentration at equilibrium and $[N_2]$ is the associated nitrogen concentration. Thus, the smaller the value of N, the more flammable the specimen, and conversely.

In this test, a sample of the material 7-15 cm. long x 6.5 ± 0.5 mm. wide x 0.035" thick (Where noted below the thickness was occasionally 0.075") was placed vertically in the center of the column filled with the gases flowing at a rate of 5 cm./sec. and ignited by a hydrogen flame.

Normally, measurements made by this method involved igniting the sample at the top. In this investigation, we modified this method and burned the sample in the selected atmospheres at both top and bottom of the specimen strip. Two samples were used for each test. The reproducibility of this method at the top is ± 0.5, and at the bottom, ± 1.

This test was designed to overcome, as far as possible, the three major drawbacks of a number of flammability tests: (1) the manner in which the sample is ignited; (2) the definition of the end point; and (3) operation under non-equilibrium conditions. Tensile and elongation properties of the formulated silicone rubbers were measured according to ASTM Method 412. The Instron tester was set at a speed of 20"/min. and the dumbell was cut with dye D.

Low-Temperature Testing

For measuring the low-temperature properties of the flame resistant silicone rubber we used the Clash and Berg flexular test (ASTM D-1043-61T). The samples were cooled in a dewar flask containing ethanol and dry ice. Measurements were then made as the samples were allowed to warm to room temperature. A torque of 0.02 lb.-in. was used for all of these tests. Sample thicknesses of the different materials were varied, as reported in the following section.

Volatility Testing

To test the elastomer's ability to withstand exposure to hard vacuum, samples measuring 0.25" x 3.0" x 0.035" were placed in separate glass chambers attached to a vacuum line capable of attaining a pressure of 1×10^{-7} torr. A mercury diffusion pump with a capacity of 5 liters/sec. was used to evacuate the system and an ion vacuum gauge was used to measure the vacuum.

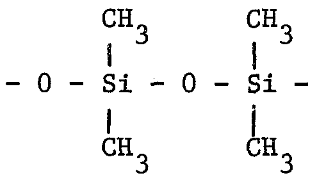
PREPARATION OF FINAL SAMPLE -- The reinforced silicone gum SE-517 (General Electric, Lot #131) was vacuum dried for four hours at 400°F/ <1 torr. and compounded with decabromodiphenyl (Michigan Chemical, Lots #647-89B and 634-57) that was recrystallized, as described above. After these ingredients were mixed on the mill for 15 minutes, Luperco CST (Lot #LVG 5281) was added and mixed for an additional 5 minutes. The ingredients were combined in the following manner: 100 pts. gum, 75 pts. D.B.D.P., and 1.2 pts. CST.

After compounding, the mixture was molded at 265°F for 15 minutes in a mold 6" x 6" x 0.075" under a pressure of 50,000 psi. Oven curing was carried out in a forced-draft oven at 400°F for 4 hours.

RESULTS AND DISCUSSION

SILICONE RUBBER TECHNOLOGY

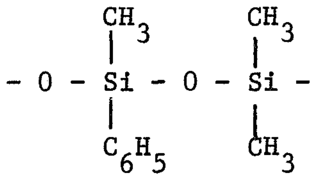
Formulation. -- Silicone rubber compounds have simple formulations as compared to those made up from the purely organic elastomers. They consist essentially of gum, fillers, and curing agents. A typical formulation contains on a weight basis 100 parts silicone rubber gum, 20-200 parts of filler, and 0.5-3 parts of curing agents. The basic skeleton of silicone rubber now on the market is a polydimethylsiloxane chain, as shown below.



$$-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-$$

These polymers have a molecular weight ranging from 300,000-700,000.

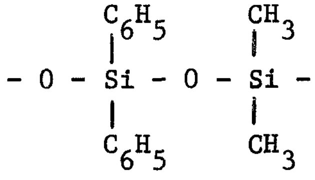
Rubbers from polydimethylsiloxanes lose their elasticity and become brittle at about -50°C. However, if some of the dimethylsiloxane units are replaced by increasing amounts of methylphenylsiloxane units,(as shown below)



$$-O-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-$$

the stiffening temperature first falls -- reaching a minimum of about -115°C at a content of 7.5 mole % of the methylphenylsiloxane units -- but rises again on further substitution. Thus, the concentration of phenyl units in the polymer chain must be optimized to obtain the best properties. As expected, the addition of phenyl groups also reduces the tendency toward crystallization.

Phenyl groups also can be incorporated in the molecule as diphenylsiloxane units, as shown below:



$$-O-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-$$

Dow's silicone rubber contains methylphenylsiloxane units, whereas that from Union Carbide and General Electric contains diphenylsiloxane units.

The introduction of phenyl groups into the polymer chain not only improves low-temperature behavior, but also increases the ability of these polymers to withstand elevated temperatures, primarily because the phenyl group is less susceptible to oxidation than the aliphatic one. Polymers containing diphenylsiloxane units have even greater heat stability than those containing methylphenylsiloxane units. Fortunately, these same polymers with phenyl groups also have superior flame resistance, and their vulcanizates have higher tensile strength and tear resistance than the vulcanizates of pure dimethylsiloxanes. However, these phenyl groups do reduce the resiliance of the rubbers somewhat and interfere with the cure. This disadvantage can be compensated to a certain extent by incorporating small amounts (0.1-0.5 mole %) of vinyl groups into the polysiloxane molecule.

Selection of the Base Formulation. -- To achieve the good low-temperature properties and stability required of the flame-resistant elastomer, we selected the silicone gum SE-54 from General Electric containing the diphenylsiloxane units. SE-54 actually contains 5.2 mole % phenyl. In addition to compounding with the pure silicone gum rubber, we have also used the so-called reinforced gum stock that has been made available by the silicone rubber producers. These stocks are master batches consisting of gum rubber and highly reinforcing silica fillers. They are prepared by the producer in a dough mixer. A low-molecular-weight reactive silicone is added to assist in the wetting-out process of the silica. All of the reinforced gums are proprietary compositions. In our investigation we have used General Electric's SE-517, which contains 22% silica or 28 PHR.

Pure unfilled silicone rubber gums have very poor mechanical properties, and reinforcing fillers are required. The highest reinforcing effect is obtained with fumed silicas which have BET surface areas of 150-400 m^2/gram. Vulcanizates containing these silica are characterized by high tensile strength. We have used Cabot's MS-7 and HS-5 as recommended by the industry.

Silicone rubber is cured or crosslinked by means of organic peroxides at elevated temperatures. The peroxides are dispersed homogeneously in the silicone rubber compound at temperatures at which they do not decompose. The compounds are then introduced into molds, and subsequently exposed to temperatures above 100°C whereupon crosslinking takes place. Benzoyl peroxide, p-chlorobenzoyl peroxide, and 2,4-dichlorobenzoyl peroxide are the three classical crosslinking agents for silicone rubber. We have selected the latter peroxide because it has a low decomposition temperature and, more importantly, its decomposition gives rise only to products with low vapor pressures. The commercial product is Luperco CST (50% active).

PRELIMINARY SCREENING OF FLAME RETARDANTS

To establish a base for the screening of potential flame retardants for silicone elastomers, we first tested the silicone gums that we planned to use in this investigation to determine their flammability according to the oxygen-index method. The results are shown in Table I. As this table shows, both SE-54 and SE-517 have an oxygen index of 22. Dow's fluorinated silicone elastomer LS-53 has a similar value. Adding auxiliary amounts of silica has very little effect on the flammability of these gums. According to the oxygen-index values, some of the commercial flame-resistant formulations have flame resistance not much greater than the unformulated products. However, these commercial products were prepared to pass very specific use tests developed by the aircraft industry, e.g., the Boeing test. According to an analysis by x-ray diffraction and fluorescence, the Union Carbide product X3901 showed the presence of chlorine and antimony oxide. The product from General Electric was presumably made flame resistent by their patented process that involves adding small amounts of chloroplatinic acid. Incidentally, a cursory examination of the flame-resistant Viton A indicated that it contains ca. 4% PbO.

In our initial screening, formulations were prepared with 15 parts of the additive (See Table II). This screening immediately revealed one of the most important problems in developing flame retardants for silicone rubbers. Any additive which is acidic or basic by itself, or forms such residues during the curing operation, reduces the physical properties of the resulting silicone rubber. Although the polysiloxane chain has good oxidative stability, it is very susceptible to degradation by acids or bases. Thus, phosphates were inappropriate additives, because they degraded during the cure cycle to give acidic residues. Although polyphosphonitrilic chloride was an effective flame retardant, it interfered with the cure of the silicone rubber gum; presumably because this chlorine-containing polymer evolves HCl at elevated temperatures. Another slightly acidic additive, ferrous sulfate hydrate, although effective as an additive, could not be used in silicone rubber formulations.

The commercial product, Krytox oil, which is a completely fluorinated polypropylene oxide, behaves as a plasticizer and, therefore, only a limited amount could be incorporated into the rubber composition without destroying the physical properties of the rubber.

Thus, according to this initial screening only copper oxide and kaolin (aluminum silicate) are effective flame retardants that can be used with silicone rubber. Other additives were tested at higher levels, as shown in Table III, but none of these appeared to be as effective as either copper oxide or kaolin. Whether adding 50 or 100 parts of glass powder, the oxygen index rose no higher than 26. The fluorinated polymers showed no benefical effect, and the chlorinated ones were poor because they degraded the silicone polymer during the cure.

TABLE I

FLAME RESISTANCE OF COMMERCIAL SILICONE ELASTOMERS

Elastomer	Silica, PHR	Oxygen Index Top
SE 54, Silicone Rubber Gum (GE)		22
SE 54, Silicone Rubber Gum (GE)	20	23
SE 54, Silicone Rubber Gum (GE)	35	23
SE-517 Reinforced Gum (GE)	28	22
SE-517 Reinforced Gum (GE)	35[a]	22
X-3-2021 Reinforced Gum (Dow)	?	22
Silastic LS-53[b]	?	22
Flame Resistant Silicone Rubber X-3901 (Union Carbide)	?	24
Flame Resistant Silicone Rubber CE 5537 (General Electric)	?	23

[a] 5 pts. Cab-O-Sil HS-5 was added to 100 pts. of SE-517.

[b] Dow's fluorinated silicone rubber.

TABLE II

FORMULATIONS[a] WITH 15 PARTS ADDITIVE

Additive	Oxygen Index Top	Remarks
Zn Dust	23	
Sn Dust	22	
$ZnSO_4 \cdot 7H_2O$	25	
$FeSO_4 \cdot 7H_2O$	26	Interfered with cure
Polyphosphonitrilic Chloride	26	Interfered with cure
Dechlorane Plus 515	24	
Dechlorane Plus 515[b] Sb_2O_3	23	
Tris (1-bromo-3-chloroisopropyl) phosphate (Firemaster T 13P)	--	Did not cure
Tris (2,3-dibromopropyl) phosphate (Firemaster T 23P)	--	Did not cure
Fiber Glass (1/8" length)	25	
CuO (dried 2 hrs. @ 400°F/ <1 torr)	26	
PbO	23	
Al_2O_3	23	
Krytox - Fluorinated Oil	26	
Busan M-11 Metaborate (Buckman Lab)	24	
Azodicarbonamide	24	
Manganese (III) Acetylacetonate	23	
Dicyclopentadienyl Iron	--	Did not cure
KI	24	
CuI	--	Did not cure
Tetraethyl orthosilicate[c]	24	
Kaolin Ultrawhite 90 (Minerals & Chemicals)	26	

a. SE-54 Gum (General Electric) 100 pts.
Silica Cab-O-Sil M-7 20 pts.
Luperco CST 1 pt.
Molded at 250°F/10 min.
Oven cured at 400°F/ <1 torr - 16 hrs.

b. 10 pts. Dechlorane and 5 pts. Sb_2O_3

c. 5 pts.

TABLE III

MISCELLANEOUS ADDITIVES[a]

Additive	Parts/ 100 pts. Gum	Oxygen Index Top	Physicals
Glass Powder	50	26	Good
(200 Mesh)-Ferro Corp	100	26	Good
PVC Powder	50	25	Degraded in oven
Chlorinated PVC	100	25	Degraded in oven
Teflon Powder	100	25	
Sb_2O_3	40		
Fluoro Compound F160 (L.N.P.)	100	26	
Sb_2O_3	40		
Vinylidene Fluoride	100	26	
Sb_2O_3	40		

[a] Formulation -

SE-54 Gum	100 pts.
Cab-O-Sil M-7	20 pts.
Luperco CST	1 pt.

Molded at 250°F/10 min.

Oven cured at 400°F/ <1 torr - 16 hrs.

Further examination of the copper-oxide system indicated that it achieved a maximum effect as a flame retardant at the 50-part level, but no advantage was obtained by increasing it beyond this point, as shown in Figure 1. To determine whether auxiliary additives would enhance the effect of copper oxide, we prepared two-component additive mixtures with 50 parts copper oxide and 50 parts of the auxiliary additive. As shown in Table IV, none of these additives were more effective than copper oxide alone.

Interestingly, among the metal oxides, the copper, nickel and boron oxides were the most effective as flame retardants for silicone rubber, as shown in Table V. Boron oxide is a low-melting glass; however, it is slightly acidic and, therefore, produces a silicone rubber with poor physical properties.

SILICATES

Single Component System. -- According to our preliminary screening, it appeared that the silicates were the best candidates as flame retardants for silicone rubber. Accordingly, we tested a number of commercial silicates (see Table VI). Although asbestos was a superior flame retardant, it contains a mixture of both magnesium and aluminum ions and therefore is slightly basic. Thus, the resulting formulated silicone rubber had poor physical properties. Mica contains magnesium and alkali-metal salts and behaves similarly. Many of the commercial silicates are deficient, because they are either slightly acidic or basic. A partial list of physical properties of some of the commercial silicates appears in Table VII. Both clays from Huber, Suprex with a pH of 4.5-5.5 and Nulok 321 with a pH of 8.5-9.0, gave products with poor properties. Clays treated with various low-molecular-weight silanes also were ineffective in yielding a product with good physical properties. Not too surprisingly, the synthetic silica-alumina catalyst (American Cyanamid) was too acidic; in fact the product containing this additive could not be cured. Barium, zirconium, copper, calcium, and magnesium silicates all produced silicone rubbers with poor physical properties. Thus, only the neutral aluminum silicates are the most outstanding both in their effectiveness in imparting flame resistance and in retaining the physical properties of the silicone rubber.

All of the neutral aluminum silicates were effective, and the list of those tested appears in Table VIII. The high-surface aluminum silicate X1657 from Minerals and Chemicals, was undoubtedly ineffective because it has base-exchange capacity equivalent to 20-25 me/100 grams. Similarly, merely washing Ultrawhite 90 with acid resulted in a product that prevented the cure of the silicone gum.

FIGURE 1

EFFECT OF CuO ON OXYGEN INDEX

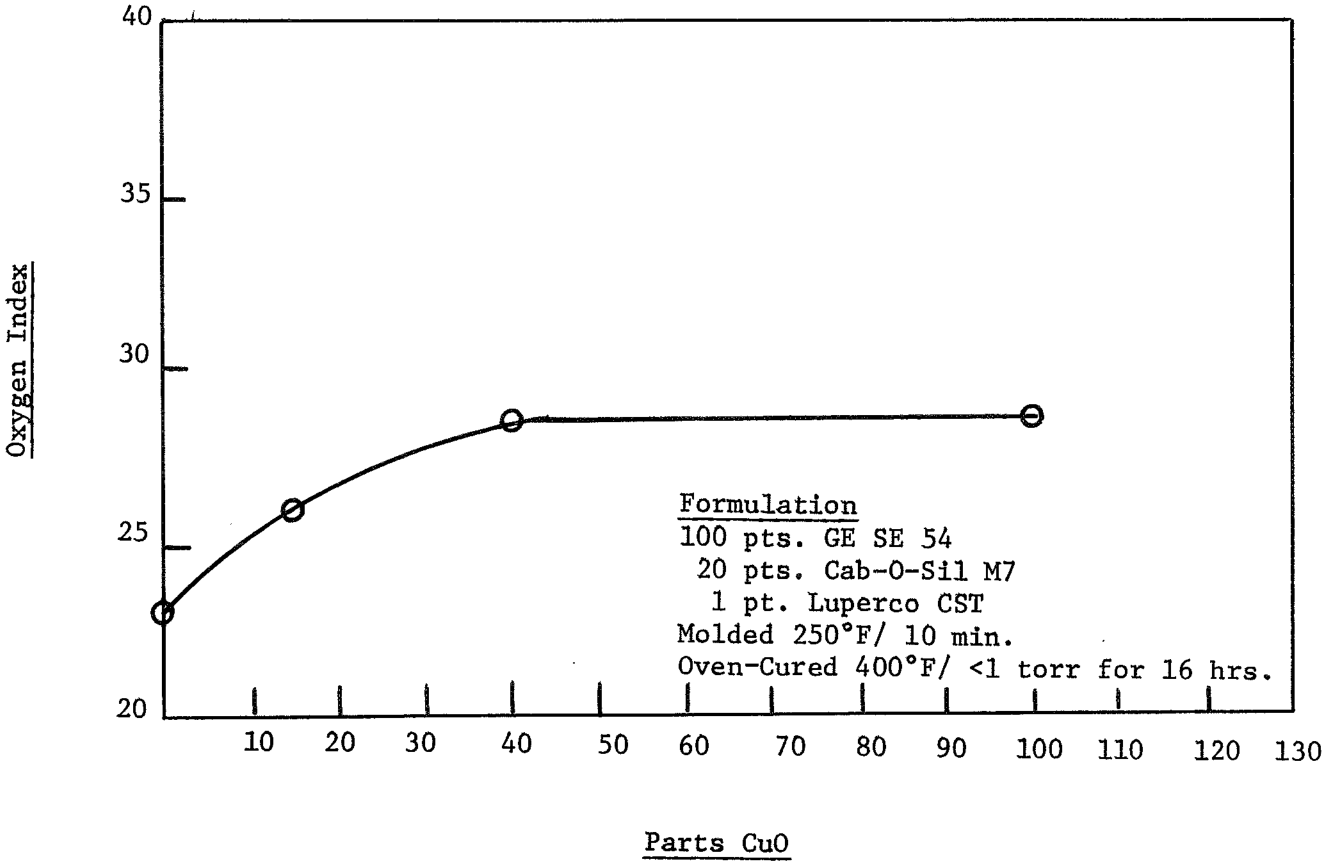


TABLE IV

TWO COMPONENT ADDITIVE MIXTURES CONTAINING CuO[a]

Additive	Oxygen Index Top	Physicals
CuO[b]	28.5	Good
$ZnSO_4 \cdot 7H_2O$[b]	27.0	Some difficulty with cure
Dechlorane Plus 515	24.0	Fair
Glass Powder (200 Mesh)	25.0	Good

a. Formulation:

SE-54 Gum (General Electric)	100 pts.
Silica Cab-O-Sil M-7	20 pts.
CuO	50 pts.
Luperco CST	1 pt.
Other Additive	50 pts.

Molded at 250°F/10 min.
Oven Cured at 400°F/ <1 torr for 16 hrs.

b. Dried at 400°F, 2 hrs., <1 torr

TABLE V

FORMULATIONS WITH OXIDES[a]

Additive	Parts	Oxygen Index Top
CuO	50	28
	100	28
PbO	50	26
Co_3O_4	50	27
I_2O_5	50	26
Ni_2O_3	50	28
MnO_2	50	24
Fe_2O_3	50	26
B_2O_3	50	28

[a] Formulation:

SE-54 Gum	100 pts.
Cab-O-Sil M-7	20 pts.
Luperco CST	1 pt.

All oxides except B_2O_3, I_2O_5, and PbO were dried at 400°F/ <1 torr for 2 hrs.

Molded at 250°F/10 min.
Oven cured at 400°F/ <1 torr for 16 hours.

TABLE VI

FORMULATIONS WITH OTHER SILICATES[a]

Silicate	Parts 100 pts. Gum	Oxygen Index Top	Physicals
Asbestos 7 RF-1	50	32	Poor
(Johns Manville)	100	35	Poor
Asbestos RG 244	50	31	Poor
(Union Carbide)	100	34	Poor
Asbestos RG-444-10	50	29	Poor
(Union Carbide)	100	30	Poor
Mica Powder (325 Mesh)	50	29	Poor
Nulok 321-SP Clay	64	26	Poor
(J.M. Huber Corp.)			
pH 8.5 - 9.0 Silane Modified	128	33	Poor
NUCAP 400 Clay	64	26	Poor
(J.M. Huber Corp.)			
pH 6.7 - 7.2 Silane Modified	128	34	Poor
Suprex Clay	64	26	Poor
(J.M. Huber Corp.)	128	34	Poor
Aiken Clay, pH 7	128	34	Poor
(C.P. Hall)			
Burgess Thermo Glace H	128	34	Poor
(Burgess Pigment Co.)			
Aerocat Triple A Catalyst[b]	128		Did not cure
(American Cyanamid)			
Aerocat	128		Did not cure
Magnesium Silicate	50	25	Poor
Avibest-Hydrated	50	32	Poor
Magnesium Silicate (FMC)			
Calcium Silicate	50	27	Poor
(Johns Manville)			
Copper Silicate	128	30	Poor
Zirconium Silicate	128	26	Fair
Barium Silicate	50	28	Poor

a. Two formulations were used. Those with 50 and 100 pts. silicate were blended with 100 pts. SE 54, 20 pts. Cab-O-Sil M-7, and 1 pt. Luperco CST. Molded at 250°F/10 min. and oven cured at 400°F/< 1 torr for 16 hrs. Formulations with 64 and 128 pts. silicate (based on pure gum) were blended with 100 pts. silicate, 100 pts. SE-517, and 1.5 pts. Luperco CST. Oven cured for 4 hrs.

b. High Alumina Cracking Catalyst (silica-alumina)

TABLE VII

PHYSICAL PROPERTIES OF COMMERCIAL SILICATES

	Particle Size (μ)			Surface Area
	% Finer Than 2	Average	pH	$m^2/g.$
Ultrawhite 90 (M&C)	92-94		6.3-7.0	
ASP 072 (M&C)	98	0.3	6.3-7.0	
Ansilex X-1663 (M&C)	90		5.0-6.0	18-19
X-1657 (M&C)	75			135-145
ASP 170 (M&C)		0.55	6.5-7.5	
ASP 172 (M&C)		0.55	6.3-7.0	
ASP 352 (M&C)		0.85	6.5-7.0	
ASP 405[a] (M&C)		4.8	6.1-6.5	
Thermoglace H (Burgess)		0.1-0.4	6.5-7.5	
Suprex (Huber)	87-92		4.5-5.5	
Nulok 321 (Huber)[b]		0.3	8.5-9.0	20-22
NUCAP 400 (Huber)[c]		0.3	6.7-7.2	20-22

a. Treated with a cationic organophilic surfactant

b. Treated with an aminosilane

c. Treated with a mercaptosilane

TABLE VIII
FORMULATIONS WITH ALUMINUM SILICATE[a]

Aluminum Silicate	Parts 100 pts. Gum	Oxygen Index Top	Physicals
Ultrawhite 90	50	28	Good
	128	35	Good
ASP 072	128	34	Good
Ansilex (X-1663)	128	35	Good
X-1657 (High Surface)	128	Did not Cure	
ASP 170	128	34	Good
ASP 172	50	27	Good
ASP 352	128	35	Good
ASP 405	50	29	Good
Ultrawhite 90 (Dehydrated at 1000°F/3 hrs.)	128	28	Poor
Laboratory Preparation-adjusted to pH 7.0	128	33	Good
Kaolin-Harshaw	50	27	Good
Fiber Frax (Kaolin Fiber)	128	28	Poor
Acid-Washed Ultrawhite 90[b]	128	Did not Cure	

a. Two formulations were used. Those with 50 pts. silicate were blended with 100 pts. SE 54, 20 pts. Cab-O-Sil M-7, and 1 pt. Luperco CST. Molded at 250°F/10 min. and oven cured at 400°F/ <1 torr for 16 hrs. Formulations with 128 pts. silicate (based on pure gum) were blended with 100 pts. silicate, 100 pts. SE-517, and 1.5 pts. Luperco CST. Oven cured for 4 hrs. Unless otherwise noted, silicate producer is Minerals & Chemicals.

b. Washed with 10% H_2SO_4 and dried

Most commercial kaolins (aluminum silicates) contain approximately 10% water of crystallization. Interestingly, when the kaolin Ultrawhite 90 was dried at 1000°F for 3 hours, it became less effective as a flame retardant. Thus, the gum with 128 parts of this kaolin had an oxygen index of 35; after the kaolin was dehydrated, the index dropped to 28 and, incidentally, the physical properties of the resulting silicone rubber became poor. Close examination of Table VI indicates a similar result. For example, the hydrated magnesium silicate, Avibest, has an oxygen index of 32, in contrast to the anhydrous magnesium silicate which has an index of 25. This observation that water plays a role in making the silicates effective as flame retardants for silicone rubbers perhaps gives us a clue concerning how the silicates operate as flame retardants. An attractive concept is that the water of hydration plays a role in bonding the silicates to the polysiloxane chain in the silicone rubber during the burning process. This crosslinking would thus reduce the amount of volatiles and decrease the flammability of the rubber.

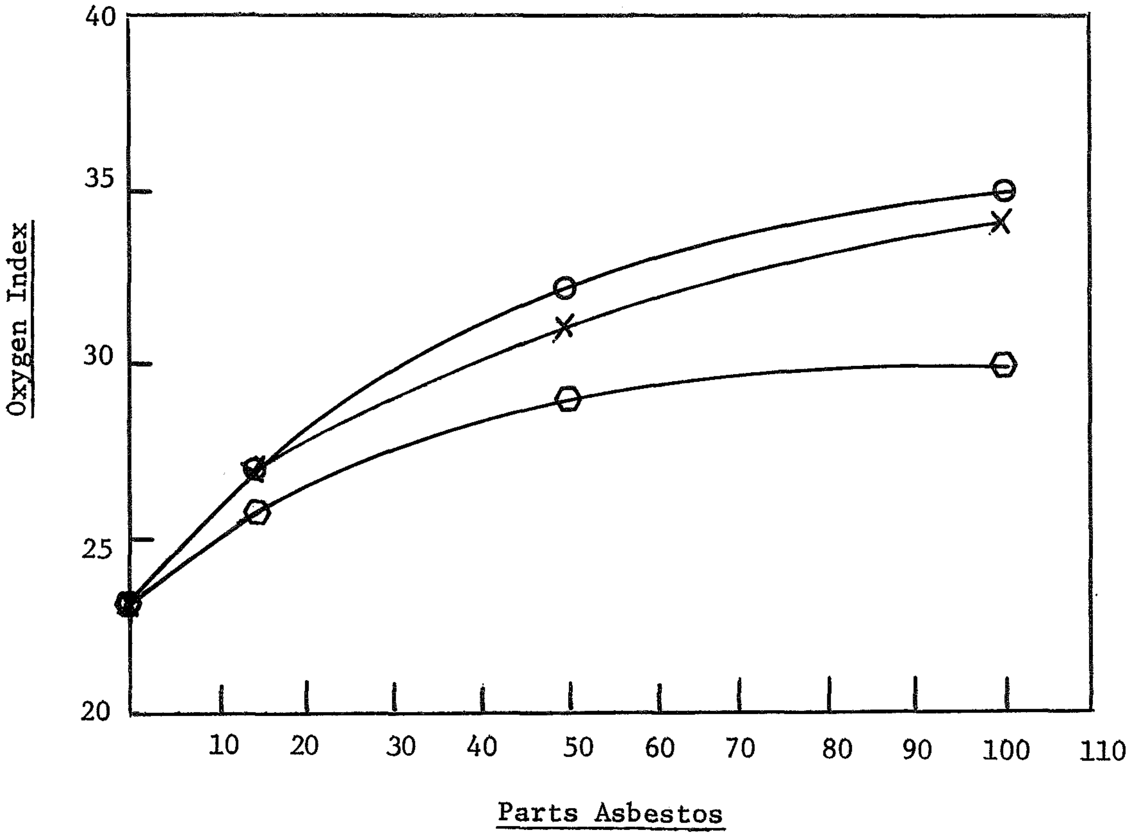
Hoping to further improve the effectiveness of the natural aluminum silicates, a number of preparations were made in our laboratories. Aluminum silicate was synthesized by treating aluminum nitrate with tetraethylsilicate in a methanol solution. The silicate was then precipitated with ammonium hydroxide. The preparations had to be carefully neutralized with dilute HCl, otherwise the resulting silicate was alkaline and ineffective as a retardant. The silicates were dried at 100°C in a vacuum oven and the neutral product was found to be an effective flame retardant, as shown in Table VIII. However, we noted no additional improvement, using this synthetic approach.

As noted above with copper oxide, not all flame retardants increased in effectiveness as their concentration in the formulated silicone rubber product was increased. One can, however, increase the concentration of asbestos in the silicone rubber and obtain increasing effectiveness in flame retardancy as shown by Figure 2. However, because of the slight basicity of asbestos, compositions containing more than 100 parts asbestos could not be cured. Adding the auxiliary additives listed in Table IX to asbestos did not help improve the physical properties of the flame-resistant rubber,either. Furthermore, mixtures containing 50 parts of asbestos and 50 parts of these auxiliary additives were not more effective in improving the flame resistance of the rubber than 100 parts of asbestos alone, as Table IX shows.

Although both aluminum silicates ASP 405 and Ultrawhite 90 were equally effective at the 50-part level; at high concentrations of aluminum silicate, Ultrawhite 90 was somewhat more effective as shown by comparing Figures 3 and 4. These curves are somewhat surprising, because they indicate that the effectiveness of the silicate increases as its concentration in the rubber is raised above the 100-part level.

FIGURE 2

EFFECT OF ASBESTOS ON OXYGEN INDEX



Asbestos

- ○ 7 RF-1 (Johns Manville)
- X RG-244 (Union Carbide)
- ⬡ RG-444-10 (Union Carbide)

Formulation

100 parts GE SE 54
20 parts Cab-O-Sil M7
1 part Luperco CST

Molded at 250°F/ 10 min.
Oven-Cured at 400°F/ <1 torr for
16 hrs.

TABLE IX

TWO COMPONENT ADDITIVE MIXTURES[a] CONTAINING ASBESTOS

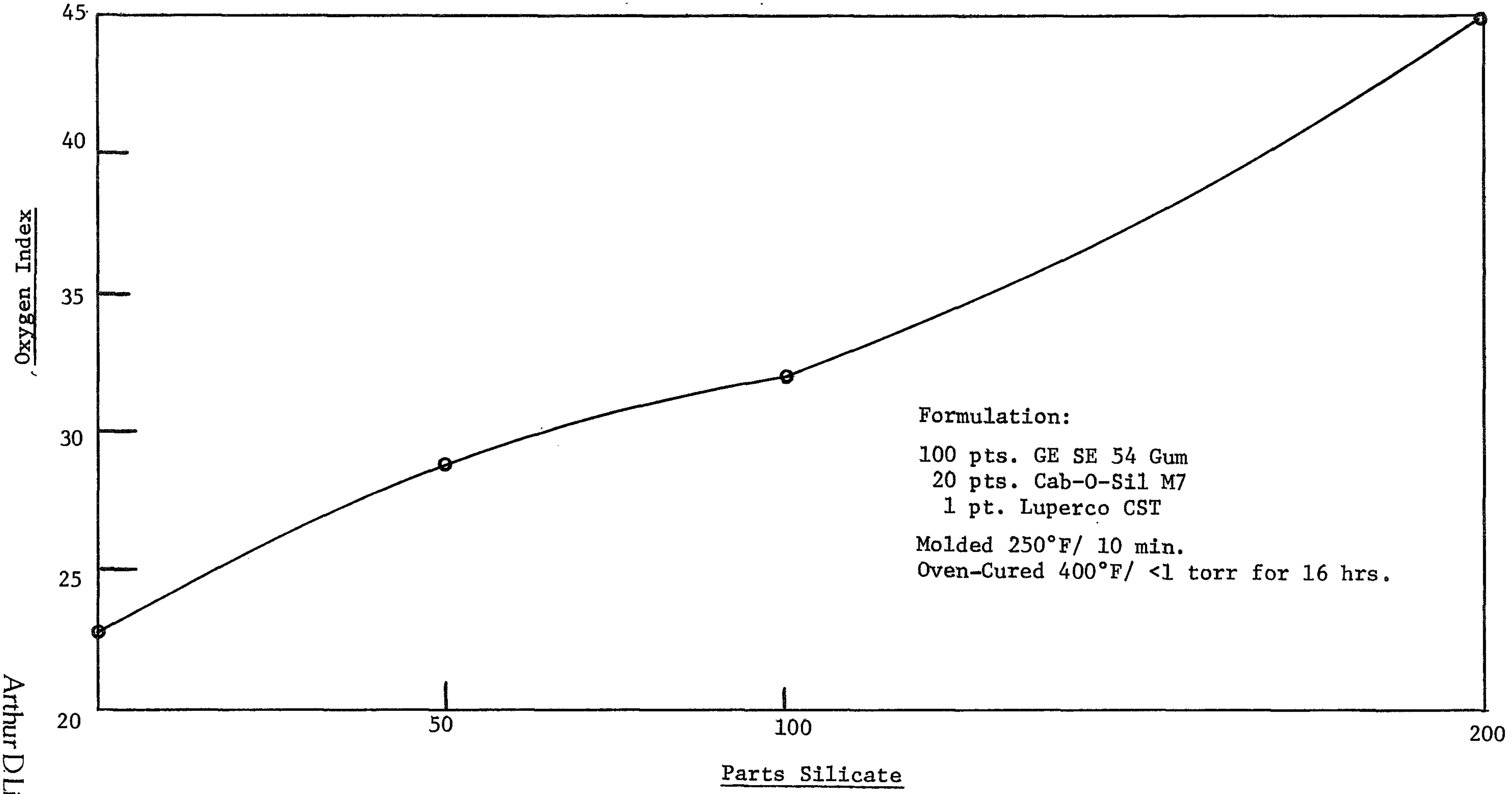
Additive	Oxygen Index Top	Physicals
Asbestos RG244	34	Poor
B_2O_3	33	Poor
Aluminum Silicate ASP 405	33	Fair
Dechlorane Plus 515	33	Poor
Mica Powder (235 Mesh)	--	Did not cure

a. Formulation:	SE-54 Gum (General Electric)	100 pts.
	Silica Cab-O-Sil M-7	20 pts.
	Asbestos RG 244 (Union Carbide)	50 pts.
	Luperco CST	1 pt.
	Other Additive	50 pts.

Molded at 250°F/10 min.
Oven Cured at 400°F/ <1 torr for 16 hrs.

FIGURE 3

EFFECT OF ALUMINUM SILICATE ASP 405 ON OXYGEN INDEX



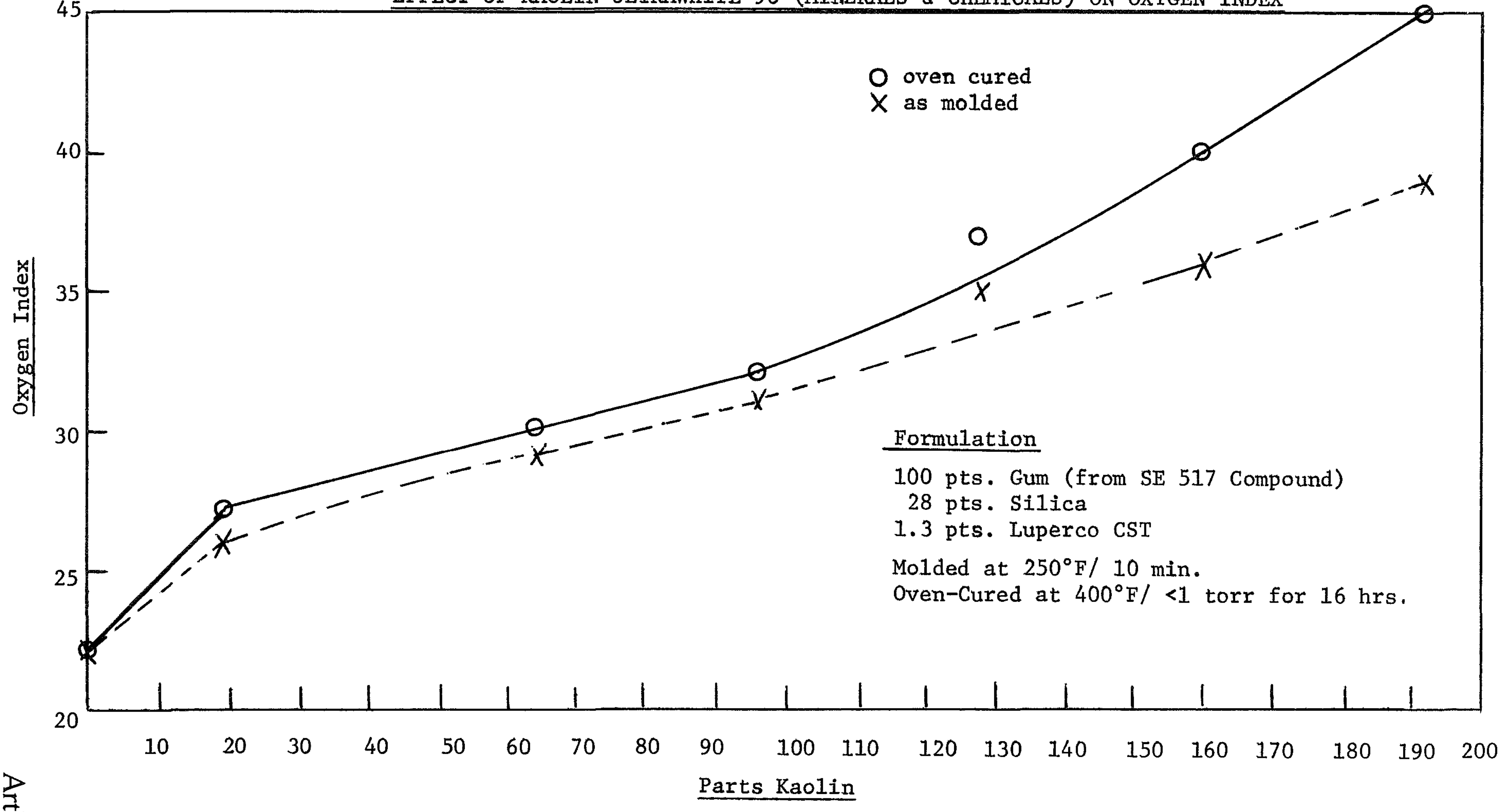
Formulation:

100 pts. GE SE 54 Gum
20 pts. Cab-O-Sil M7
1 pt. Luperco CST

Molded 250°F/ 10 min.
Oven-Cured 400°F/ <1 torr for 16 hrs.

FIGURE 4

EFFECT OF KAOLIN ULTRAWHITE 90 (MINERALS & CHEMICALS) ON OXYGEN INDEX



Formulation

100 pts. Gum (from SE 517 Compound)
28 pts. Silica
1.3 pts. Luperco CST

Molded at 250°F/ 10 min.
Oven-Cured at 400°F/ <1 torr for 16 hrs.

As expected, oven curing the silicone rubbers under the conditions we used in this program (400°F/<1 torr. for 16 hours) increased the flame resistance of the silicone rubber. Flammable volatiles were apparently removed during this stage. This effect is well illustrated by the curves in Figure 4, where the oxygen index has been measured before and after the oven cure.

Note from Figures 3 and 4 that different rubber stocks were used in compounding with Ultrawhite 90 and ASP 405: SE-54 with 20 parts of Cab-O-Sil M-7; and SE-517, a reinforced gum stock containing a similar base gum but with 28 parts of a treated silica already added. Over the years, the silicone-rubber producers have developed considerable technology in compounding gums to produce rubbers with high-strength properties. This is well shown by Table X.

In the first formulation, which was prepared by mixing the ingredients in our laboratory, the resulting rubber had a tensile strength of only 410 psi. In contrast, starting with the formulated SE-517 from General Electric, the tensile strength of the resulting silicone rubber was raised to 1200 psi. Although in our initial screening we were not greatly concerned with the physical properties of the formulated flame-resistant silicone rubber, we now felt that it was best to use the reinforced guy, SE-517. With 100 parts SE-517 and 100 parts of Ultrawhite 90, a tensile strength of approximately 600 psi and an elongation of 160% was obtained, as shown in Table X. Formulations containing other commercial kaolins that were effective as flame retardants are also included in this table. According to these results, Ultrawhite 90 appears to be superior in obtaining an elastomer with reasonable elongation.

Although we did not attempt to optimize the compounding conditions in the initial phase, we were interested to determine the effect of the concentration of peroxide in these kaolin systems on the flame resistance of the resulting silicone rubber. As shown by Figure 5, when the concentration of peroxide was increased from 1 to 5 parts, the flame resistance of the rubber decreased somewhat, as measured by the oxygen index. Normally, we used approximately 1.5 pts. in formulations containing this quantity of filler. We should point out that the effect of peroxide concentration on the oxygen index depends on the particular flame retardant used in the silicone-rubber formulation.

The rubber prepared from SE-517 and 100 parts of Ultrawhite 90 had good low-temperature properties as tested by the torsion-pendulum method (ASTM D-2236-64T). The results of this test are plotted in Figure 6. In this figure, a comparison has been made between the flame-resistant Viton A and the flame-resistant silicone rubber. As the curves show, the flame-resistant silicone rubber is considerably more flexible than Viton A at temperatures below -112°F.

TABLE X

PHYSICAL PROPERTIES OF SILICONE RUBBER CONTAINING KAOLIN[a]

	Formulation	Parts	Tensile, psi	Elongation %
1.	SE-54	100	410	500
	Cab-O-Sil M-7	20		
	Luperco CST	1		
2.	SE-517	100	1200	450
	Luperco CST	1		
3.	SE-517	100	570 (600)[b]	160 (160)[b]
	Kaolin Ultrawhite 90	100		
	Luperco CST	1		
4.	SE-517	100	500	75
	Kaolin ASP 072	100		
	Luperco CST	1.5		
5.	SE-517	100	570	75
	Kaolin X1663	100		
	Luperco CST	1.5		

a. Molded at 250°F/10 min. Oven cured at 400°F/ <1 torr for 16 hrs.

b. 1.5 pts. Luperco CST

FIGURE 5

EFFECT OF PEROXIDE CONCENTRATION ON OXYGEN INDEX
KAOLIN SYSTEM

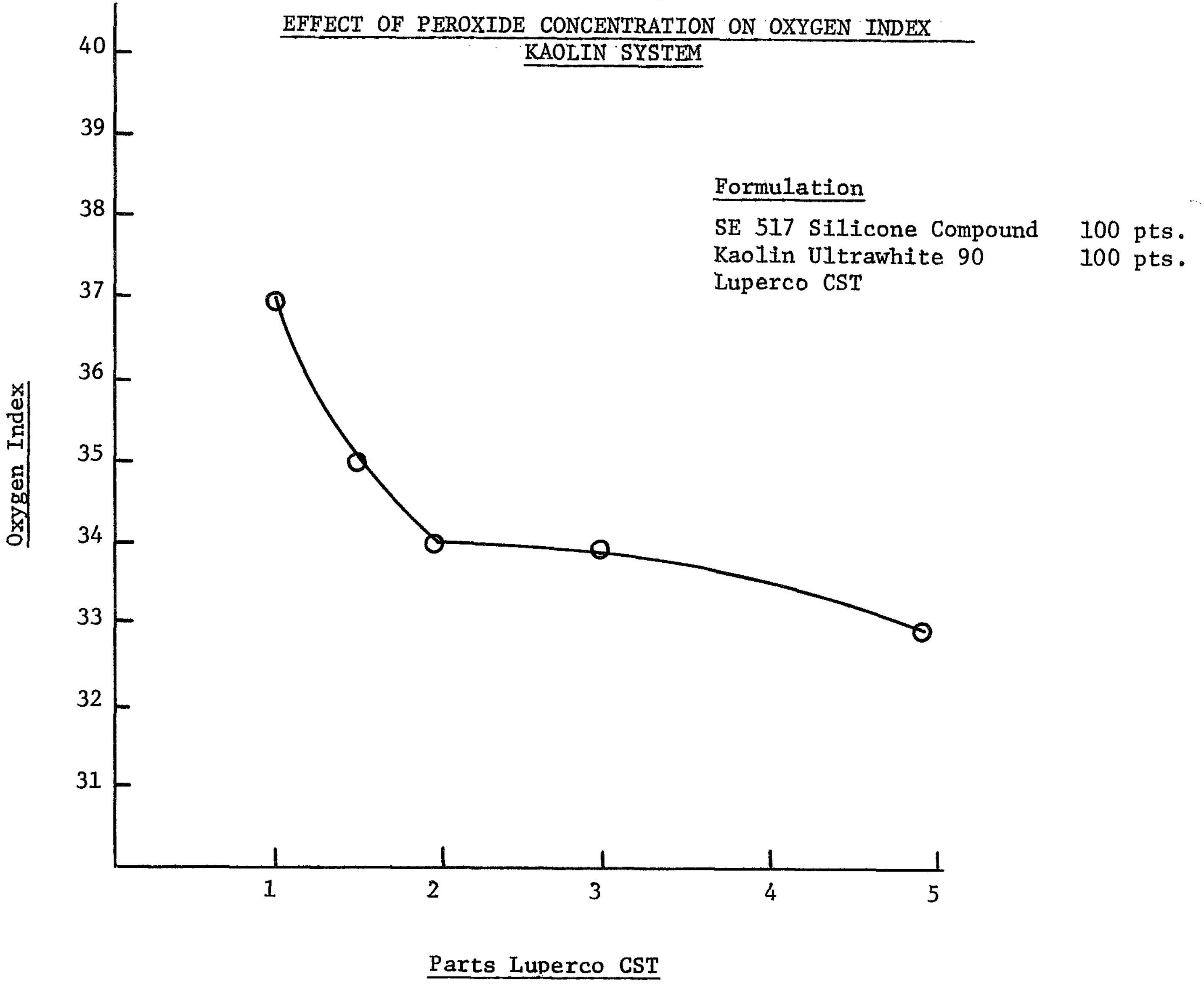
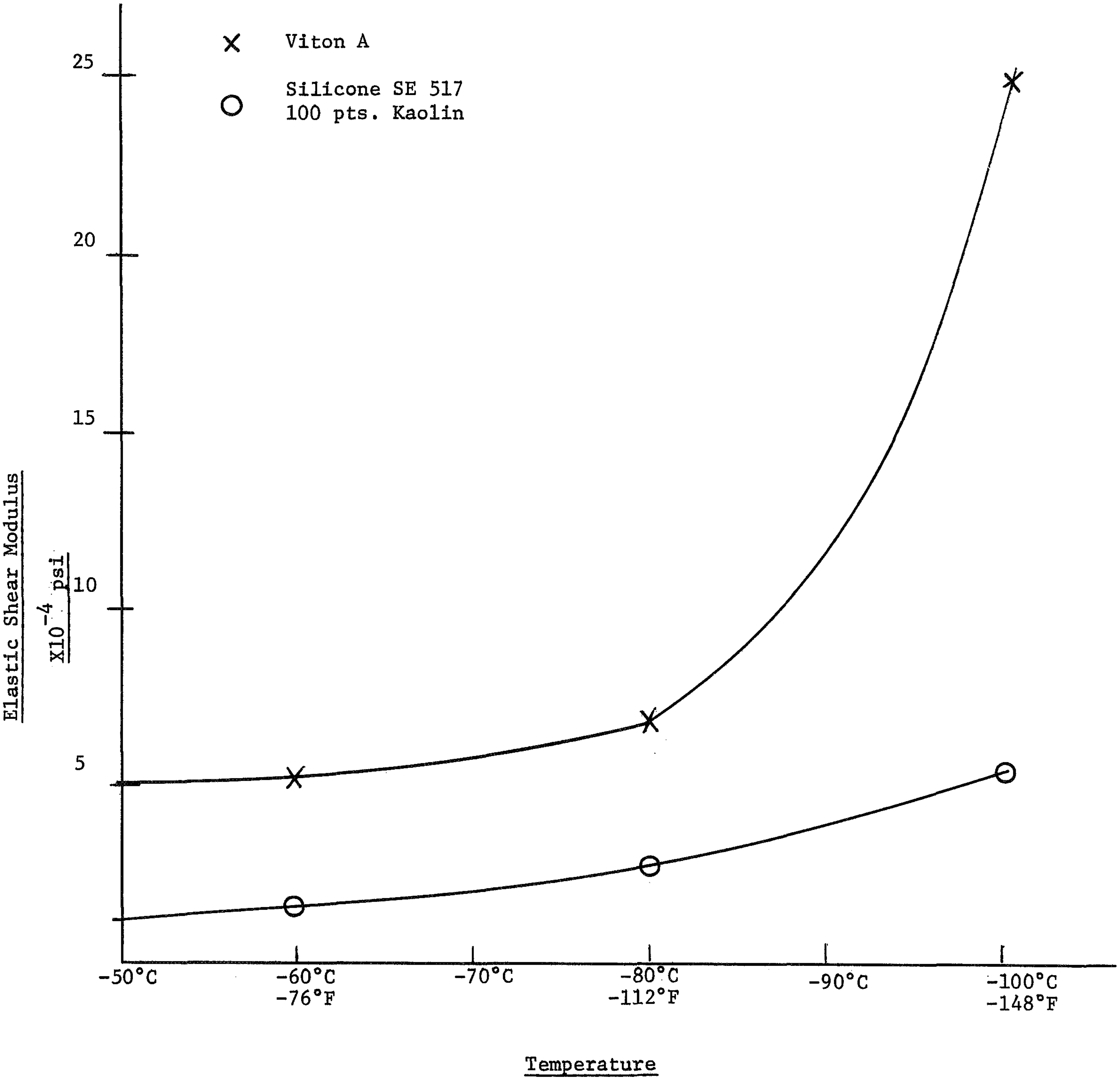


FIGURE 6

ELASTIC SHEAR MODULUS VS. TEMPERATURE



Two-Component Systems. -- In an attempt to develop a synergistic flame-retardant system we examined two-component mixtures, containing aluminum silicate and an auxiliary additive. With the aluminum silicate ASP 405, none of the auxiliary additives such as glass powder, Dechlorane plus, or boron oxide were effective synergists at the level tested, as shown in Table XI. The addition of 5-15 parts of an auxiliary additive to mixtures of SE-517 with 100 parts of Ultrawhite 90 did show that products such as ammonium chloride and bromide appear to behave synergistically. For example, with ammonium chloride at the 15-parts level, the oxygen index was 39 (see Table XII). With Ultrawhite 90 alone, the rubber had an oxygen index of 35. The comparison is on a no-oven-cure system. Unfortunately, silicone rubbers made with these halides lose their strength on oven curing, even when levels as low as 5 parts are used and are, therefore, of little practical interest. Surprisingly, the addition of as little as 1 part of the fluorinated Krytox oil to the system containing 100 parts of Ultrawhite 90 reduced the physical strength of the silicone rubber. Other additives examined with SE-517 are listed in Table XII.

With two-component additive mixtures containing 50 parts of Ultrawhite 90 auxiliary additives were tested at both the 50-and 15-parts levels. As shown in Table XIII, none of these auxiliary additives were effective synergists. Note that the combination of 50 parts Ultrawhite 90 and 50 parts Dechlorane plus 515 yielded a silicone rubber with poor physical properties. Apparently this chlorinated derivative is not sufficiently stable to endure the cure conditions. At higher levels, many of the inorganic additives gave ineffective cures, as shown in Table XIV. Combinations of the auxiliary inorganic additive and Ultrawhite 90 were also ineffective.

When Ultrawhite 90 was added to reinforced gums similar to SE-517, the products had poor physical properties, as shown in Table XV. This result is very surprising and not well understood, and suggests that General Electric's compound has a unique composition. Perhaps one of the additives in the commercial product behaves as a buffer to maintain a neutral pH.

AROMATIC BROMIDES

In testing the flame-restant silicone rubber containing kaolin at NASA, we discovered that the flame resistance of these rubbers was good when samples were burned at the top. In fact, NASA's values correlated with the oxygen-index values determined in our laboratories. However, when these same samples were burned at the bottom, they were unsatisfactory according to NASA tests and the modified oxygen-index method (samples burned at the bottom rather than the top). Table XV shows these oxygen-index values when the kaolin samples were burned at the bottom. The index remained at 21.

TABLE XI

TWO-COMPONENT ADDITIVE MIXTURES[a] CONTAINING ALUMINUM SILICATE

Additive	Oxygen Index Top	Physicals
Aluminum Silicate ASP 405	36	Fair
Glass Powder (Ferro)	33	Fair
Dechlorane Plus 515	34	Fair
B_2O_3	--	Did not cure

a. Formulation:		
	SE 54 Gum (General Electric)	100 pts.
	Silica Cab-O-Sil M7	20 pts.
	Aluminum silicate ASP 405 (Minerals & Chemicals)	100 pts.
	Luperco CST	1 pt.
	Other Additive	50 pts.

Molded at 250°F/10 min.
Oven cured at 400°F/ <1 torr for 16 hrs.

TABLE XII

TWO-COMPONENT ADDITIVE MIXTURES CONTAINING 100 PARTS KAOLIN[a] AND 100 PARTS SE-517[b]

Additive	Parts	Oxygen Index Top	Remarks
-----	--	35	115 pts. Kaolin, no oven cure[c]
-----	--	38	115 pts. Kaolin, oven cure[c]
NH_4Br[d]	15	37	Physicals poor, did not oven cure
NH_4Cl[d]	15	39	Physicals poor, loses strength on oven cure
NH_4Cl[d]	5	37	Physicals Good
$(CH_3)_4$ NBr[d]	15	34	Did not cure well
$(CH_3)_4$ NCl[d]	15	34	Did not cure well
NaCl	15	37	Physicals Good
Na_2SO_3	15	38	Some reduction in physicals
$ZnCO_3$	15	34	Physicals Good
$PbCO_3$	15	33	Some reduction in physicals
Krytox Oil	5	38	Some reduction in physicals
Krytox Oil	1	37	Some reduction in physicals
Cab-O-Sil HS-5	7	37	Some reduction in physicals
Dechlorane Plus 515	7.5	39	Some reduction in physicals
RF-1 (Cyanamid)[e]	7.5		
Glass Fiber 1/8"	5	39	Some reduction in physicals
SbF_3	15	--	Did not cure
Fe_2O_3	2	36	

a. Ultrawhite 90 (Minerals and Chemicals)

b. 1 Part Luperco CST, molded at 250°F/ 10 min. Oven cure 400°F/ <1 torr for 16 hrs.

c. From graph Figure 4

d. Sample was not oven-cured

e. A phosphorous and halogen-containing derivative

TABLE XIII

TWO-COMPONENT MIXTURES WITH 50 PTS. KAOLIN-ULTRAWHITE 90[a]

Auxiliary Additive	Parts/ 100 pts. Gum	Oxygen Index Top	Physicals
Ultrawhite 90	50	32	Good
CuO	50	28	Good
Dechlorane Plus 515	50	29	Poor
I_2O_5	15	27	Good
$BaSiF_6$	15	28	Poor
Ultrawhite 90	15	30	Good
Glass Fiber 1/8" length	10	30	Poor
Tetraethyl orthosilicate	5	28	Good

[a] Formulation:

SE 54	100 pts.
Cab-O-Sil M-7	20 pts.
Luperco CST	1 pt.

Molded: 250°F/10 min.

Oven cured: 400°F/ <1 torr - 16 hrs.

TABLE XIV

THE FOLLOWING INORGANIC ADDITIVES GAVE INEFFECTIVE CURES[a]

	Additive	Parts
1.	NH_4Br (Fisher Scientific)	50
2.	NH_4Br	50
	Kaolin Ultrawhite 90	50
3.	LiBr	50
4.	LiBr	50
	Kaolin Ultrawhite 90	50
5.	Sb_2S_3	50
6.	Sb_2S_3	50
	Kaolin Ultrawhite 90	50
7.	Chromated $ZnCl_2$ (DuPont)	50
8.	Chromated $ZnCl_2$	50
	Kaolin Ultrawhite 90	50
9.	$CuBr_2$	50
10.	$CuBr_2$	50
	Kaolin Ultrawhite 90	50
11.	V-Bor (Borax) - American Potash	50
12.	V-Bor (Borax) - American Potash	50
	Kaolin-Ultrawhite 90	50
13.[b]	$ZnSO_4 \cdot 7H_2O$	50
	Kaolin Ultrawhite 90	50
14.[b]	Polyphosphonitrilic Chloride	50
	Kaolin Ultrawhite 90	50

[a] Formulation - SE 517 Silicone Rubber Compound 100 parts
Luperco CST 1.5 parts
Molded 250°F/10 min.
Oven cured 400°F/ <1 torr, 4 hrs.

[b] Formulation: SE-54 100 parts
Cab-O-Sil M7 20 parts
Luperco CST 1 part
Oven cured 16 hrs.

TABLE XV

EFFECT OF DIFFERENT SILICONE RUBBER COMPOUNDS[a]

Formulation	Parts	Oxygen Index		Physicals
		Top	Bottom	
1. Dow X-3-2021	100	22	18	Good
2. Dow X-3-2021	100	35	21	Fair
Kaolin Ultrawhite 90	100			
3. Dow 955U	100	35	21	Fair
Kaolin Ultrawhite 90	100			
4. KW 1200 (Union Carbide)	100	34	21	Fair
Kaolin Ultrawhite 90	100			
5. SE-517	100	35	21	Good
Kaolin Ultrawhite 90	100			

[a] 1.5 parts Luperco CST

Our first approach to improve the flame resistance of the silicone rubbers when burned at the bottom was to incorporate a heat stabilizer, such as red iron oxide. This offered little improvement. The composition containing 100 parts SE-517, 100 parts Ultrawhite 90, and 2 parts iron oxide had an oxygen index of only 22 when burned at the bottom. We then screened many of our older samples by the bottom-burning test; the only promising sample was one that contained the halogenated flame retardant from Hooker, Dechlorane plus (65% chlorine). A sample containing 15 parts of Dechlorane plus and 100 parts SE-54 gum had an oxygen index of 24 when burned at the bottom.

Hexabromobenzene. -- With the encouraging results obtained with the chlorine containing additive, we immediately formulated with and tested the more effective bromo derivatives. Hexabromobenzene, which is available commercially, was selected as a good candidate for this application because we believed an aromatic bromide could best endure the high temperatures of the curing process. Unfortunately, hexabromobenzene sublimes under oven-cure conditions. Therefore, samples containing this derivative were not oven cured. Furthermore, we noted that the gum samples containing hexabromobenzene had to be cured immediately after the samples were milled, otherwise the physical properties of the cured sample were reduced. This could be an effect of the impurities in the hexabromobenzene rather than the aromatic bromide itself; the sample was not of the highest purity.

Table XVI summarizes some of the results obtained with hexabromobezene, with and without kaolin and antimony oxide. As this table shows, 50 parts of hexabromobenzene is more effective than 100 parts of kaolin. The comparison has been made on samples that have not been oven cured. The oxygen index rose from 21 to 30 when the sample was burned from the bottom, and the index rose from 33 to 36 when the sample was burned at the top. Generally, one can see that the improvement in flame resistance, as tested by burning from the bottom, is proportional to the concentration of the halogenated derivative. Of most significance was the observation that the physicals of the formulated silicone rubber with the bromo derivative were better than that obtained with kaolin alone. As the table illustrates, using a combination of antimony oxide and hexabromobenzene offers no advantages and, as expected, hexabromobenzene is more effective than the chlorinated derivative, Dechlorane plus. Moreover, the product obtained with 50 parts Dechlorane plus and 100 parts kaolin did not have the physical strength of the analogous product made with hexabromobenzene.

In order to directly compare the effectiveness of aromatic bromo derivatives with those containing chlorine, the SE-517 silicone compound was formulated with hexachlorobenzene. As mentioned above, because these benzene derivatives are relatively volatile, we compared the silicone rubber samples after they were molded. The silicone rubber contained 100 parts of the halogenated derivative and 100 parts of the reinforced

TABLE XVI

EFFECT OF HALOGEN-CONTAINING COMPOUNDS ON FLAMMABILITY (SAMPLES BURNED FROM BOTTOM)[a]

Additive System	Parts Additive[b]	Oxygen Index Top	Oxygen Index Bottom	Physicals
Kaolin Ultrawhite 90[c]	100	33	21	Good
Dechlorane Plus 515[c]	12.5[d]	26	24	Good
Hexabromobenzene	50	36	30	Good
Kaolin Ultrawhite 90 Hexabromobenzene	50 50	45	27	Good
Kaolin Ultrawhite 90 Hexabromobenzene	100 50	45	29	Good
Kaolin Ultrawhite 90 Hexabromobenzene Antimony Oxide	100 33 17	42	26	Good
Kaolin Ultrawhite 90 Dechlorane Plus 25	100 50	40	27	Fair
Kaolin Ultrawhite 90 Dechlorane Plus 25 Antimony Oxide	100 33 17	Did not cure		

---

a. Formulation:

SE-517 Compound (General Electric)	100 pts.
Luperco CST	1.5 pts.

Molded at 250°F/10 min. No oven cure

b. Based on 100 pts. of SE-517 Compound (silica and gum)

c. Sample Post Cured 16 hrs.

d. Formulation: SE-54 gum 83.3 pts; Silica (Cab-O-Sil M-7) 16.7 pts.

gum. As the table below indicates, hexabromobenzene is by far superior to hexachlorobenzene in terms of improving the flame resistance of the rubber.

Halogen Derivative	Oxygen Index Top	 Bottom	Physical Properties Tensile psi	 % Elongation
Hexachlorobenzene	34	28	320	400
Hexabromobenzene	44	35	450	500

Table XVII illustrates how the oxygen index as measured by the bottom-burning test, increases as one gradually increases the concentration of hexabromobenzene in a mixture of kaolin and hexabromobenzene. This further confirms that there is no advantage in using a mixture of kaolin and hexabromobenzene. At an additive level of 100 parts, the oxygen index, as measured by burning sample on top, remains relatively constant with different mixtures of kaolin and hexabromobenzene. However, the index drops sharply when kaolin is used alone.

On the other hand, increasing the concentration of kaolin in the mixture does increase the tensile strength of the cured silicone rubber, as Table XVII illustrates. Note again that all of these comparisons have been made on a "no-oven-cure" basis. It was difficult to cure samples containing more than 100 parts of hexabromobenzene. However, a satisfactory product was prepared with 100 parts of hexabromobenzene and 50 parts of kaolin. This product had outstanding flame resistance, as shown by the table, although its physical strength was rather poor.

When hexabromobenzene was used in combination with other inorganic compounds such as copper oxide and iron oxide instead of kaolin, the flame resistance of the cured silicone rubber was reduced. Thus, as illustrated by Table XVIII, the flame resistance gradually decreased as one mixed 50 parts of hexabromobenzene with 50 parts of kaolin, copper oxide, or iron oxide.

Figure 7 illustrates the effect of peroxide content on the physical properties of the cured silicone rubber, containing 75 parts of hexabromobenzene and 25 parts of kaolin. This curve is typical of most rubber systems. The elongation gradually decreases as the peroxide concentration and the degree of cure increases, and the tensile strength usually reaches a maximum value and then tends to gradually decrease as the degree of cure increases. As Figure 7 shows, with this particular system, the level of 2 parts of peroxide is optimum.

Decabromodiphenyl (D.B.D.P.). -- To avoid the volatility of hexabromobenzene and yet retain its superior flame resistance, we were fortunate to obtain samples of decabromodiphenyl from Great Lakes Chemical.

TABLE XVII

KAOLIN AND AROMATIC BROMO COMPOUNDS[a]

(No Oven Cure)

	Additive System	Parts Additive	Oxygen Index		Tensile psi	Elongation %
			Top	Bottom		
1.	Hexabromobenzene	100	44	35	450	500
2.	Hexabromobenzene Kaolin Ultrawhite 90	75 25	47	33	485	450
3.	Hexabromobenzene Kaolin Ultrawhite 90	50 50	45	27	515	500
4.	Kaolin Ultrawhite 90	100	33	21	525	425
5.	Hexabromobenzene	50	36	30	492	460
6.	Decabromodiphenyl	50	35	30	600	900
7.	Decabromodiphenyl Kaolin Ultrawhite 90	50 50	42	27	436	550
8.	Decabromodiphenyl Kaolin Ultrawhite 90	75 25	43	33		
9.	Decabromodiphenyl	100	46	36		
10.	Hexabromobenzene Kaolin Ultrawhite 90	100 50	55	40	324	300

a. Formulation -	SE 517	100 pts.
	Luperco CST	1.5 pts.

Molded 250°F/10 min.

TABLE XVIII

THE USE OF DIFFERENT INORGANIC COMPOUNDS WITH HEXABROMOBENZENE[a]

(No Oven Cure)

Inorganic Additive	Parts	Oxygen Index	
		Top	Bottom
Kaolin (Ultrawhite 90)	50	45	27
CuO	50	37	25
Fe_2O_3	50	30	21

[a] Formulation:

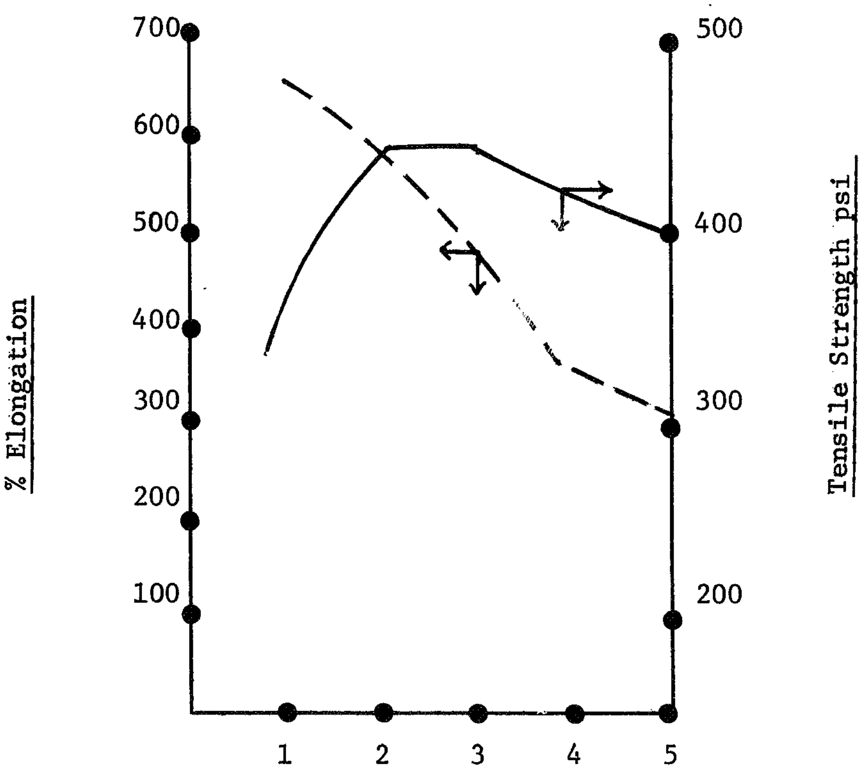
SE 517 Silicone Rubber Compound	100 pts.
Hexabromobenzene	50 pts.
Luperco CST	1.5 pts.

FIGURE 7

EFFECT OF PEROXIDE CONTENT ON PHYSICAL PROPERTIES

Hexabromobenzene -	75 parts
Kaolin	25 parts

(No Oven Cure)



Parts Luperco CST/100 Parts SE-517 Compound

The decabromo derivative that was made available to us was purer than the hexabromobenzene. As a result, the silicone rubber compositions containing decabromodiphenyl had better physical properties than that with hexabromobenzene (see Table XVII). Again, note that the comparison is being made with samples that have not been oven-cured. Under these conditions, the flame resistance of the products containing either of the two bromo derivatives is about equivalent. Decabromodiphenyl contains 84.8% bromine and hexabromobenzene contains 87.5%. As Table XVII shows, mixtures of kaolin and decabromodiphenyl gave results similar to those obtained with hexabromobenzene. Again, we noted no advantages in using the mixture rather than the pure bromo compound.

As noted above, the gum samples containing hexabromobenzene had to be cured immediately after the samples were milled, otherwise the sample was not effectively cured. We were pleased to observe that with decabromodiphenyl the silicone rubber compounds were stable, and an immediate cure was not required. Furthermore, we noted little difference whether the formulated product was cured immediately or after 24 hours. These results suggest that the impurities in the hexabromobenzene may be responsible for the ineffective cure.

To further confirm the improved stability of the decabromodiphenyl in the silicone rubber systems, we prepared mixtures of dichlorobenzoyl peroxide (Luperco CST) and decabromodiphenyl, and titrated the peroxide immediately after mixing, after 24 hours and after 48 hours, at room temperature. Essentially, no change was observed in the peroxide concentration. These results are significant, for often in the fabrication of silicone rubber products, the silicone rubber compound is left on the shelf with the peroxide. Therefore, this customary procedure may be followed with these flame resistant silicone compounds.

The formulated silicone rubber containing decabromodiphenyl, as expected, could be oven cured. As noted above, oven curing invariably increases the flame resistance of the composition. Thus, when the gum rubber was compounded with 50 parts of decabromodiphenyl, the following improvements were obtained:

	Oxygen Index		Tensile	Elongation
	Top	Bottom	psi	%
Before Post Cure	35	30	600	900
After Post Cure	36	31	640	870

With 50 parts dodecabromodiphenyl and 50 parts Ultrawhite 90 analogous results were obtained

	Oxygen Index		Tensile	Elongation
	Top	Bottom	psi	%
Before Post Cure	42	27	436	550
After Post Cure	43	27	496	350

With the system containing Ultrawhite 90 alone at the 100-part level, the tensile strength increased from 525 to 600 psi when the formulated rubber was oven cured.

Table XIX summarizes the results obtained with the decabromodiphenyl system when the samples were oven cured. Adding increasing amounts of decabromodiphenyl to the silicone rubber composition invariably decreased the physical properties of the cured rubber. The data derived from Table XIX is illustrated by Figure 8. Both tensile strength and elongation decrease as one increases the decabromodiphenyl concentration from 50 to 150 parts.

With the aluminum silicate system, we noted a 3-point drop in the oxygen index value when the concentration of peroxide was increased from 1-5 parts. In contrast, the compositions containing decabromodiphenyl alone or a mixture of hexabromobenzene and kaolin showed only a slight decrease in index values -- a drop of 1 unit. The effect of peroxide content on the physical properties of the system containing 100 parts of decabromodiphenyl is illustrated by Figure 9, which is similar to Figure 7. However, with the decabromodiphenyl system, the percent elongation drops rapidly as the concentration of peroxide is increased. Again, the tensile strength of the cured rubber remains essentially constant. On the basis of this study, we selected a level of 1.5 parts of Luperco CST for the SE-517 compound with 100 parts of additive. The data related to mixtures of kaolin and decabromodiphenyl in Table XIX have been plotted in Figure 10. Here, you can see the effect of mixing decabromodiphenyl with kaolin on the physical properties of the resulting rubber. At the 100-part additive level, the rubber containing kaolin alone has the highest tensile strength. Mixing the kaolin with decabromodiphenyl produces products with intermediate physical properties.

Some of the oxygen index values listed in Table XIX for the decabromodiphenyl-silicone rubber system are plotted in Figure 11. This plot shows how the oxygen index values for the sample burned both at the top and bottom increase as the percent decabromodiphenyl increases in the rubber compositions. Fortunately, these curves have a good positive slope. This plot also includes oxygen-index values for rubber compositions containing a mixture of the bromo derivative and Ultrawhite 90. These results indicate clearly how the oxygen-index values obtained by burning the sample at the bottom are strictly dependent on the concentration of the bromo derivative. On the other hand, the values obtained when the sample was burned at the top were substantially increased when Ultrawhite 90 was added. At the 100-part additive level, the oxygen-index values (top) were higher for a mixture of the bromo derivative with Ultrawhite 90 than for Ultrawhite 90 alone as indicated by Table XIX.

The superiority of the decabromo derivative as a flame retardant for silicone rubber is shown in Figure 12, as compared to Ultrawhite 90. Rubber containing kaolin Ultrawhite 90 alone has good flame resistance only when the sample is burned at the top, as this figure shows very clearly.

TABLE XIX

EFFECT OF VARIOUS BROMO COMPOUNDS ON FLAME RESISTANCE AND PHYSICAL PROPERTIES[a]

(All Samples Oven Cured)

		Parts	Oxygen Index		Tensile	
	Additive System	Additive	Top	Bottom	psi	Elongation %
1.	Decabromodiphenyl	100	47	40	435	950
2.	Decabromodiphenyl	75	45	34	470	800
	Kaolin-Ultrawhite 90	25				
3.	Decabromodiphenyl	50	43	27	496	350
	Kaolin-Ultrawhite 90	50				
4.	Kaolin-Ultrawhite 90	100	35	21	600	160
5.	Decabromodiphenyl	50	36	31	640	870
6.	Decabromodiphenyl	125	50	44	395	895
7.	Decabromodiphenyl	150	53	48	278	775
8.	Decabromodiphenyl	200	60	54	Poor	
9.	Octabromodiphenyl	200	57	48	Poor	
10.	Octabromodiphenyl	100	44	34	Fair	
11.	Octabromodiphenyl	50	36	30	Fair	
12.	Octabromodiphenyl	50	41	27	Fair	
	Kaolin-Ultrawhite 90	50				
13.	Octabromodiphenyl	75	44	32	Fair	
	Kaolin-Ultrawhite 90	25				
14.	Tetrabromobisphenol S	100	40	32	Poor	
15.	Tetrabromobisphenol S	75				
	Kaolin-Ultrawhite 90	25	36	30	Poor	

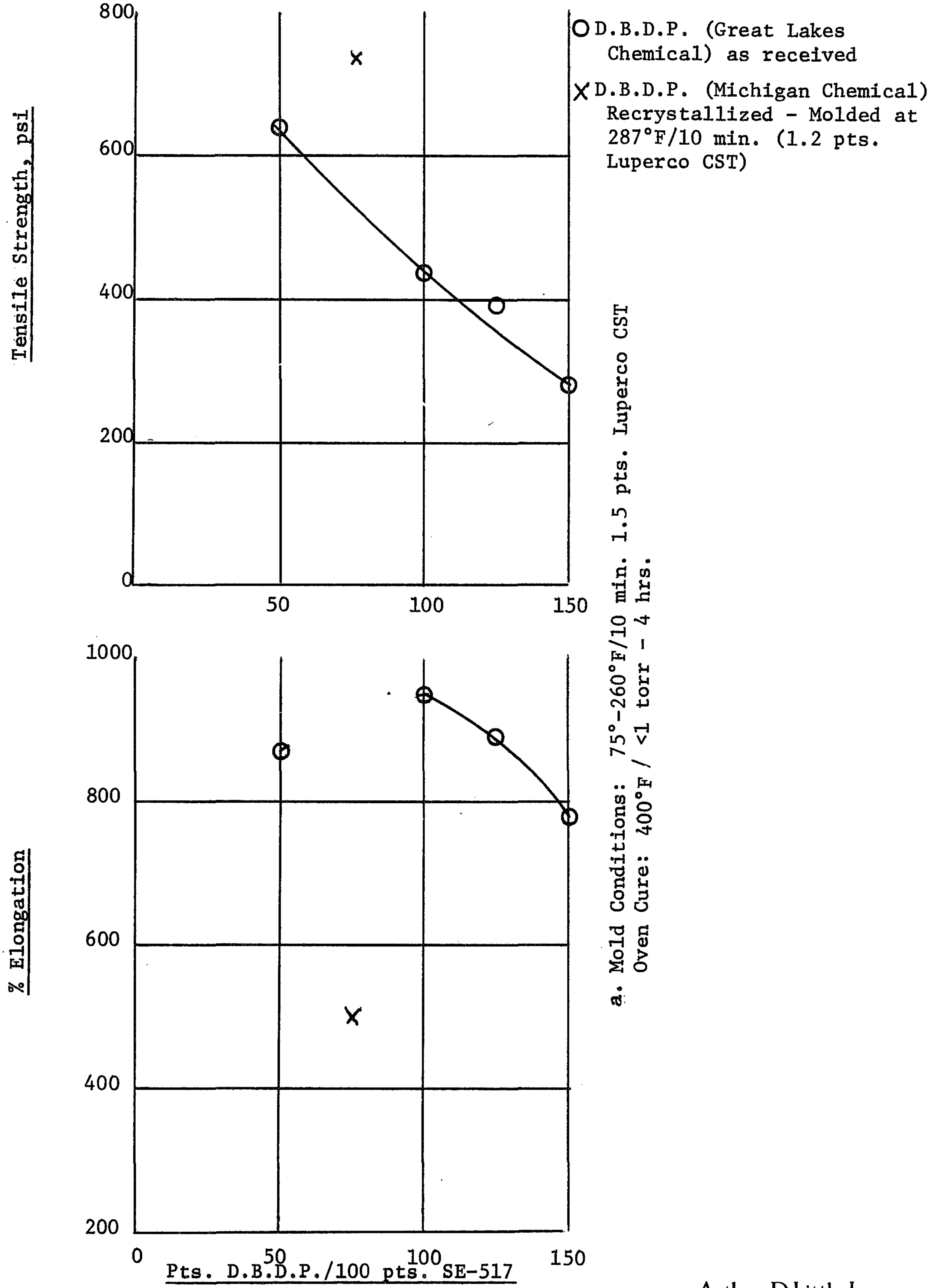
a. Formulation: SE 517 Silicone Rubber Compound 100 parts
Luperco CST 1.5 parts

Mold Conditions: 75° - 260°F/10 min.

Oven Cure: 400°F/ <1 torr - 4 hrs.

FIGURE 8

EFFECT OF DECABROMODIPHENYL CONCENTRATION[a]



a. Mold Conditions: 75°-260°F/10 min. 1.5 pts. Luperco CST
Oven Cure: 400°F / <1 torr - 4 hrs.

FIGURE 9

EFFECT OF PEROXIDE CONTENT ON PHYSICAL PROPERTIES

Decabromodiphenyl - 100 parts
(Samples Oven Cured)

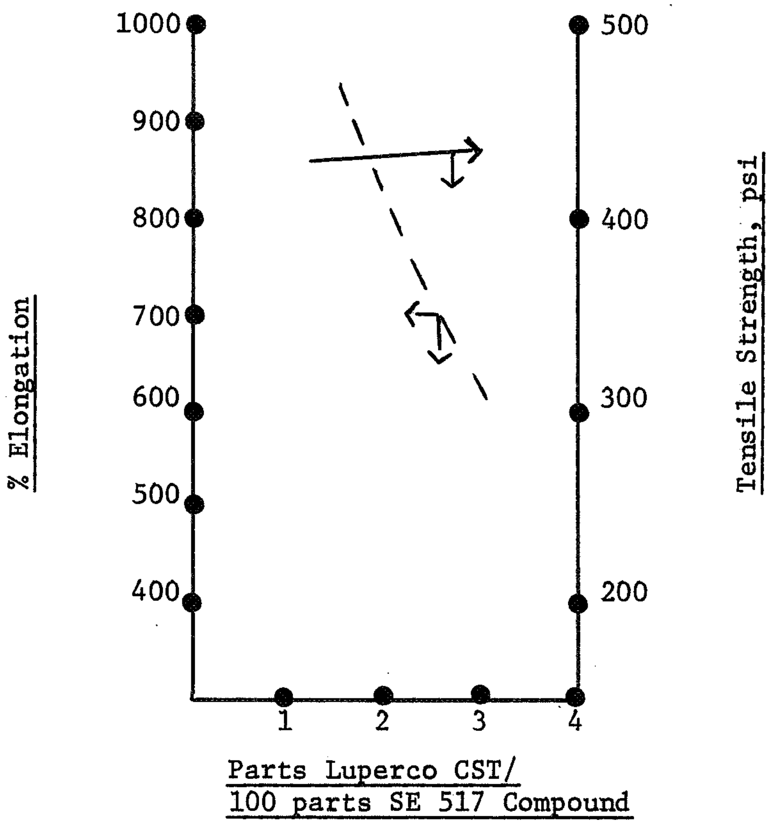
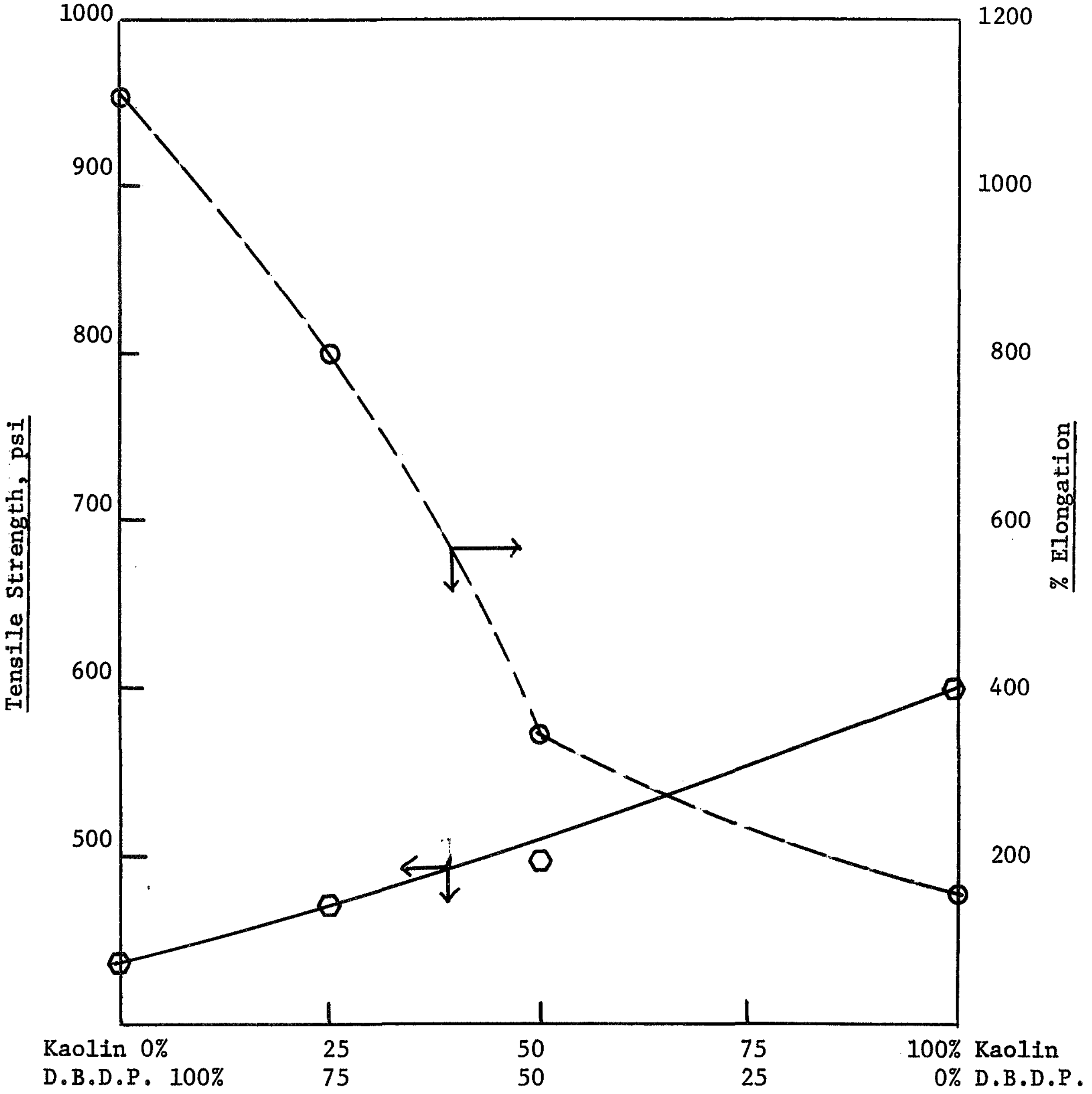


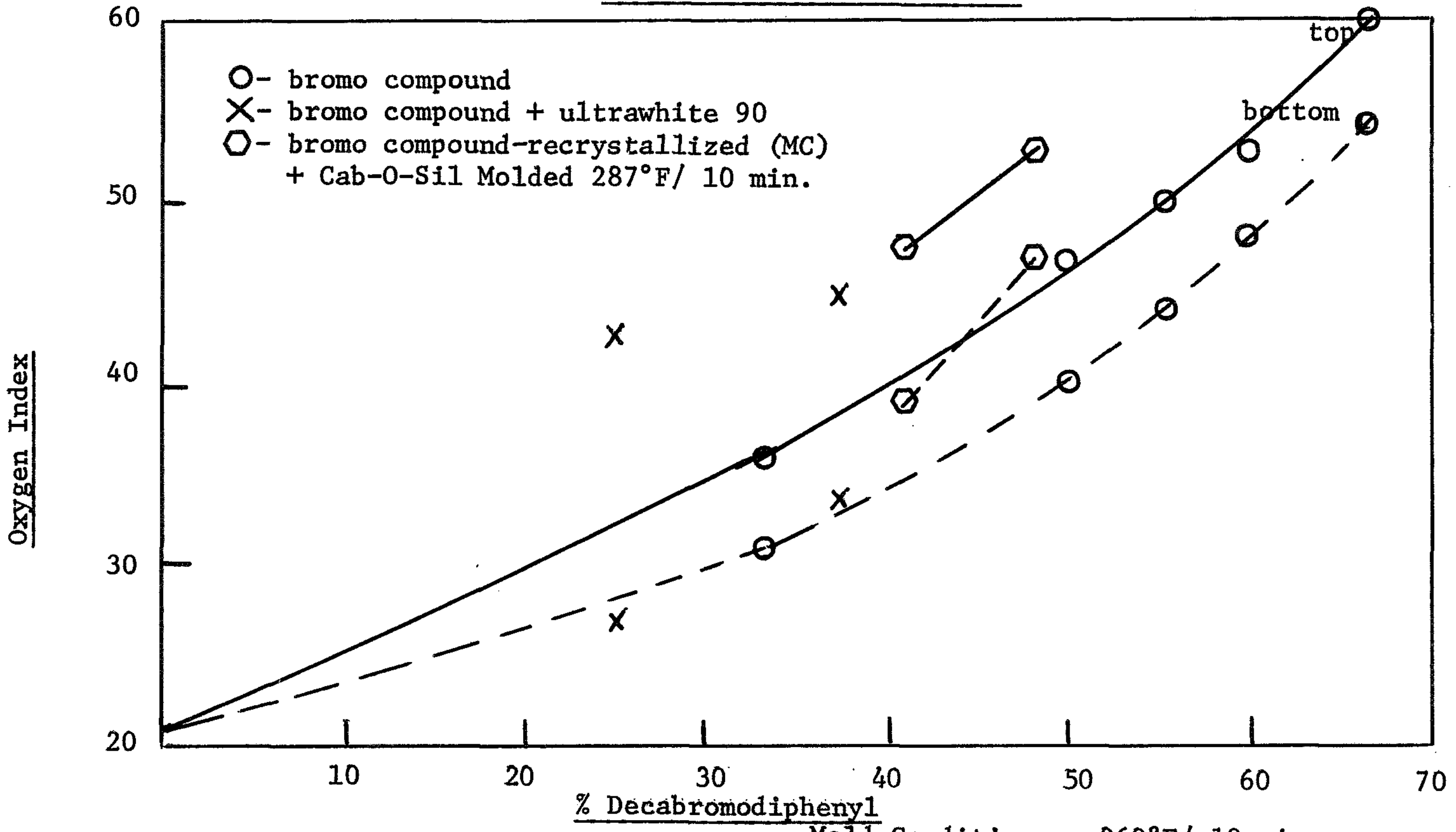
FIGURE 10

EFFECT OF MIXING DECABROMODIPHENYL WITH KAOLIN (ULTRAWHITE 90) ON PHYSICAL PROPERTIES[a]



[a] 100 pts. Additive/100 pts. SE-517 Silicone Rubber Compound (1.5 pts. Luperco CST)
Mold Conditions: 260°F/10 min.
Oven Cure: 400°F/ <1 torr - 4 hrs.

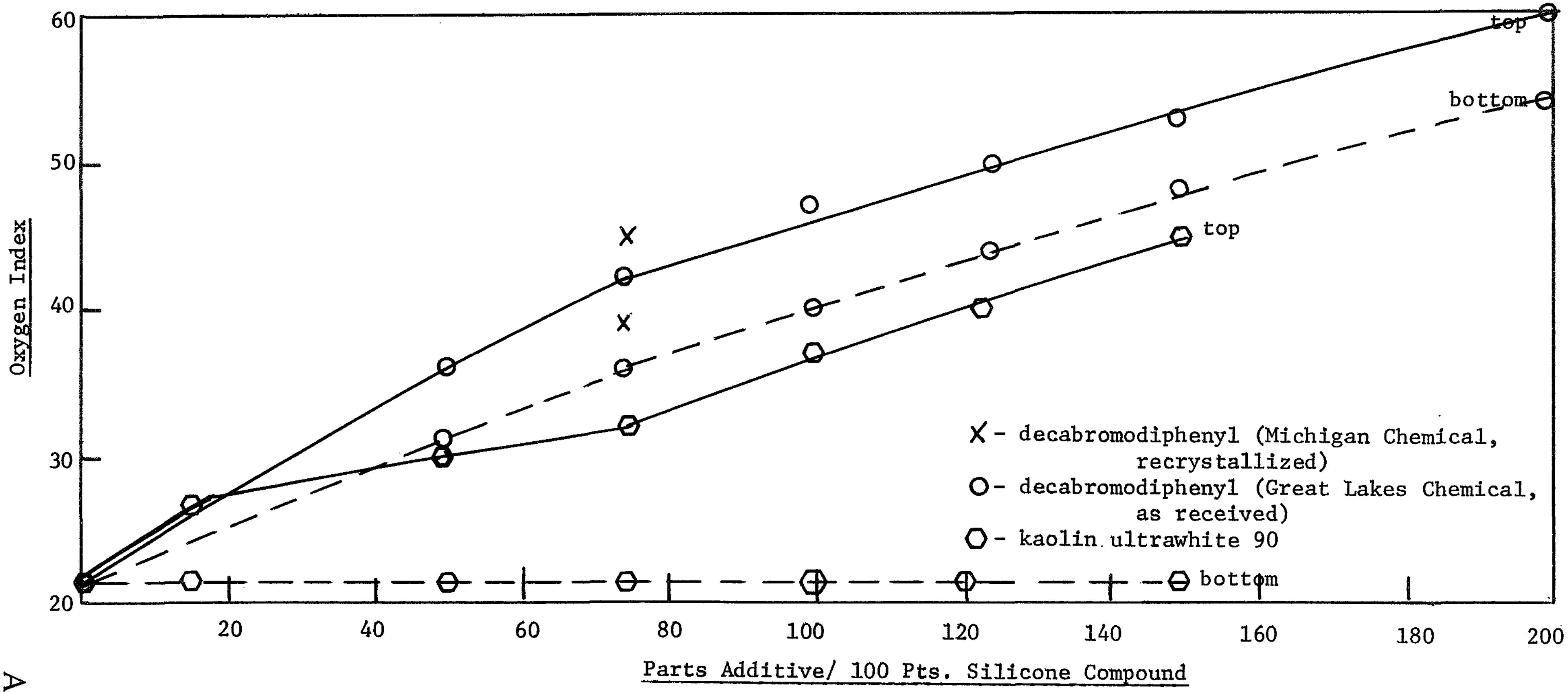
FIGURE 11
ADDITION OF DECABROMODIPHENYL TO SILICONE RUBBER COMPOUND
EFFECT ON FLAME RESISTANCE



Mold Conditions: 260°F/ 10 min.
1.5 pts. Luperco CST
Oven Cure: 400°F/ <1 torr - 4 hrs.

FIGURE 12

EFFECTIVENESS OF DIFFERENT FLAME RETARDANTS



The oxygen-index values obtained by burning this sample at the bottom remain constant at 21, even with high concentrations of Ultrawhite 90. With decabromodiphenyl, at the same concentration levels, the oxygen-index values for the sample burned at the bottom are even higher than those obtained by burning the Ultrawhite 90 samples at the top.

OTHER BROMO DERIVATIVES

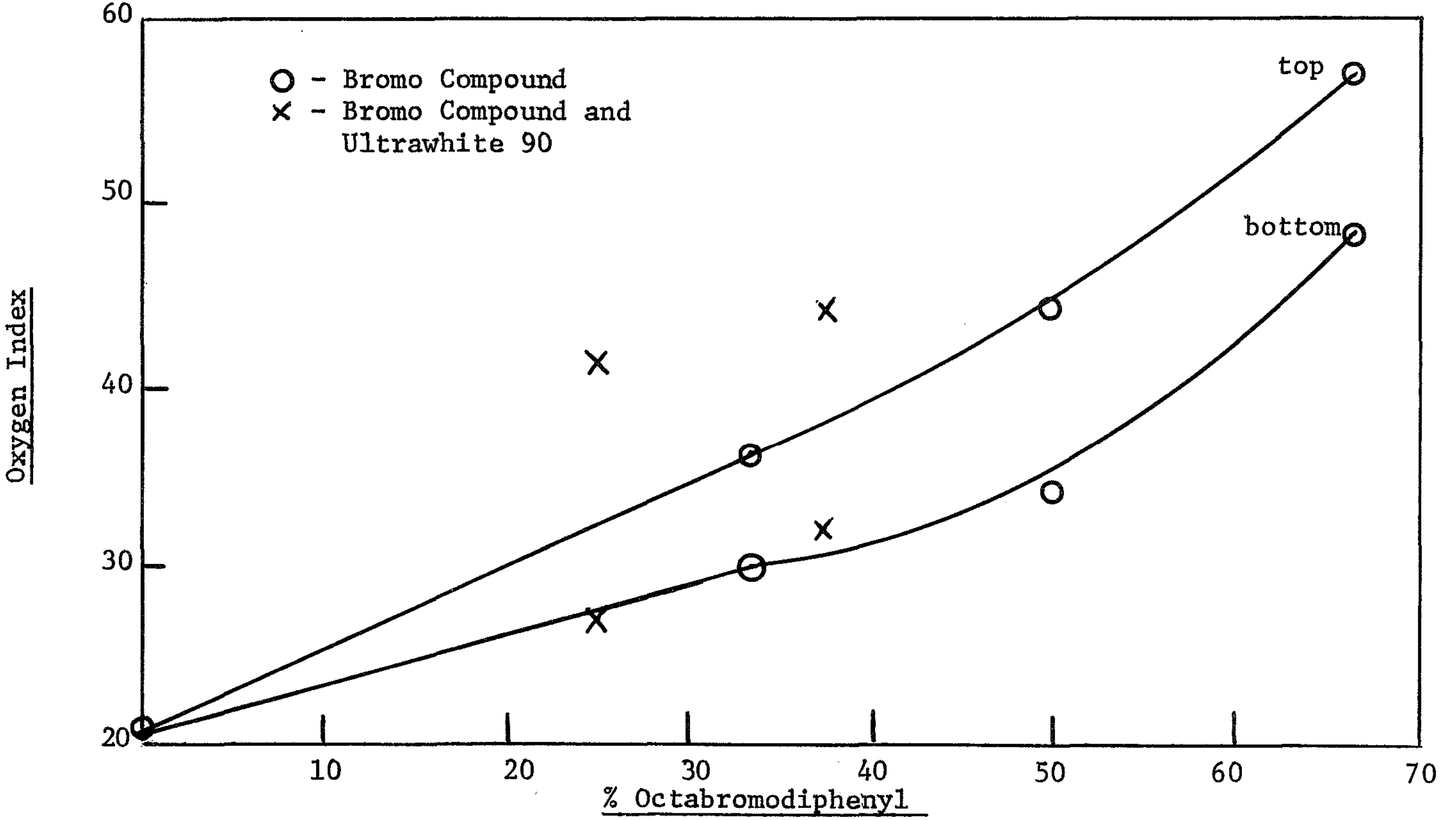
When octabromodiphenyl was substituted for the deca derivative, the flame resistance of the formulated rubbers was very good, but the physical properties were either fair or poor, as shown in Table XIX. The oxygen-index values for this additive are plotted in Figure 13. This set of two curves is similar to that obtained by adding decabromodiphenyl to silicone rubber. This figure also includes data points for a mixture of octabromodiphenyl and Ultrawhite 90. Here again, observe that adding Ultrawhite 90 further improved the flame resistance of the silicone rubber when the sample was burned at the top.

The use of the aromatic bromo compound, tetrabromobisphenol S, (See Table XIX) also resulted in a silicone rubber with poor physical properties. These negative results with the aromatic bromo compounds containing hydrogen atoms suggest that these derivatives impart an instability to the silicone rubber during the high-temperature curing cycle. A reasonable supposition is that the presence of hydrogen atoms in the brominated flame retardant can produce HBr during the cure cycle. The resulting acidic HBr can then degrade the silicone polymer.

Further confirmation of this hypothesis was obtained when we noted that other aromatic bromides, such as tetrabromomethylene dianiline and tetrabromobisphenol A, gave completely ineffective cures with or without kaolin (See Table XX). This table further illustrates that shifting from aromatic bromides to aliphatic ones, whether cyclic or acyclic, results in unsatisfactory cures. Note that this effect was obtained even though compounds such as hexabromocyclohexane and tetrabromomethane contain no hydrogen atoms. Thus, according to our investigation, the only satisfactory bromo derivatives effective as flame retardants for silicone rubber are aromatic ones, containing no hydrogen atoms.

Interestingly, with silicone rubber compounds containing bromo derivatives that did not completely interfere with the cure cycle, namely, deca and octabromodiphenyl and tetrabromobisphenyl S, the flame resistance does correlate with the bromine content of the silicone-rubber composition (See Figure 14). As the figure illustrates, the values for the oxygen indices of samples of rubber containing octabromodiphenyl are somewhat lower than those obtained with the decabromoderivative, at the same bromine concentration. This effect could be ascribed to the lower stability of the silicone rubber containing octabromodiphenyl; the high concentration of decomposition products could increase the flammability of the sample.

FIGURE 13
ADDITION OF OCTABROMODIPHENYL TO SILICONE RUBBER COMPOUND SE-517
EFFECT ON FLAME RESISTANCE



Mold Conditions: 75-260°F/ 10 min.
1.5 pts. Luperco CST
Oven Cure: 400°F / <1 torr - 4 hrs.

TABLE XX

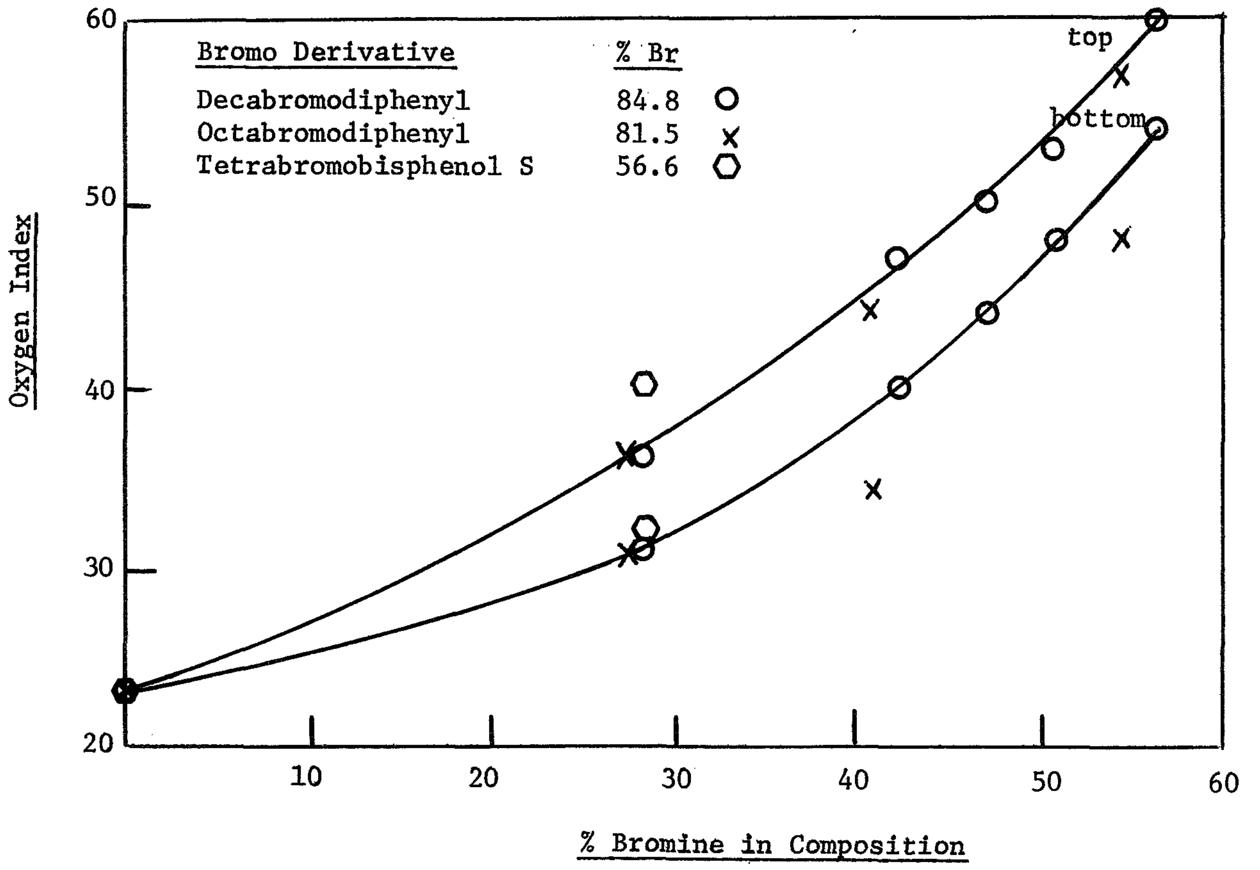
THE FOLLOWING BROMO COMPOUNDS GAVE INEFFECTIVE CURES*

	Additive	Parts
1.	Tetrabromoethylenedianiline	50
2.	Tetrabromomethylenedianiline Kaolin Ultrawhite 90	50 50
3.	Tetrabromobisphenol A	100
4.	Tetrabromobisphenol A Kaolin Ultrawhite 90	75 25
5.	Hexabromocyclohexane	100
6.	Hexabromocyclohexane Kaolin Ultrawhite 90	75 25
7.	Tetrabromomethane	100
8.	Tetrabromomethane Kaolin Ultrawhite 90	75 25
9.	Tetrabromobutane	100
10.	Tetrabromobutane Kaolin Ultrawhite 90	75 25
11.	Hexabromocyclododecane	100
12.	Hexabromocyclododecane Kaolin Ultrawhite 90	75 25

* Formulation: SE 517 Silicone Rubber Compound 100 pts.
Luperco CST 1.5 pts.
Molded 250°F/10 min.

FIGURE 14

EFFECT OF BROMINE CONCENTRATION ON FLAME RESISTANCE



OPTIMIZING THE DECABROMODIPHENYL SYSTEM

Auxiliary Additives. -- Having selected decabromodiphenyl as the preferred additive for preparing flame-resistant silicone rubbers, we next attempted to find a synergistic auxiliary additive. Unfortunately, this search was not successful, as shown by the examples in Table XXI. Antimony oxide does have a slightly positive effect. Compare sample No. 69B with the one below for a normal inert filler. Surprisingly, the physical properties of the formulation containing antimony oxide was superior to those containing the other additives. The tensile strength was increased by 200 psi. This particular antimony oxide is very finely divided and apparently when it was added to the mixture of decabromodiphenyl and the silicone rubber compound, it behaved as a reinforcing filler. The cadmium-barium stabilizer was used as an auxiliary additive in an attempt to neutralize the deleterious effect of HBr that could evolve from the bromo derivative during the cure cycle. However, as Table XXI shows, the physical properties were reduced, if anything.

Purification of Decabromodiphenyl From Great Lakes Chemical. -- Realizing that the purity of the aromatic bromide can affect the physical properties of the resulting formulated rubber, we therefore decided to recrystallize a portion of the decabromodiphenyl. This derivative is soluble in hot trichlorobenzene and was, therefore, easily recrystallized from this solvent. As shown in Table XXII, the recrystallized product, sample No. II-74B had a tensile strength of 700 psi as compared to 640 for the decabromodiphenyl as received. Furthermore, the percent elongation was reduced from 870 to 500% by the recrystallization process. Apparently the oxygen index as measured from the top was also increased, from 36 to 40.

Surprisingly, a similar result was obtained by merely washing the sample: washing the decabromodiphenyl first with water and then with isopropyl alcohol (sample No. III-32B). We suspect that washing with water removed residual HBr from the product, whereas the alcohol could have removed unreacted diphenyl. A water dispersion of the decabromodiphenyl received from Great Lakes Chemical was slightly acidic (1% concentration in water); in contrast, both the recrystallized product and that prepared by washing were essentially neutral products.

Addition of Cab-O-Sil Silica. -- A more dramatic result was obtained with the system containing 75 parts of the purified decabromodiphenyl and 8 parts of Cab-O-Sil. Here the tensile strength was increased from 695 to 835 psi. In these formulations, the Cab-O-Sil was added to the mill after the bromo derivative.

TABLE XXI

DECABROMODIPHENYL SYSTEM--EFFECT OF AUXILIARY ADDITIVES[a]

Sample No.	Additive System	Parts Additive	Oxygen Index Top	Oxygen Index Bottom	Physical Properties Tensile psi	Physical Properties % Elongation
II-63A[b]	Decabromodiphenyl	100	47	40	435	950
II-69A[b]	Decabromodiphenyl	100	46	38	175	200
	Cd-Ba Stabilizer[c]	3.0				
II-72A	Decabromodiphenyl	100	47	39	450	450
	Cab-O-Sil HS-5	5.0				
II-69B	Decabromodiphenyl	90	45	38	625	430
	Antimony Oxide[d]	10				
ef	Decabromodiphenyl	90	43[e]	37[e]	450[f]	840[f]
	Inert Filler	10				

a. Formulation: Silicone Compound SE-517, 100 pts; Luperco CST, 2.0 pts; molded 260°F/10 min
Oven Cure - 400°F <1 torr-4 hrs. Decabromodiphenyl (Great Lakes, as received)

b. 1.5 pts. Luperco CST

c. Ferro Corp.

d. Thermogard F-R, M&T Chemicals

e. Values obtained from graph (Figure 11)

f. Values obtained from graph (Figure 10)

TABLE XXII

EFFECT OF PURIFYING DECABROMODIPHENYL[a]

Sample No.	Additive System	Parts Additive	Decabromodiphenyl Purification Method	Oxygen Index		Physical Properties	
				Top	Bottom	Tensile PSI	% Elongation
II-52A[bc]	Decabromodiphenyl	50	None	36	31	640	870
II-74B[b]	Decabromodiphenyl	50	Recrystallized From Trichlorobenzene	40	31	700	500
III-32B[b]	Decabromodiphenyl	50	Washed With Water & Isopropyl Alcohol	40	31	700	460
III-5B[d]	Decabromodiphenyl Cab-O-Sil HS-5	75 8	None	42	36	695	483
III-2A[d]	Decabromodiphenyl Cab-O-Sil HS-5	75 8	Washed With Water & Isopropyl Alcohol	43	37	835	517

a. Formulation: 100 pts. Silicone Rubber Compound SE-517; Molded 10 min. at 287°F;
Oven Cure - 400°F, <1 torr, 4 hrs.
Decabromodiphenyl (Great Lakes Chemical)

b. Luperco CST - 1.5 pts.

c. Curing Temp. Initial: 75°F; Final: 287°F, Time 10 min.

d. Luperco CST - 1.2 pts.

During this investigation, we noted that the time of addition of the Cab-O-Sil is very significant. To obtain the beneficial effect of this additional silica, it must be added to the compounding mill as the last component in this three-component system containing gum, decabromodiphenyl, and Cab-O-Sil. Cab-O-Sil HS-5 was selected for this application because it is known to be one of the most reactive reinforcing fillers for silicone rubber.

When 8 parts of Cab-O-Sil was added to the pure gum, the tensile strength was increased 300 psi, (See Table XXII). This table includes the values for the tensile strength after molding and after the oven cure. Under optimum cure conditions, the oven cure value should be higher than that obtained after molding. Because of the limited availability of the decabromodiphenyl, we did not always determine optimum cure conditions in every study of a variable.

Realizing that the physical properties of the formulated silicone rubber depend upon the concentration of decabromodiphenyl, we decided that the 75-part level would be the best compromise in terms of flame resistance and physical properties. At this level, adding 8 parts of Cab-O-Sil in the optimum manner boosted the tensile strength approximately 200 psi to a value of 860 psi. This is a very substantial increase in tensile strength, considering that the rubber, free of auxiliary fillers, gives a tensile of approximately 1200-1300 psi. The concept of adding a small amount of base such MgO (See sample No. III-7A) did not prove to be a fruitful approach. As the table shows, the physical properties were reduced after the oven cure.

Increasing the Cab-O-Sil content of the flame-resistant rubbers to 12 parts did not further improve their physical properties. The slight improvement in oxygen-index values in this case for the samples burned at the bottom may be due to the dilution effect of the filler. Comparison of the last two items in Table XXIII indicates that samples can be cured in an oven with or without vacuum to produce a product with approximately equivalent physical properties.

Purification of Decabromodiphenyl from Michigan Chemical. -- At this time in our program, we were no longer able to obtain samples of decabromodiphenyl from Great Lakes Chemical. Fortunately, Michigan Chemical made a decision to enter the market, and they provided us with two shipments of material. As Table XXIV illustrates, the product received from Michigan Chemical was of higher purity than the one from Great Lakes Chemical. Melting points were determined by DTA. As the table shows, the melting point of the Michigan Chemical product was 379°C, whereas that received from Great Lakes was 358°C, and the latter sample melted over a wider range (compare the DTA curves in Figure 15 and Figure 16 for these two products-as received). Drying these samples in a vacuum oven at 200°C under full vacuum conditions for 4 hours also yielded information concerning the relative purity of the samples. The product from Great Lakes had 16%

TABLE XXIII

SYSTEMS CONTAINING CAB-O-SIL HS-5[a]

Sample No.	Additive System	Parts Additive	Oxygen Index		Tensile Strength		% Elongation	
			Top	Bottom	As Molded	Oven Cure	As Molded	Oven Cure
III-4A	Cab-O-Sil HS-5	8			1332	1080	625	437
III-3B	--------------	--			1000	970	537	400
III-4B	Decabromodiphenyl	75	43	36	617	600	500	475
III-2A	Decabromodiphenyl	75	43	37	860	835	550	517
	Cab-O-Sil HS-5	8						
III-3A[b]	Decabromodiphenyl	75	43	36	800	765	525	437
	Cab-O-Sil HS-5	8						
III-7A	Decabromodiphenyl	75	42	37	835	670	575	375
	Cab-O-Sil HS-5	8						
	MgO - Maglite D[c]	0.5						
III-8A	Decabromodiphenyl	75	43	38	867	700	600	358
	Cab-O-Sil HS-5	12						
III-8B[d]	Decabromodiphenyl	75	43	38	890	680	587	392
	Cab-O-Sil HS-5	12						

a. Formulation: 100 pts. SE-517 Silicone Compound and 1.2 pts. Luperco CST. D.B.D.P. (Great Lakes Chemical) was washed with alcohol. Mold Conditions: 287°F/10 min. Oven cure: 400°F/ <1 Torr/4 hrs.

b. Formulation was aged without peroxide for 24 hrs. Peroxide then added and formulation cured

c. Whittaker, Clark, and Daniels, Inc.

d. Sample was post cured in ordinary oven without vacuum

TABLE XXIV

DECABROMODIPHENYL - SAMPLE PURITY[a]

Source	Treatment	Melting Point °C	% Volatiles*
Great Lakes Chemical	As Received	358	16.0
Great Lakes Chemical	Washed	368	12.8
Michigan Chemical Lot #1	As Received	379	5.3
Michigan Chemical Lot #1	Washed	381	5.1
Michigan Chemical Lot #1	Recrystallized	381	---
Michigan Chemical Lot #2	As Received	380	---
Michigan Chemical Lot #2	Recrystallized	382	---

a. Volatility determined by drying sample 4 hours at 200°C/ <1 Torr.

FIGURE 15

DECABROMODIPHENYL (GREAT LAKES CHEMICAL)

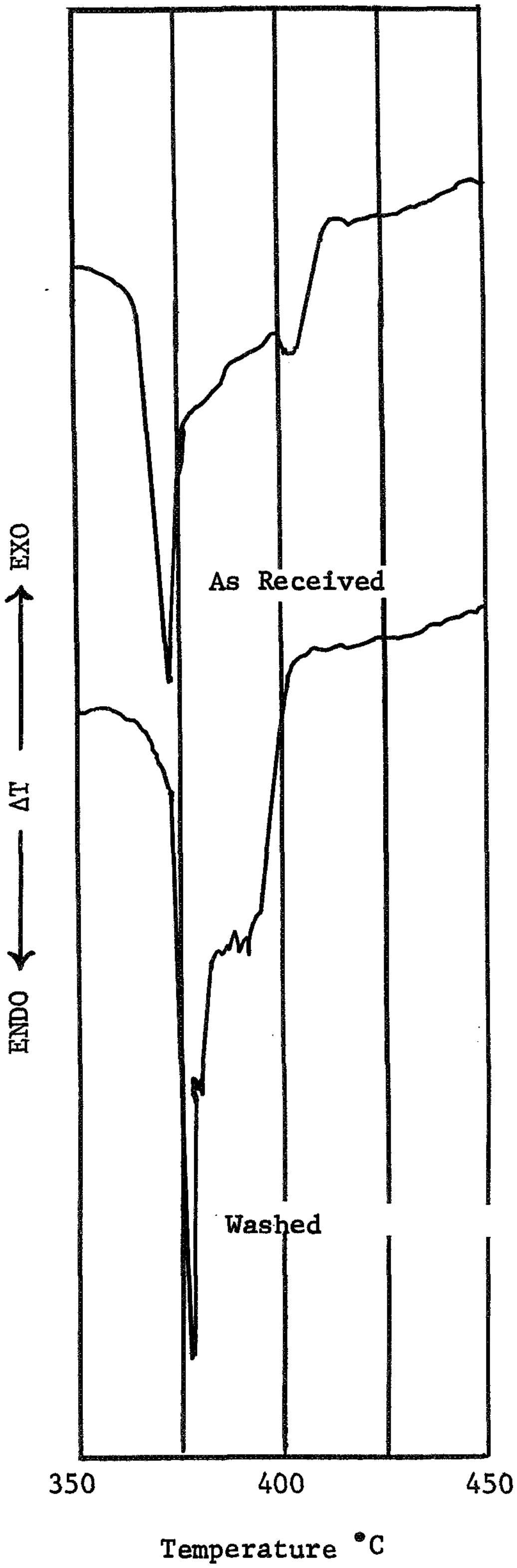


FIGURE 16

DECABROMODIPHENYL (MICHIGAN CHEMICAL LOT #1)

Temperature °C

volatiles under these conditions, whereas that received from Michigan Chemical had only 5% volatiles.

Washing the Great Lakes material as described above raised the melting point, according to the DTA curves shown in Figure 15, and reduced the volatiles. Recrystallizing the Michigan Chemical product raised the melting point only slightly and, as shown in Figure 16, some of the impurities were removed. Lot #2 Michigan Chemical appeared to have the highest purity. Note the very sharp melting points on both the recrystallized and as-received products as shown in Figure 17.

In spite of this high purity, we were surprised to learn that the physical properties of the flame-resistant rubber containing 75 parts of decabromodiphenyl were actually worse with the Michigan Chemical product as compared to that from Great Lakes (See Table XXV). Compare samples III-4B and III-33A. Even when the formulated product containing the washed decabromodiphenyl from Michigan Chemical (III-34A) was compared with that from Great Lakes, we noticed very little improvement in physical properties. Apparently, merely washing the Michigan Chemical product was inadequate. However, when the decabromodiphenyl from Michigan Chemical was recrystallized by first dissolving it in hot trichlorobenzene and then precipitating it rapidly by adding it to cold isopropyl alcohol, the resulting silicone rubber had greatly improved physical properties. The tensile value of 735 psi was obtained even without the additional Cab-O-Sil. Note also that in every instance the silicone rubber containing the Michigan Chemical decabromodiphenyl had improved flame resistance when measured from the top and from the bottom. A graphic representation of this improvement in flame resistance is indicated in Figures 8, 11, and 12 where these new data points have been included. A comparison of the different decabromodiphenyls with Cab-O-Sil either at the 8- or 5-parts level further confirms the advantages of utilizing the recrystallized product from Michigan Chemical, as shown in Table XXV.

These strange results obtained with the purer product from Michigan Chemical were very puzzling. Only after examining the decabromodiphenyl samples under an optical microscope did we realize that the purity of the decabromodiphenyl was not the only requirement for a flame-resistant silicone rubber. These photographs are shown in Figure 18. Washing the diphenyl derivative does not affect the particle size; therefore, Photographs I and II can be compared. The differences between these products made by Michigan Chemical and Great Lakes is very obvious now. That from Great Lakes has an extremely fine particle size with an average particle size of perhaps 3 microns, whereas the sample from Michigan Chemical has some very large particles. Note from the photograph that these large particles are actually chunks.

When the product from Michigan Chemical was recrystallized and rapidly precipitated, the resulting decabromodiphenyl precipitated as very fine platelets (See Photograph III). Although these platelets are relatively large, they have high surface, and it is the surface effect that is most important in determining the interaction of a filler with silicone gums. Thus,

FIGURE 17

DECABROMODIPHENYL (MICHIGAN CHEMICAL LOT #2)

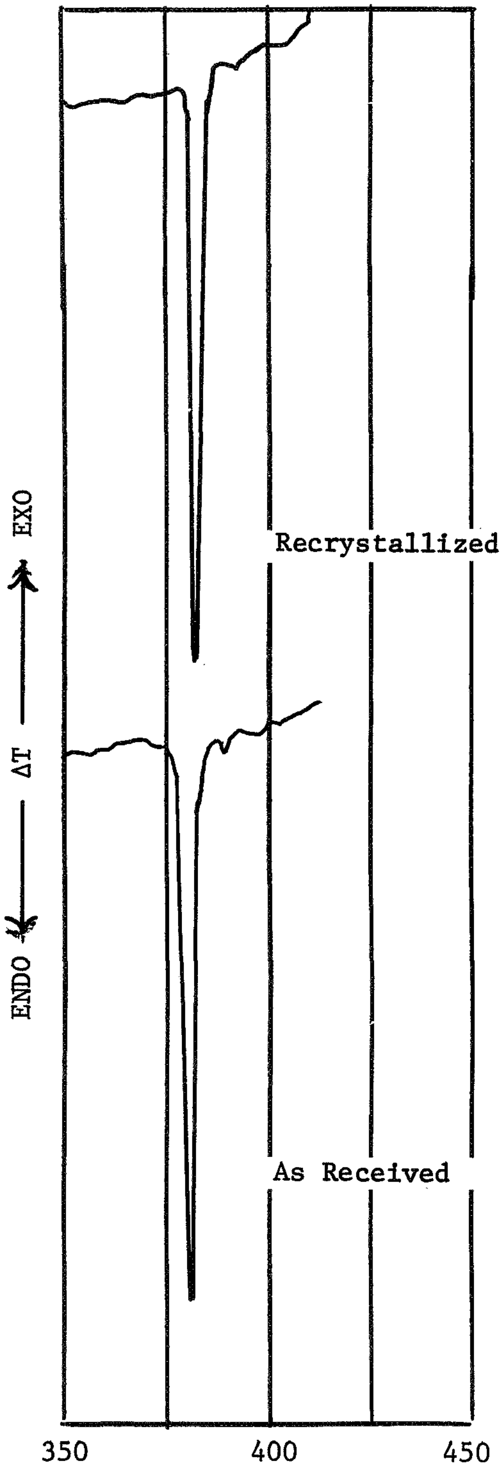


TABLE XXV

DECABROMODIPHENYL (D.B.D.P.) PURITY: EFFECT ON PROPERTIES[a]

Sample No.	D.B.D.P. Source[b]	Purification Method	Cab-O-Sil Pts./100	Oxygen Index		Tensile Strength		% Elongation	
				Top	Bottom	As Molded	Oven Cure	As Molded	Oven Cure
III-4B	GL	Washed	None	42	36	617	600	500	475
III-34A	MC-1	Washed	None	46	38	560	565	500	475
III-33A	MC-1	None	None	46	38	540	440	590	600
III-64[cd]	MC-2	Recrystallized	None	45	39	700	735	500	500
III-2A	GL	Washed	8	43	37	860	835	550	517
III-35A[e]	MC-1	Washed	8	47	39	650	685	565	485
III-40	MC-1	Recrystallized	8	48	39	815	875	525	525
III-55B[cd]	MC-1	Recrystallized	5	47	40	773	851	500	464
III-66[cd]	MC-2	Recrystallized	5	45	40	733	810	500	475

a. Formulation: 100 pts. SE-517 gum, 75 pts. D.B.D.P., 1.2 pts. Luperco CST molded 287°F/10 min, mold 0.035" thick Oven cured at 400°F/ <1 torr - 4 hrs.

b. GL = Great Lakes Chemical; MC = Michigan Chemical; number indicates different lots

c. SE-517 gum vacuum dried 400°F/ < 1 torr 4 hrs. Cured rubber in forced draft oven 400 °F/4 hrs.

d. Molded at 265°F/10 min.

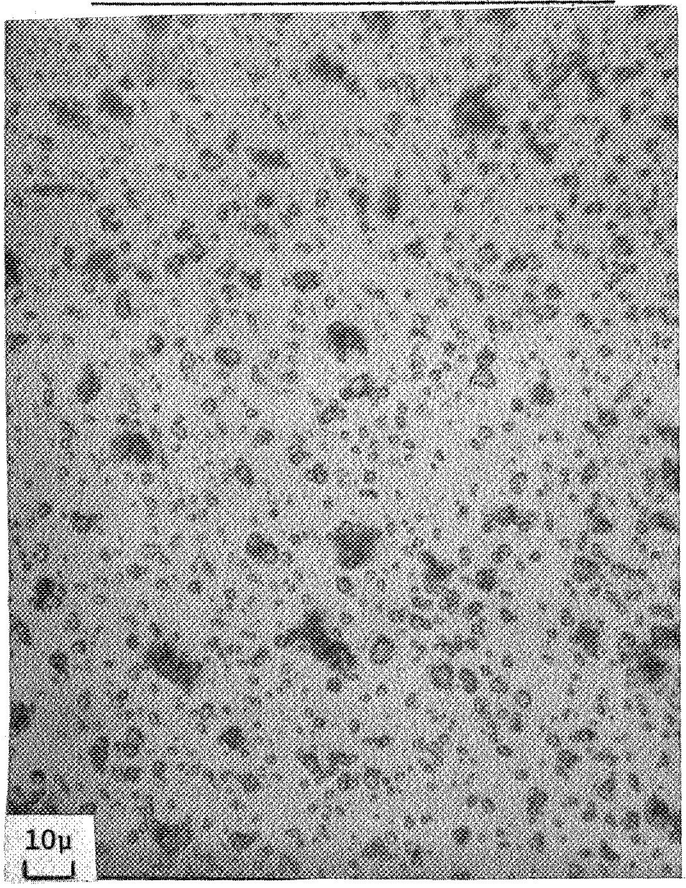
e. Mold 0.075" thick

FIGURE 18

DECABROMODIPHENYL SAMPLES

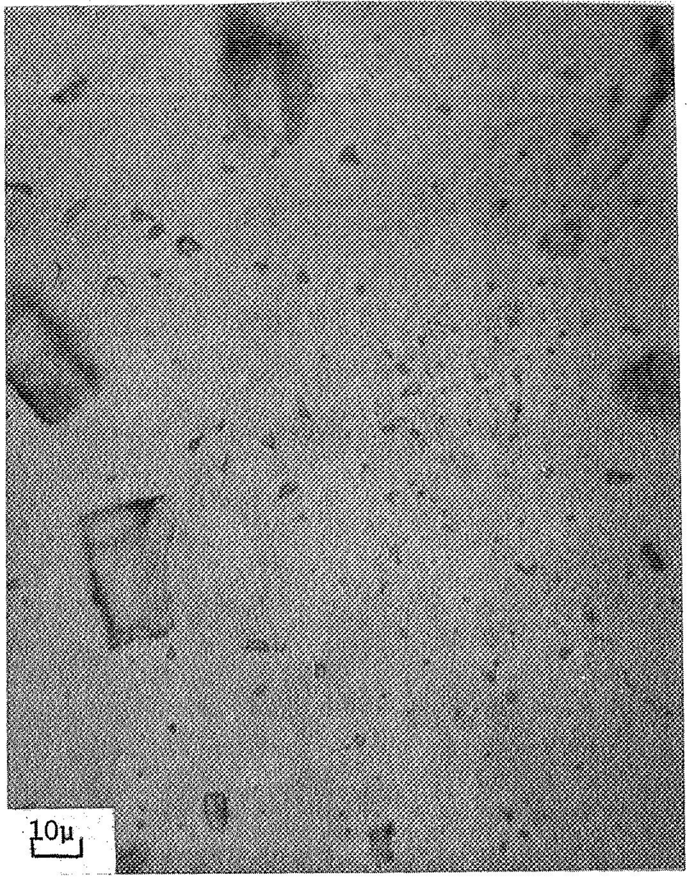
I

Great Lakes Chemical Co., Washed



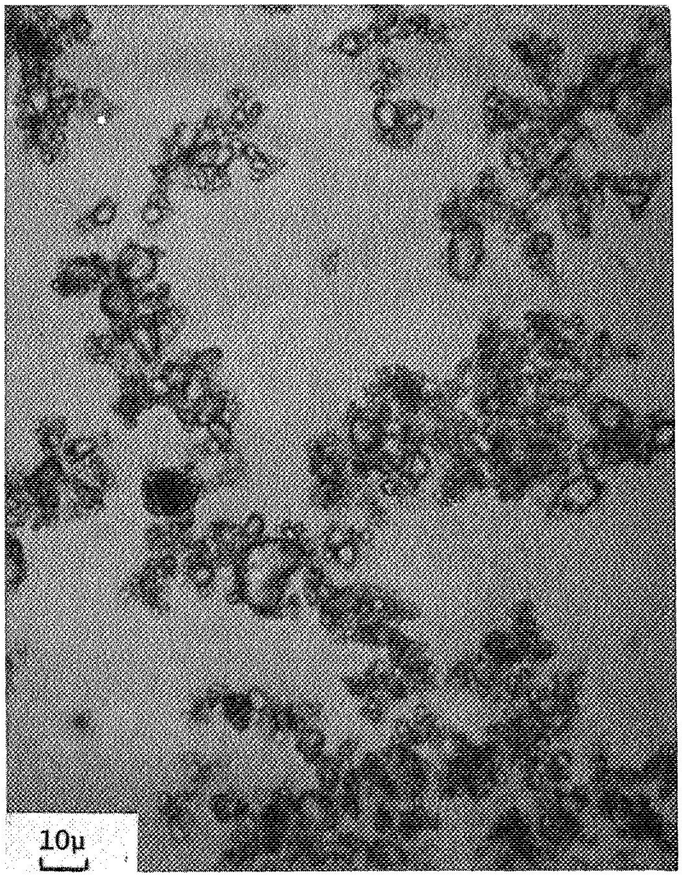
II

Michigan Chemical, As Received



III

Michigan Chemical, Recrystallized



the recrystallization of the Michigan Chemical product yielded a silicone rubber with good physical strength, not because the decabromodiphenyl was more pure, but because it had been precipitated in a new high-surface form. To further reinforce this argument, a portion of the decabromodiphenyl from Michigan Chemical was not purified but merely powdered by a micronizer. This product is shown in Photograph IV in Figure 18. Here the average particle size has been reduced to dimensions approaching the Great Lakes product. Using the decabromodiphenyl powdered by the micronizer resulted in a silicone rubber with physical properties similar to that obtained with the recrystallized material.

Effect of Pre-drying Silicone Gum. -- As mentioned earlier in the report, because the application of flame resistant silicone rubbers in a space environment requires that these materials have a low-volatile content, we always cured the rubber in a vacuum oven at an elevated temperature. However, most fabricators of silicone rubber products cure their products in a forced-draft oven. Therefore, we examined the approach where the silicone gum was first vacuum dried before mixing it with the other ingredients. Thus, vacuum curing by the fabricator would not be required.

We have found that this approach is workable, as indicated by the results in Table XXVI. Under the optimum cure conditions the process of first vacuum drying the gum, (The gum was vacuum dried at 400°F/ < 1 torr. for 4 hours), and then curing it in a forced-draft oven is probably preferred. Compare samples III-61B and III-48B. These samples were molded at 265°F, which is the preferred molding temperature. At 287° the rubber sheets were often "scorched" in the mold. According to the results shown in Table XXVI, either using the vacuum oven before the curing operation or using the vacuum oven during the curing operation makes little difference in terms of the physical properties of the resulting silicone rubber. The pre-dried gum may have a slight edge in yielding the stronger rubber. One interesting observation shown in this table is that the 265° mold temperature appears to give a product with better flame resistance as measured by burning the sample on the bottom.

Optimization of Cure Conditions and Formulation. -- To establish basic information concerning the effect of curing conditions on the physical properties of SE-517 silicone rubber, we examined the effect of various variables such as peroxide content, mold temperature, and mold time on the physical properties of the rubber containing no additional filler other than that incorporated by the rubber producer. These results are summarized in Table XXVII. As mentioned previously, molding temperatures should be lower than 287°F with this particular rubber composition. The lower temperature prevents scorching and it also allows for a more

TABLE XXVI

EFFECT OF DRYING SILICONE GUM COMPOUND AND CURING IN FORCED-DRAFT OVEN[a]

Sample No.	Vacuum Drying of Gum	Vacuum Cure	Mold Temp. °F	Tensile Strength As Molded	Tensile Strength Oven Cure	% Elongation As Molded	% Elongation Oven Cure	Oxygen Index Top	Oxygen Index Bottom
III-61B	No	Yes	265	719	812	537	487	46	40
III-48B	Yes	No	265	855	843	569	437	46	40
III-40	No	Yes	287	815	875	525	525	47	39
III-42	Yes	No	287	810	808	500	500	48	39
III-36B[b]	No	Yes	287	615	568	500	415	47	39
III-37A[b]	Yes	Yes	287	663	606	440	375	47	39

a. Formulation: SE-517 100 pts., D.B.D.P. (Michigan Chemical Lot #1) Recrystallized 75 pts., Cab-O-Sil HS-5 8 pts., Luperco CST 1.2 pts.
Drying Conditions: Vacuum dried gum prepared by drying in vacuum oven at 400°F/ <1 torr for 4 hrs.
Forced-Draft Oven Cure: 400°F/4 hrs.
Vacuum Oven Cure: 400°F/ <1 torr for 4 hrs.

b. D.B.D.P. was washed rather than recrystallized

TABLE XXVII

EFFECT OF CURING CONDITIONS ON PHYSICAL PROPERTIES OF SE-517 SILICONE RUBBER COMPOUND

Sample No.	Parts Luperco CST	Initial Temp. of Mold, °F	Final Temp. of Mold, °F	Time Min.	Tensile Strength, psi		% Elongation	
					As Molded	Oven Cure[a]	As Molded	Oven Cure
III-47AB	0.6	260	260	10	1133	1227	890	919
II-73A-1	0.6	75	287	10	1300	1000	900	850
73A-2	0.6	75	287	15	950	800	800	800
73A-3	0.6	287	287	10	1200	900	900	800
III-3B	1.2	287	287	10	1000	970	537	400
II-73B	1.5	287	287	10	1000	800	500	400
II-70A	1.5	75	260	10	----	760	---	800

a. 4 hrs. at 400°F (<1 torr)

efficient use of the peroxide during the oven-cure stage. Sample No. III-47AB appears to be the best one in the series. Note also that with the SE-517 alone the concentration of Luperco CST should not be much greater than 0.6 parts.

Some of the results on this table have been graphed in Figures 19 and 20. Figure 19 shows that the rubber was not cured under optimum cure conditions because the tensile values for the oven-cured samples are always lower than that obtained by testing the rubber after molding. The values represented in this figure are for samples molded at 287°F. At this temperature increasing the level of Luperco CST beyond 1.2 parts reduces the strength of the vulcanizate. The conditions illustrated by Figure 20 are more near optimum. Note that the curve for the oven-cured samples is above that for the samples having no oven cure. Here, the mold temperature was 260°F. The curve clearly indicates that under these conditions a molding time of 10 minutes is optimum.

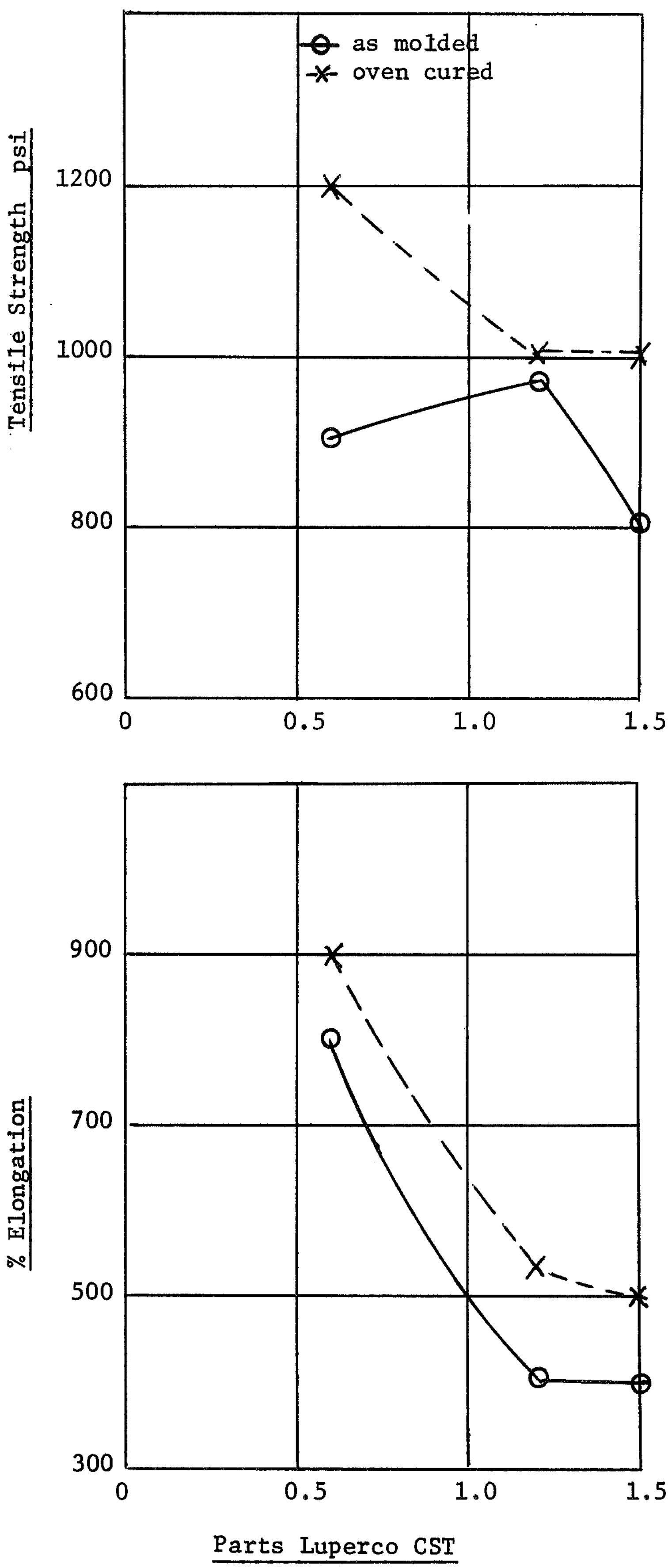
The next set of curves was obtained by measuring properties of the flame-resistant silicone rubber containing recrystallized decabromodiphenyl from Michigan Chemical. The solid line in Figure 21 shows the effect of vacuum drying the silicone gum on the physical properties as one cures the product in a forced-draft oven over a 16-hour period. The dashed line shows what occurs to the physical properties as one cures the rubber in a vacuum oven over the same period; however, in this instance, the silicone gum was not predried before it was compounded.

Under the experimental conditions cited in Figure 21, vacuum drying of the gum is preferred. Note that it is only after 4 hours in the vacuum oven that the product,prepared from the gum as received from the supplier, obtains tensile properties similar to that obtained from the product prepared with the vacuum-dried gum.

The effect of varying the amount of Cab-O-Sil added to the formulation on the properties of the flame-resistant silicone rubber is shown in Figure 22. Apparently the effect of Cab-O-Sil does not become significant until more than 3 parts of Cab-O-Sil are added. The tensile strength then rises rapidly, as shown by the curves in this figure. Vacuum-dried silicone gum was used in this investigation and in the formulations cited in the next series of figures. Although there is little advantage in adding 8 parts versus 5 parts of Cab-O-Sil to the flame-resistant compositions, Figure 23 shows that the only real difference is evident when one compares the samples immediately after molding. Under these conditions, the formulation containing 8 parts of Cab-O-Sil is superior.

We know that the physical properties of the flame-resistant rubber are reduced when the concentration of decabromodiphenyl is increased. This is clearly shown in Figure 24, but this figure also demonstrates the effect of using a peroxide concentration for the curing higher than

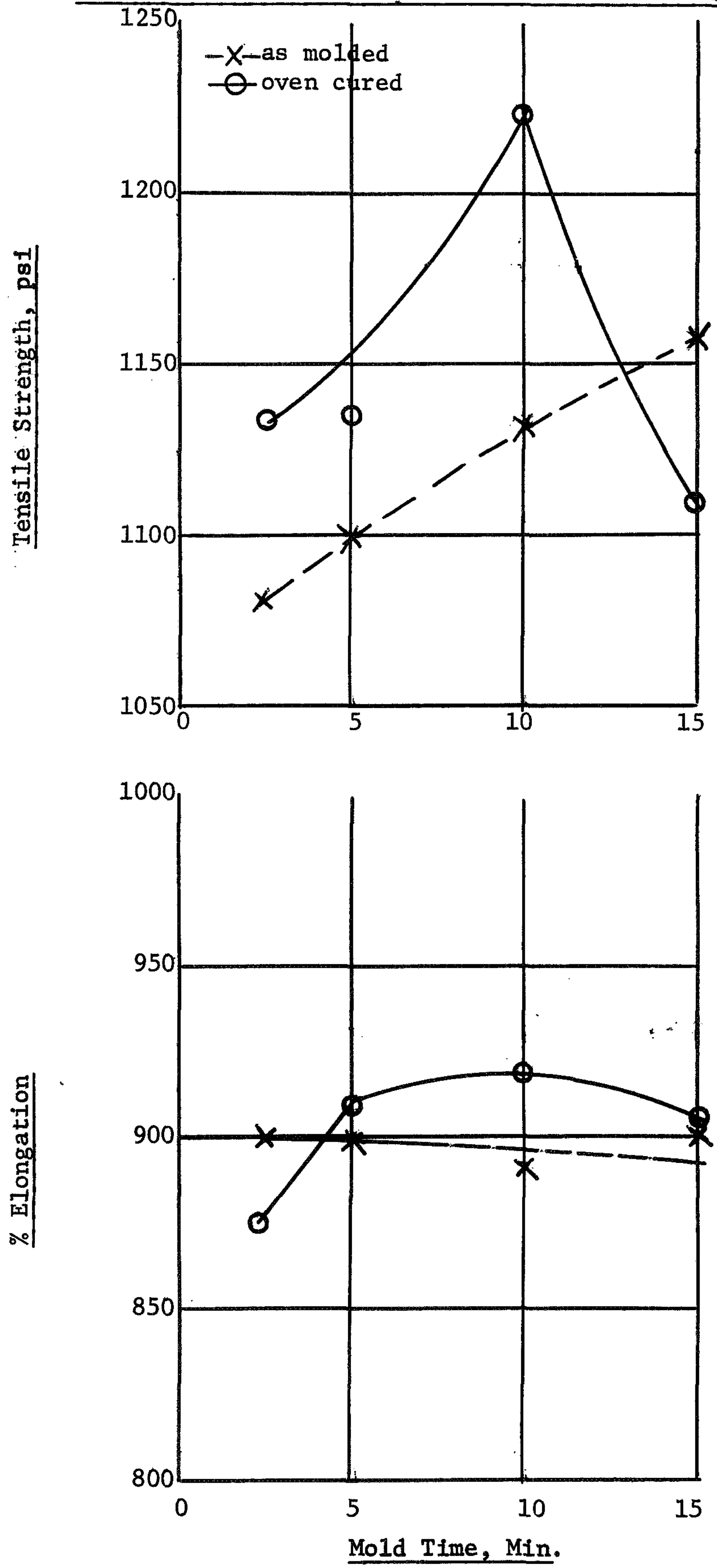
FIGURE 19
EFFECT OF VARYING AMOUNT OF VULCANIZING AGENT - BASE COMPOUND[a]



a. Formulation - SE-517 100 pts.
Mold Conditions: 287°F/ 10 min.
Oven cured at 400°F/ <1 torr for 4 hrs.

Figure 20

EFFECT OF MOLDING TIME:BASE SILICONE COMPOUND[a]

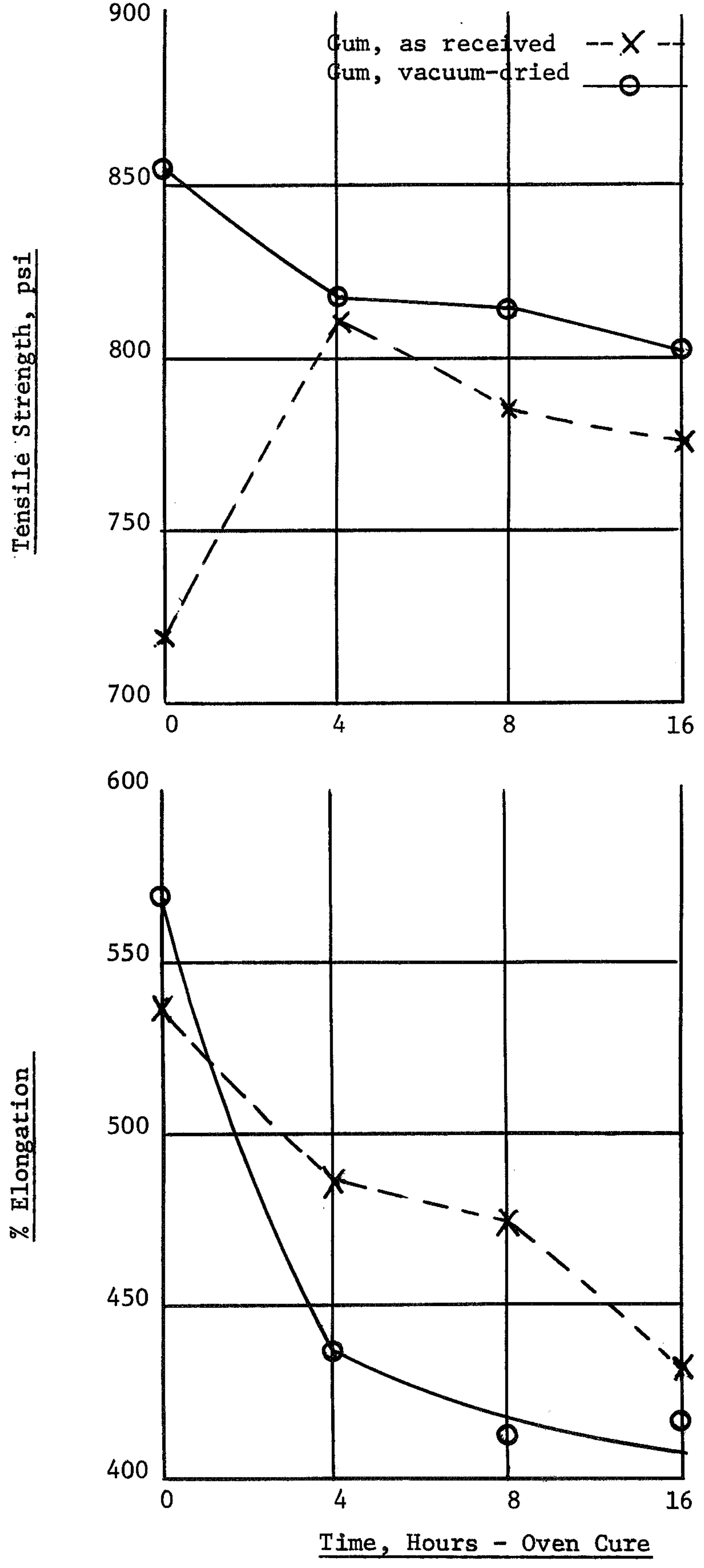


a. Formulation: SE-517 100 pts.
Luperco CST 1.2

Mold Temp. 260°F, .075 in mold

Figure 21

EFFECT OF DRYING SILICONE GUM[a]

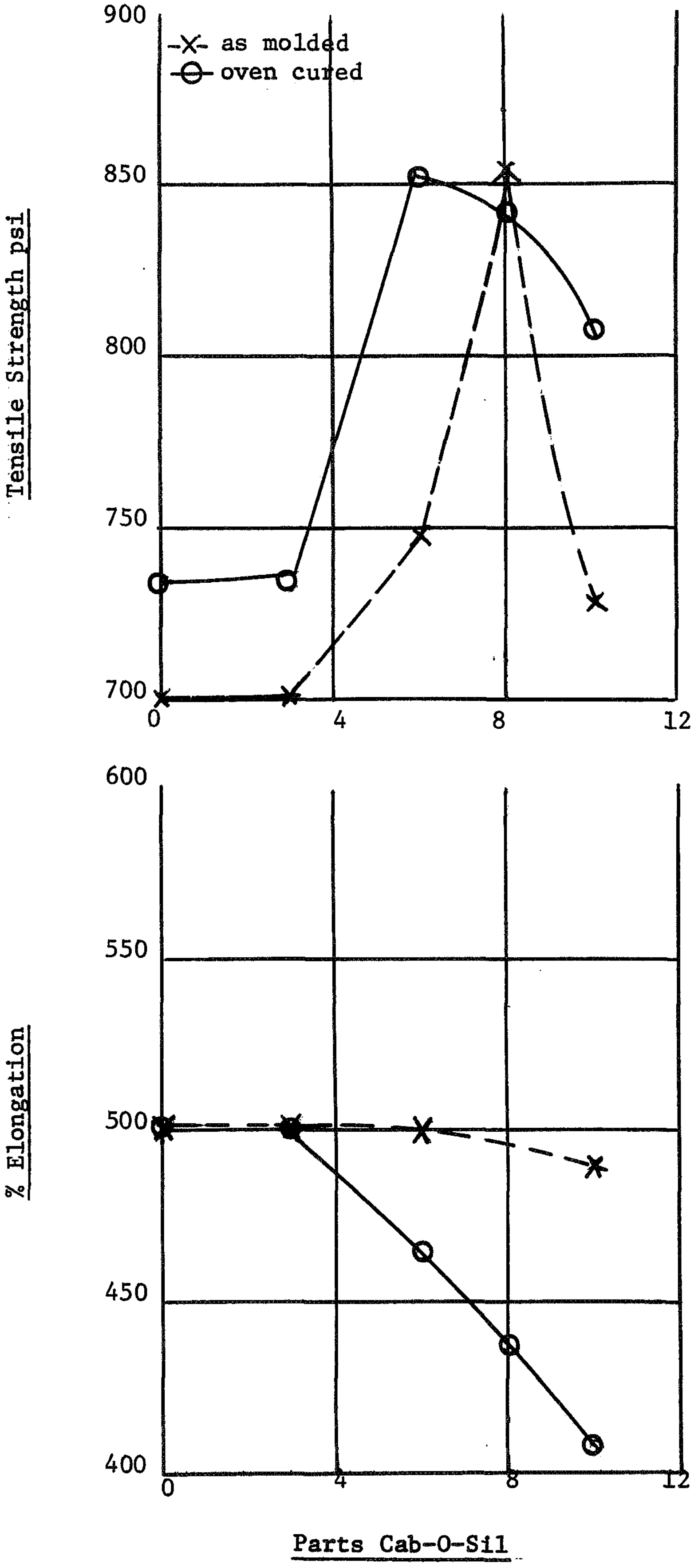


a. Formulation: SE-517 100 pts.
D.B.D.P. 75
Cab-O-Sil HS-5 8
Luperco CST 1.2

Mold Conditions: 265°F/10 min.

Figure 22

EFFECT OF VARYING THE AMOUNT OF CAB-O-SIL HS-5[a]

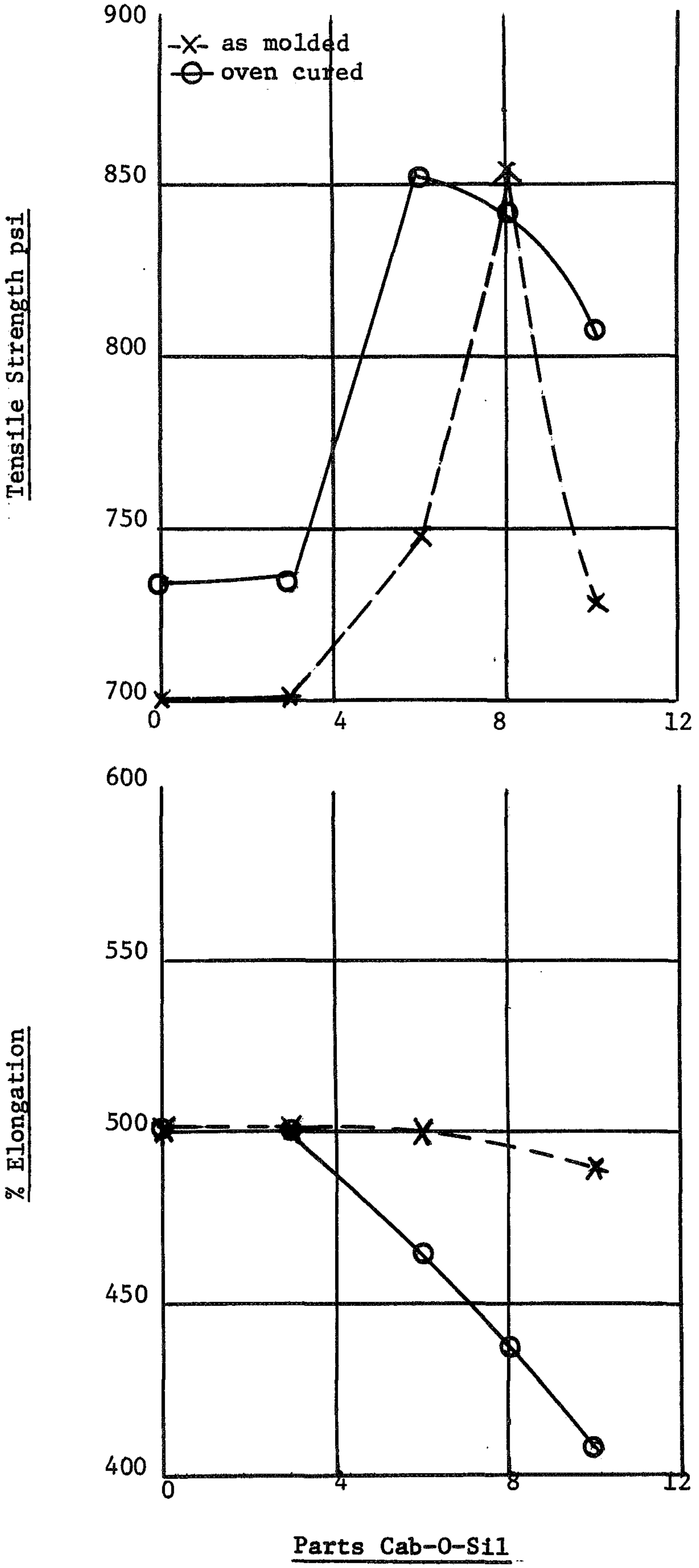


a. Formulation: SE-517 100 pts.
D.B.D.P. 75
Luperco CST 1.2

Molded: 265°F/10 min.

Figure 22

EFFECT OF VARYING THE AMOUNT OF CAB-O-SIL HS-5[a]



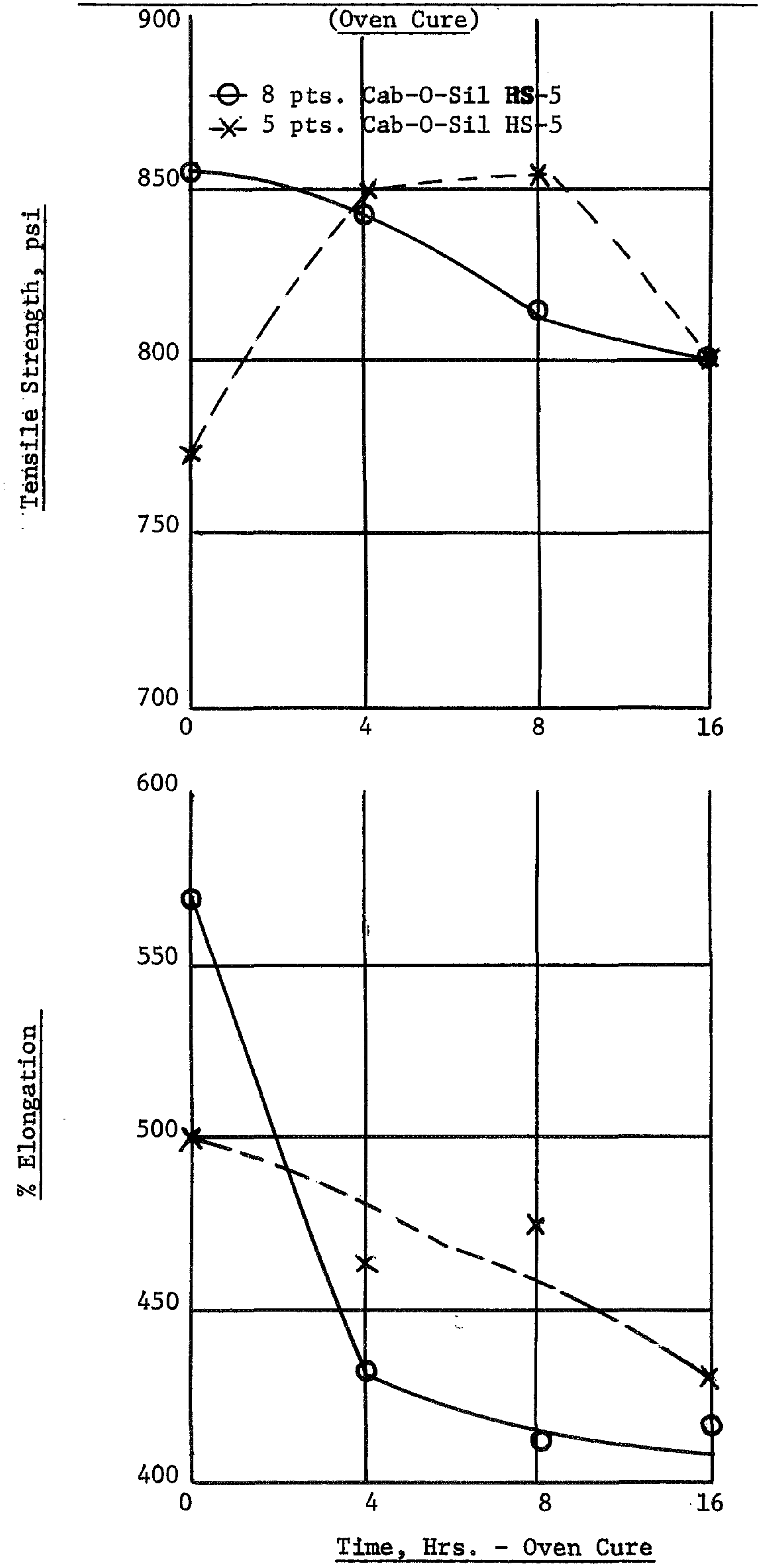
a. Formulation: SE-517 100 pts.
D.B.D.P. 75
Luperco CST 1.2

Molded: 265°F/10 min.

Figure 23

EFFECT OF VARYING THE AMOUNT OF CAB-O-SIL HS-5[a]

(Oven Cure)



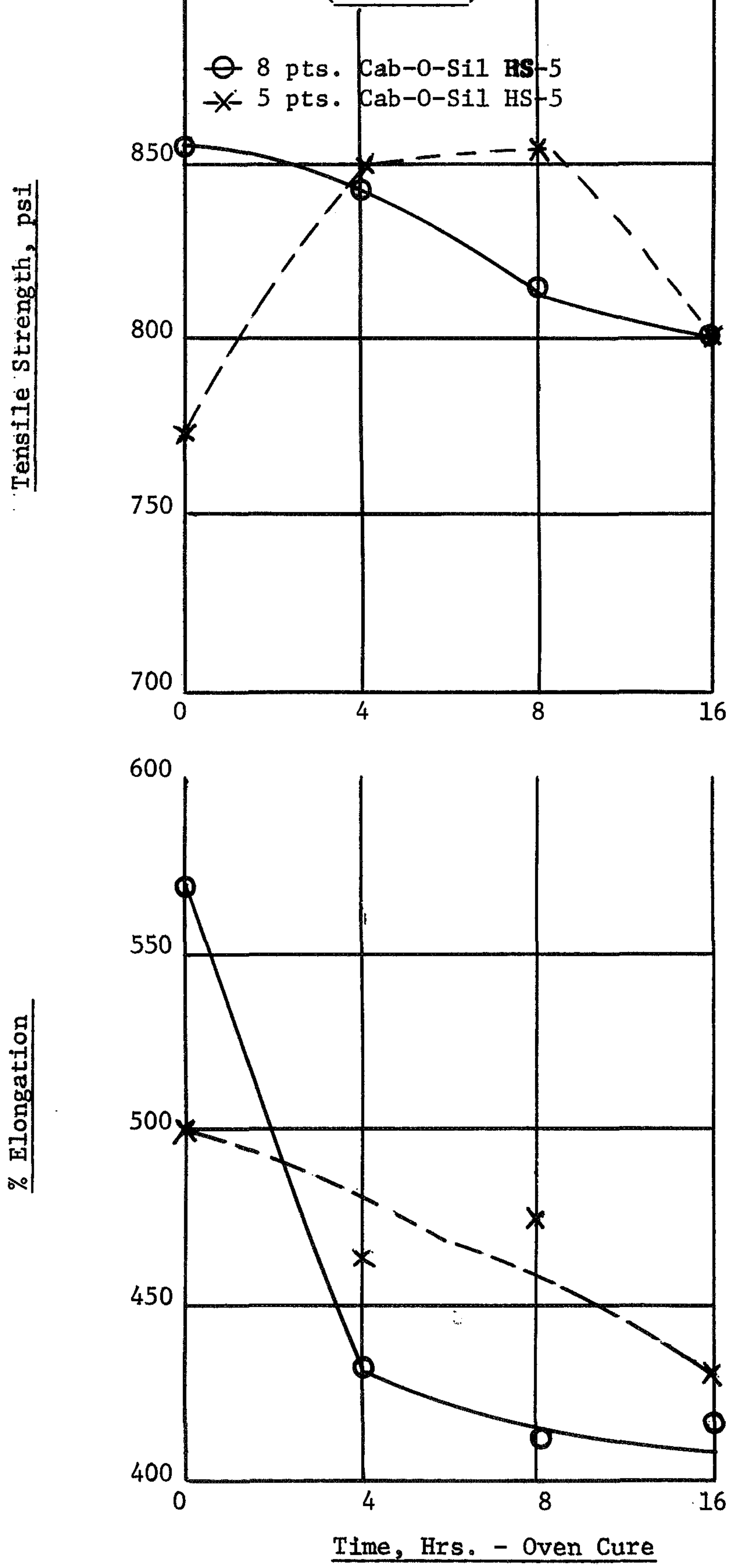
a. Formulation	SE-517	100 pts.
	D.B.D.P.	75
	Luperco CST	1.2

Mold
Conditions 265°F/10 min.
Oven Cure: 400°F

Figure 23

EFFECT OF VARYING THE AMOUNT OF CAB-O-SIL HS-5[a]

(Oven Cure)

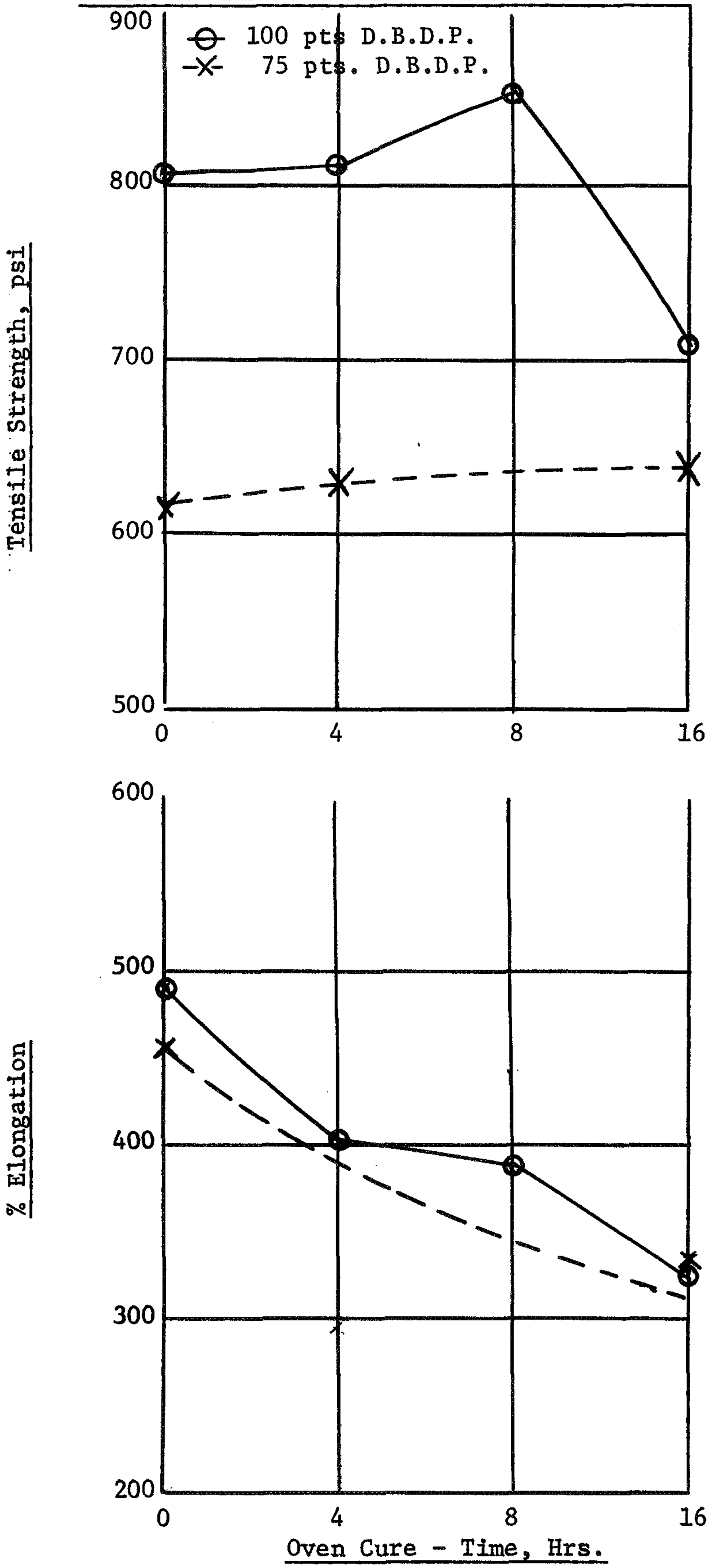


a. Formulation	SE-517	100 pts.
	D.B.D.P.	75
	Luperco CST	1.2

Mold
Conditions 265°F/10 min.
Oven Cure: 400°F

Figure 24

EFFECT OF DECABROMODIPHENYL CONCENTRATION[a]



a. Formulation SE-517 (Dried)100 pts.
Cab-O-Sil HS-5 8
Luperco CST 1.5
Mold Conditions: 265°F/10 min.

that required by the system. Note that with 75 parts of the bromo derivative the tensile strength begins to drop after 8 hours in the oven. These formulations were prepared with 1.5 parts of Luperco CST. While this is appropriate for formulations containing 100 parts of decabromodiphenyl, one can damage the strength of the rubber using 75 parts of decabromodiphenyl, if the oven cure is allowed to proceed over an extended period. This is more clearly shown in Figure 25, where the effect of varying the amount of peroxide on the physical properties of this same system is shown. With 75 parts of decabromodiphenyl, a peroxide (Luperco CST) concentration of 1.2 parts is optimum.

Although these studies of the variables involved in the cure of the flame-resistant rubber were usually carried out with formulations containing 75 parts decabromodiphenyl and 8 parts silica; in most instances the same conclusions are also valid for formulations containing 75 parts decabromodiphenyl alone.

Figures 26 and 27 show the effect of molding time on the decabromodiphenyl-silica formulation at 265°F and at 287°F. At 265° the compositions can be molded over a 10- to 15-minute period without damaging the strength properties of the rubber. In contrast, at 287° the 10-minute molding time is preferred, and continuing molding beyond this time can cause a reduction in physical properties.

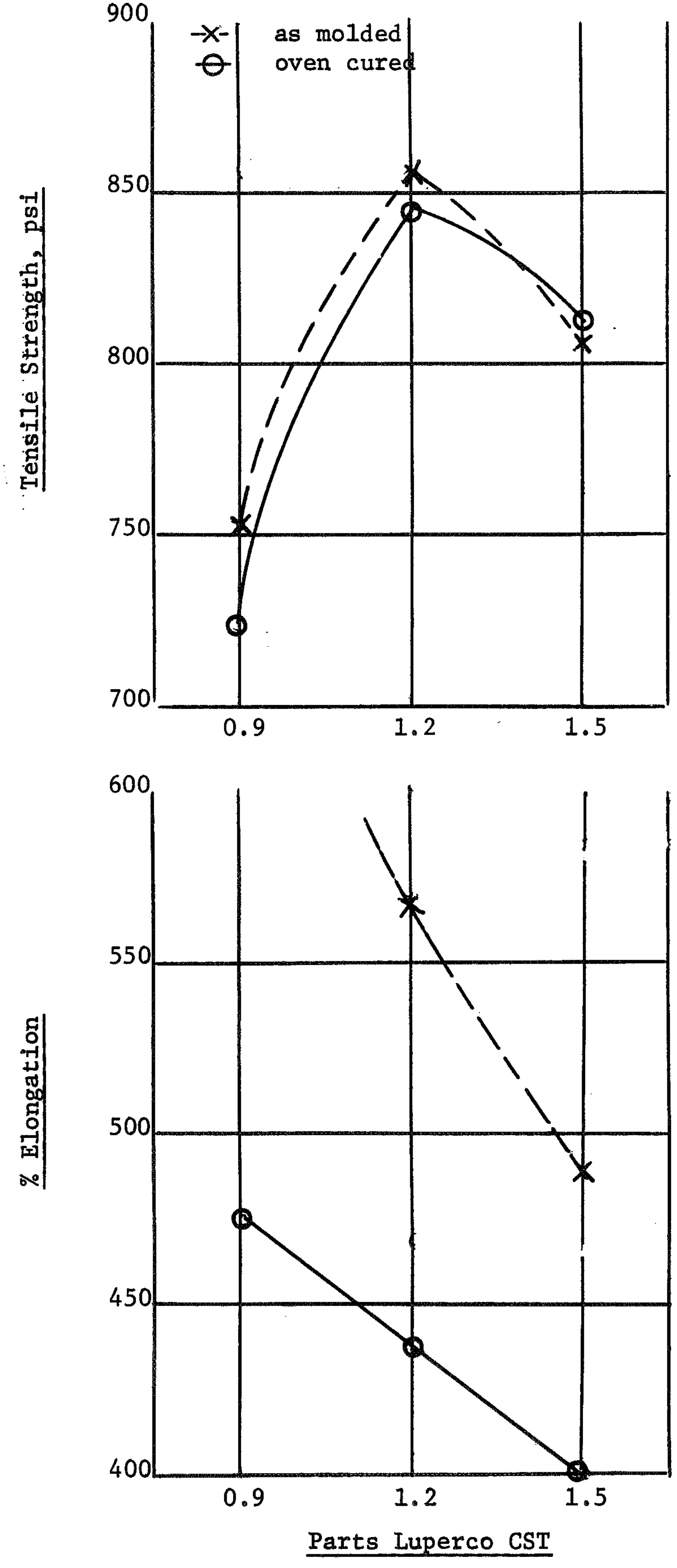
PHYSICAL PROPERTIES OF THE FLAME-RESISTANT SILICONE RUBBER

Flame Resistance. -- Flame-resistant rubbers containing various levels of decabromodiphenyl were tested for flame resistance at NASA, Manned Spacecraft Center, Houston. These results are summarized in Table XXVIII. This table also includes the oxygen-index values for these same samples when they were burned on the bottom. Generally, the ADL and NASA tests correlate very well. For example, compare the results with sample No. III-39. This sample, when burned at the bottom with a silicone ignitor at NASA in a 40% oxygen environment (10 psia), was self-extinguishing. It did not pass the test in a 50% oxygen environment. When tested at ADL, this same sample had an oxygen index of 40. Our final sample, No. III-70, passed the self-extinguishing test in a 50% oxygen atmosphere, although the ADL rating was 40. This difference may be accounted for by the difference in thickness of the two samples: No. III-63 has a thickness of 35 mils and No. III-70 has a thickness of 75 mils. Note from Table XXVIII that sample No. III-12B, which has a thickness of 75 mils and an oxygen index of 44, burned exceedingly slowly in an atmosphere of 100% oxygen at a pressure of 6.2 psia. The propagation rate of burning was 0.011"/sec. These results are very encouraging and indicate that with articles as thick as boot soles the flame-resistant silicone rubber may not burn in a 100%-oxygen atmosphere.

Data obtained by NASA at different total pressures in different atmospheres with our final flame-resistant elastomer have been plotted in Figure 28. This figure clearly shows the regions where the flame-

Figure 25

EFFECT OF VARYING THE AMOUNT OF VULCANIZING AGENT[a]

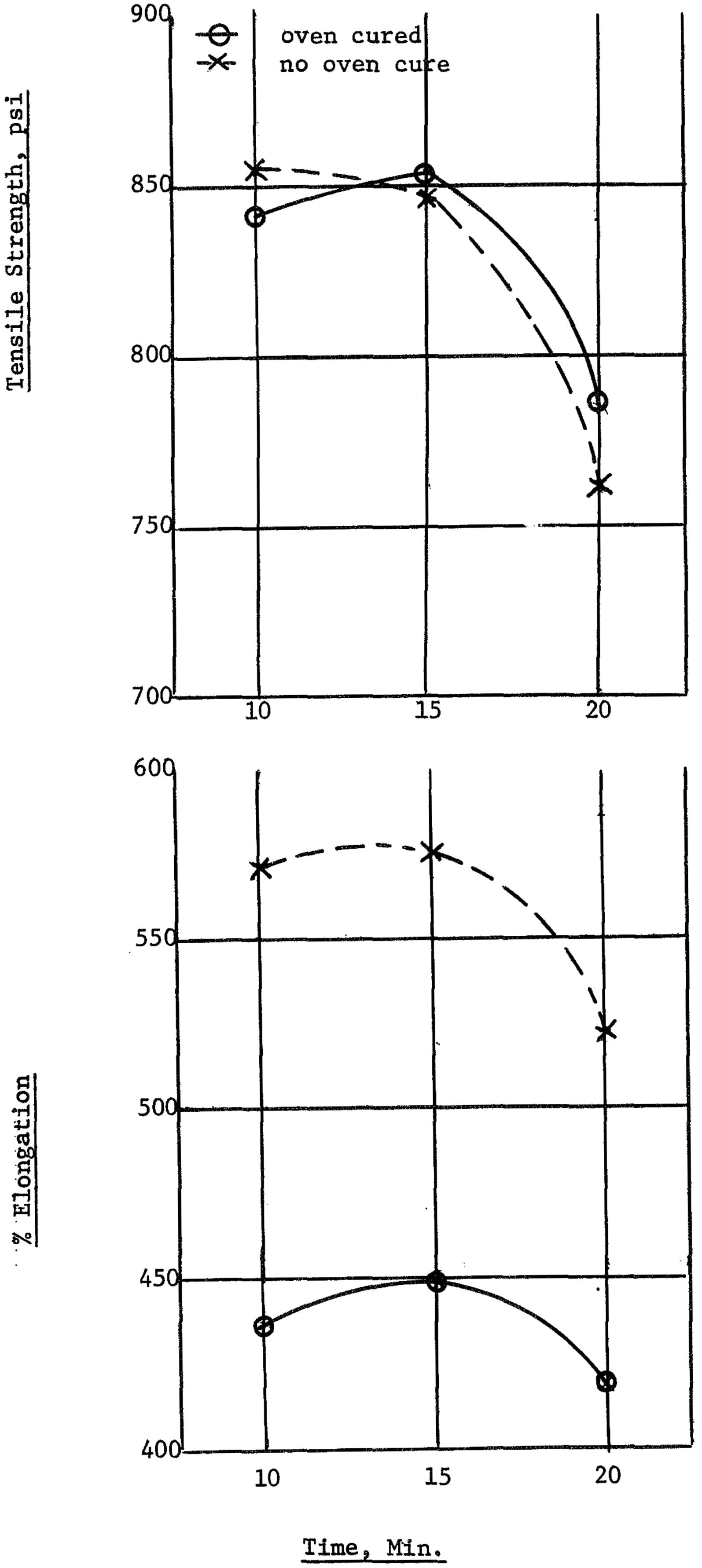


a. Formulation: SE-517 (Dried) 100 pts.
D.B.D.P. 75
Cab-O-Sil HS-5 8
Luperco CST

Mold Conditions: 265°F/10 min.

Figure 26

EFFECT OF MOLDING TIME: MOLD TEMP. 265°F [a]



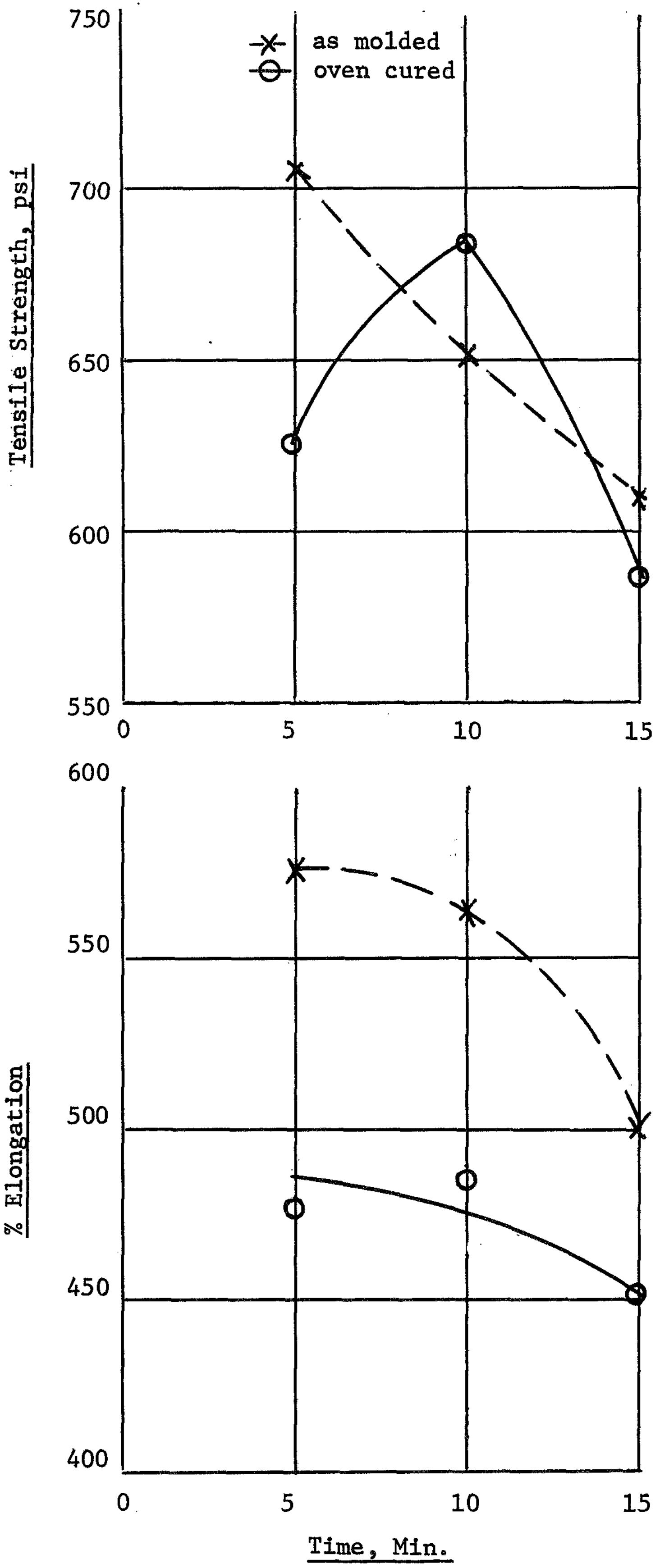
[a] Formulation:

SE-517 (dried)	100 pts.
D.B.D.P.	75
Cab-O-Sil HS-5	8
Luperco CST	1.2

Mold Temp. 265°F

Figure 27

EFFECT OF MOLDING TIME
MOLD TEMP. 287°F a



a. Formulation:	SE-517	100 pts.
	D.B.D.P.	75 pts.
	Cab-O-Sil HS-5	8 pts.
	Luperco CST	1.2 pts.

FLAME RETARDANCE-OXYGEN INDEX VS. NASA MSC (HOUSTON)

				Mold		NASA MSC (HOUSTON)				ADL
Sample No.	Decabromodiphenyl Pts./100	Source[a]	Cab-O-Sil Pts./100	Temp °F	Thickness	% Oxygen	Pressure PSIA	Ignitor Bottom	Propagation Rate, in/sec.	Oxygen Index Bottom
III-21	75	GL	8	287	0.075"	30	10	Tissue	S/E	37
III-39	75	MC	8	287	0.035"	35	10	Silicone	S/E	40
						40	10	Silicone	S/E	
						50	10	Silicone	0.013	
III-63	75	MC[b]	8	265	0.035"	35	10	Silicone	S/E	40
						40	10	Silicone	S/E	
						50	10	Silicone	0.013	
III-70[b]	75	MC	-	265	0.075"	35	10	Silicone	S/E	40
						50	10	Silicone	S/E	
						60	10	Silicone	0.029	
III-12A[c]	100	GL	8	287	0.075"	35	10	Tissue	S/E	41
						35	10	Silicone	S/E	
						100	6.2	Tissue	0.018	
III-12B[c]	125	GL	8	287	0.075"	35	10	Tissue	S/E	44
						35	10	Silicone	S/E	
						100	6.2	Tissue	0.011	
II-64A	150	GL	-	255	0.035"	35	10	Tissue	S/E	48
						35	10	Silicone	S/E	
						100	6.2	Tissue	0.051	

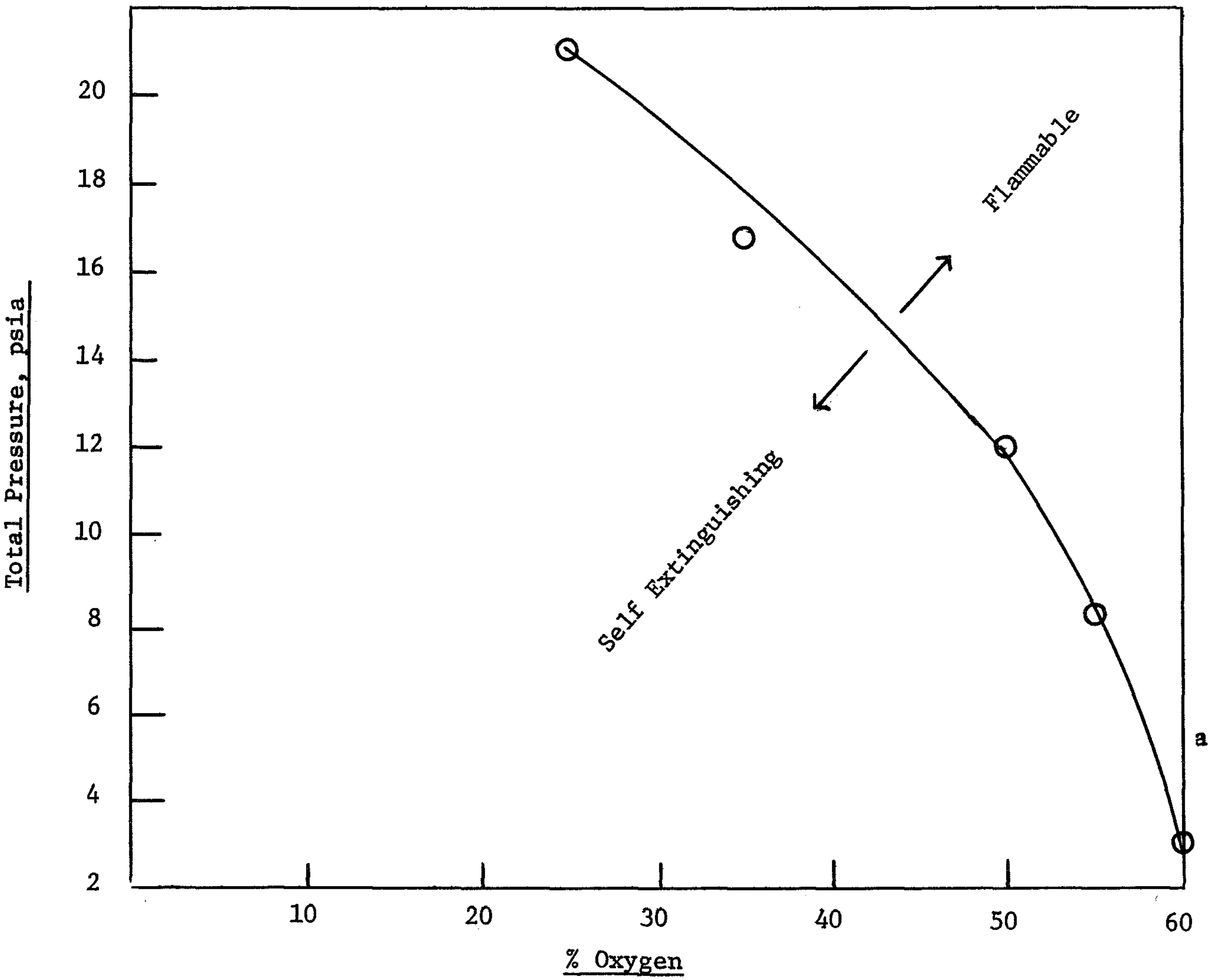
a. GL = Great Lakes Chemical, washed; MC = Michigan Chemical (recrystallized)

b. Vacuum dried gum compound. Oven cure: forced-draft oven, 4 hrs./400°F

c. Oven cured 1 hr. instead of 4

Figure 28

FLAME-RESISTANT SILICONE ELASTOMER^a - FLAMMABILITY (NASA TEST RESULTS)



a. Final Sample No. III-70-71

resistant silicone rubber becomes flammable. Thus, at high pressures above atmospheric pressure, this silicone rubber will burn in atmospheres containing as little as 25% oxygen, whereas at low pressures below 6 psia, this flame-resistant elastomer will be self extinguishing in atmospheres containing as much as 55-60% oxygen.

Low-Temperature Properties. -- Low-temperature properties of the flame-resistant elastomer were tested according to ASTM-D1043-61T, which is a Clash and Berg flexular test. Because of the limitations of our instrument, low-temperature measurements were made at temperatures no lower than -80°C or -112°F. The results are plotted in Figure 29. Samples of different thicknesses were taken in order to make comparisons between different formulations on one graph. Viton A loses all of its elastomeric properties at temperatures as low as -112°F. On the other hand, all of the silicone rubber formulations maintain elastic properties in this region. The final sample had the best low-temperature flexibility, as measured at room temperature and at -112°F. Note that with the final sample, the deflection in the curve at the point where elasticity changes rapidly occurs at the lowest temperature of any of the silicone rubbers in this series. Adding 8 parts of Cab-O-Sil drastically reduces the flexibility of the elastomer and, interestingly, this formulation still has better low-temperature properties than the silicone rubber containing no decabromodiphenyl.

Another comparison of these formulations is shown in Figure 30. In this figure, all of the formulations can be compared readily in spite of the fact that measurements were made with samples of varying thicknesses, because the calculation of the apparent modulus of rigidity includes a value for the thickness of the sample. A sample calculation of these apparent modulus values is shown in the Appendix. A comparison of the two best formulations for the flame-resistant silicone rubber shows that the elastomer containing decabromodiphenyl alone, namely the final sample, loses only 15% of its elasticity as it is cooled from room temperature to -115°F. The sample containing both decabromodiphenyl and Cab-O-Sil loses approximately 120% of its elasticity during the same cooling operation.

Permanent-Set Properties. -- This effect of small amounts of Cab-O-Sil also shows up in its effect on the general resiliency of the elastomer and the permanent-set properties. To give some indication of resiliency, the test for permanent-set was modified. Normally, these measurements are made by elongating the elastomer specimen 200%, where it is held for 10 minutes in the elongated state. The specimens are then allowed to recover and the extent of elongation is measured 10 minutes later. We have modified this permanent-set measurement by taking readings of the elongation 30 seconds, 1 minute, 3 minutes and 6 minutes after the elastomer sample was allowed to recover.

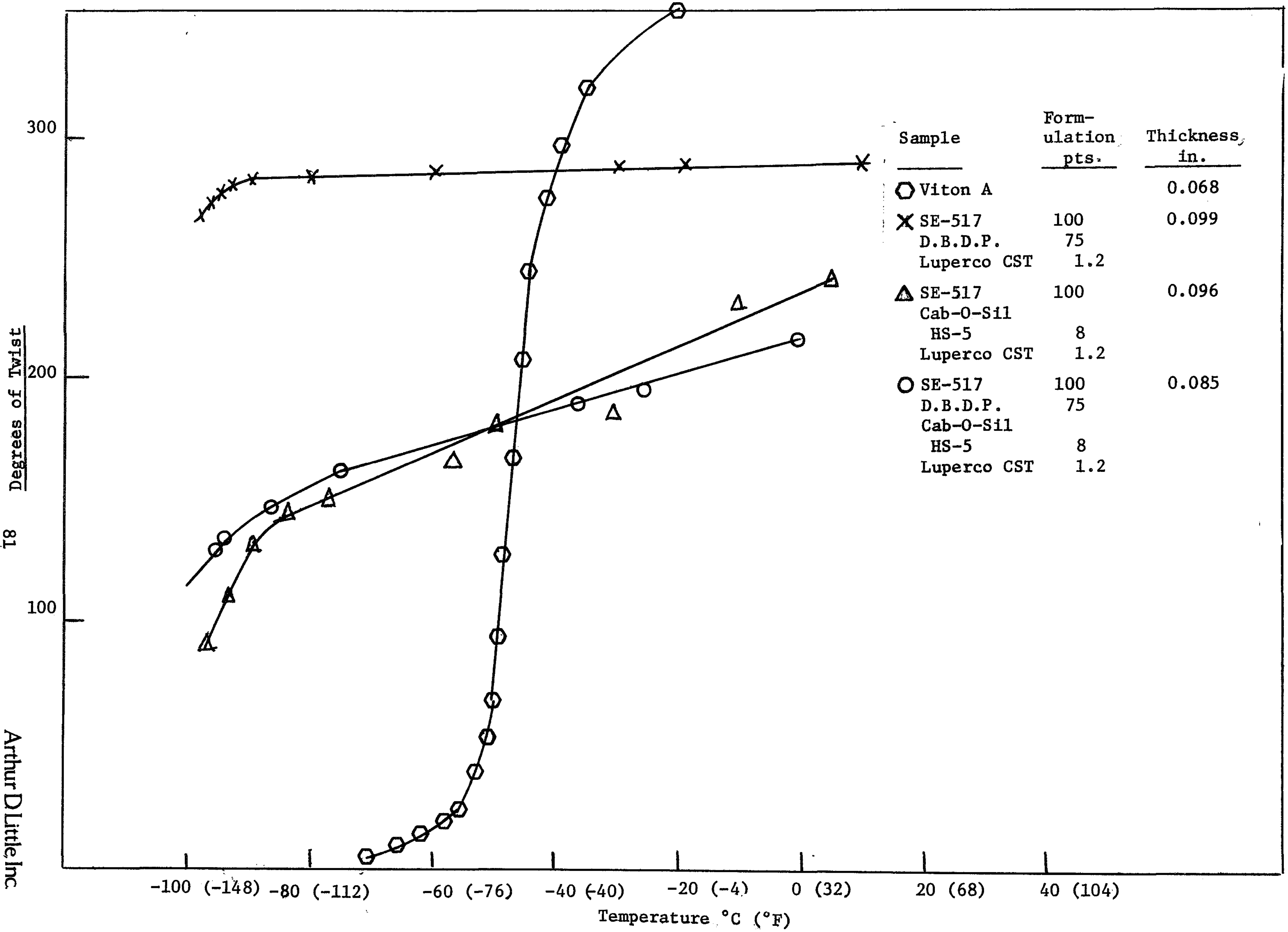
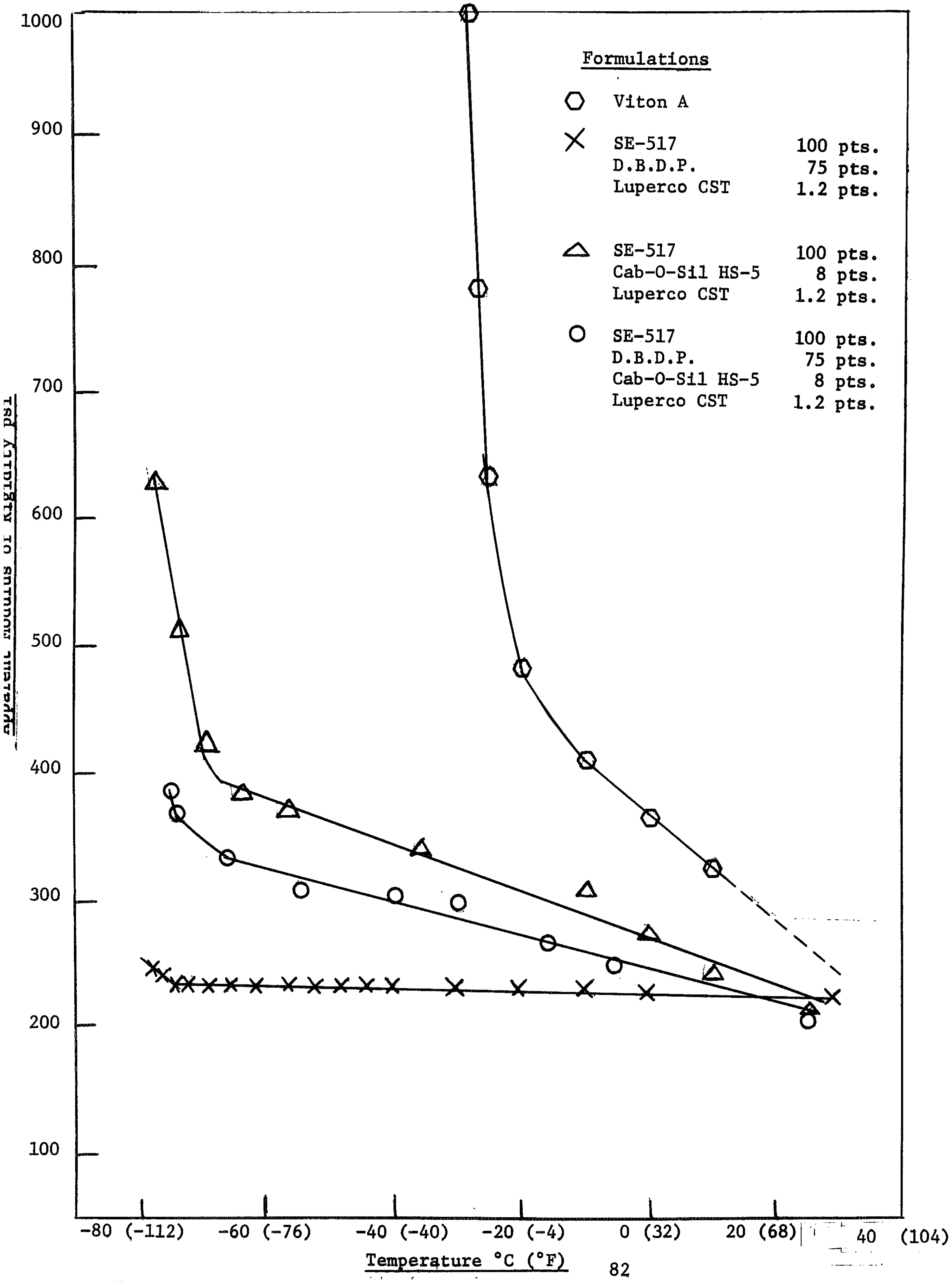

300
200
100
Degrees of Twist
-100 (-148)
-80 (-112)
-60 (-76)
-40 (-40)
-20 (-4)
0 (32)
20 (68)
40 (104)
Temperature °C (°F)
Sample
Formulation pts.
Thickness in.
⬡ Viton A 0.068
✕ SE-517 100 0.099
D.B.D.P. 75
Luperco CST 1.2
△ SE-517 100 0.096
Cab-O-Sil HS-5 8
Luperco CST 1.2
○ SE-517 100 0.085
D.B.D.P. 75
Cab-O-Sil HS-5 8
Luperco CST 1.2

Figure 30

APPARENT MODULUS OF RIGIDITY VS. TEMPERATURE



As shown in Table XXIX, samples containing as little as 3 parts of Cab-O-Sil have a permanent set of 8.4-8.2%, whereas cured SE-517 gum has a permanent set of 4%, and the final NASA sample containing 75 parts of decabromodiphenyl has a permanent set of 5%. As the table shows, according to the modified test the final NASA sample has resiliance properties almost as good as the cured SE-517 itself. Adding the small amount of Cab-O-Sil to the formulation greatly affects the resiliance. The values of elongation measured after 30 seconds and 1 minute show dramatically the beneficial effect of leaving the silica out of the formulation.

Aging Characteristics. -- Early in the program, we studied the effect of aging the flame-resistant silicone elastomer on physical properties and in this particular test we used a formulation containing 100 parts of decabromodiphenyl. As Table XXX illustrates, samples of this formulation aged for 7 days in a forced-draft oven at 150°C maintained their physical properties rather well.

Volatility Characteristics. -- Because the flame-resistant elastomer has to have the capability of withstanding repeated exposure to hard vacuum (10^{-7} torr), a sample of the formulated silicone rubber was subjected to a screening test, in which it was exposed to this vacuum for 72 hours. The formulation used in this test was the following: 100 parts SE-517, 75 parts decabromodiphenyl (Great Lakes - washed), 8 parts HS-5 silica, and 1.2 parts Luperco CST. After 72 hours this sample, which had been previously post-cured at 400°F in a vacuum oven for 4 hours, lost only 0.06% of its weight. In comparison, a sample of the pure SE-517 gum vacuum cured under the same conditions lost 0.44%.

PROPOSED COST OF THE FLAME-RESISTANT SILICONE RUBBER

Because decabromodiphenyl is still an experimental product, we have been unable to obtain a firm price quotation from Michigan Chemical. They have informed us that they now have a process that has been completely worked out in the laboratory, and this process is being readied for pilot-plant operation. Michigan Chemical has every intention to produce decabromodiphenyl as a commercial product, and it should become available in reasonable quantities in the very near future. At that time, a firm price quotation will also be available. Michigan Chemical has estimated the price of this bromo derivative in the range of $2 per pound. In any case, it will invariably be cheaper than the base gum stock, SE-517.

TABLE XXIX

DECABROMODIPHENYL[a] SYSTEMS - PERMANENT SET PROPERTIES

Sample No.	Pts./100 Pts. SE-517		Tensile	% Elongation	% Permanent Set Measured At				
	D.B.D.P.	Cab-O-Sil	psi		30 sec.	1 min.	3 min.	6 min.	10 min.
III-47B[b]	--	--	1227	919	4.0	4.0	4.0	4.0	4.0
III-70	75	--	705	500	6.2	6.2	6.2	5.0	5.0
III-65	75	3	735	500	12.6	10.4	8.4	8.4	8.4
III-66	75	5	810	475	12.3	10.2	8.2	8.2	8.2

a. D.B.D.P. - Michigan Chemical, recrystallized. SE-517 vacuum dried 400°F/ <1 torr for 4 hrs. Formulations molded with 1.2 pts. Luperco CST at 265°F/ 10 min. and oven cured at 400°F for 4 hrs.

b. 1 pt. Luperco CST

TABLE XXX

EFFECT OF AGING THE FLAME-RESISTANT SILICONE COMPOUND[a]
(7 Days, 150°C)

	Physical Properties		Oxygen Index	
	Tensile, psi	% Elongation	Top	Bottom
Before	446	825	46	39
After	432	575	46	39

a. Formulation:	GE SE 517 Silicone Rubber Compound	100 pts.
(Ref. II-64B)	Decabromodiphenyl (Great Lakes Chem.)	100 pts.
	Luperco CST	2 pt.

Molded at 260°F/10 min.

Oven cured at 400°F/ <1 torr - 4 hrs.

Using the $2.00 figure, we estimate the cost of the flame-resistant silicone rubber at $2.49 per pound; on a pound-volume basis it is $4.73. These computations are shown below.

Ingredient	Parts By Weight	Ingredient Cost/lb	Total Cost	Cost/ Pound	Specific Gravity	Pound Volume Cost
SE-517	100	$3.63	363.00	518.5		
D.B.D.P.	75	2.00	150.00	176.2	1.61	1.61 X $2.94 = $4.73
Luperco CST	1.2	4.55	5.46			
	176.2		518.46	$2.94		

Cost per pound does not tell the complete story about a silicone rubber. The pound volume cost is a more meaningful figure and, as shown above, it is determined by multiplying the cost per pound of a rubber by its specific gravity. This figure gives the compounder a truer picture of the cost per unit of rubber products which he can make from a given amount of material.

CONCLUSION

We have found that the flame retardant of choice for silicone rubber compounds is decabromodiphenyl. Decabromodiphenyl is preferred, because it is an aromatic bromide and is free of any hydrogen atoms. Therefore, this additive does not evolve HBr during the high-temperature curing cycle, and yet it is a very effective flame retardant when samples of the rubber are burned in oxygen rich atmospheres.

In this application the decabromodiphenyl must be extremely pure. Purity, as characterized by the melting point of the derivative, can be measured easily by DTA. For the optimum physical strength of the rubber, the bromo derivative should be used in a finely divided state: the minimum particle size should be equal to or less than 3 microns; and the preferred particle size equal to or less than 1 micron.

Silicone rubbers containing 75 parts of the bromo derivative are flame resistant and do not burn in an atmosphere containing 50% oxygen at 10 psia. Products containing this level of flame retardant have good physical properties, with tensile strengths between 700 and 800 psi and elongations of 500%. Furthermore, this product has good permanent-set properties and resilience. Drying the silicone gum stock at 400°F at <1 torr. prior to compounding it with additives yields a rubber that loses less than 0.1% of its weight at pressures as low as 10^{-7} torr.

We have found that the reinforced gum stocks containing silica incorporated by the rubber producers are those preferred for use in formulating the flame-resistant silicone rubbers. SE-517 stock from General Electric has proven to be a very acceptable product. Unfortunately, because of the limitations imposed by the inadequate supply of decabromodiphenyl, we were unable to fully explore the use of the competitive reinforced gum stocks.

With 75 parts of decabromodiphenyl, optimum cure of the rubber is obtained with 1.2 parts of the dichlorobenzoyl peroxide catalyst, Luperco CST (50% active), at a mold temperature of 260° - 265°F. A molding time of between 10 and 15 minutes is preferred under these conditions, and an oven cure of 4 hours in a forced-draft oven is adequate to produce a rubber with good physical properties.

If a rubber of higher tensile strength is required, a highly reinforcing silica, such as Cab-O-Sil HS-5, can be added in portions varying from 5 to 10 parts. The silica must be added to the mill after the decabromodiphenyl. This produces a rubber with a tensile strength approximately 100 psi higher than the rubber containing decabromodiphenyl alone. However, this additional silica greatly reduces the resilience of the cured rubber and causes poor permanent-set properties. The silica also reduces the low-temperature flexibility of the flame-resistant rubber. In terms of low-temperature flexibility, the rubber containing decabromodiphenyl alone is superior.

RECOMMENDATIONS

In future work, other reinforced gum stocks should be investigated more completely. Most of the work reported in this study was carried out with SE-517. Each of the rubber producers sells reinforced silicone gum stocks and General Electric makes several. These differ in base gum, concentration of filler, type of filler, and type of low molecular weight silicone. The limited availability of decabromodiphenyl during this study did not allow us to study a variety of stocks.

Because the time and mode of addition of silica and other fillers is important, the merits of combining decabromodiphenyl with the gum, either before or after adding the reinforcing silica in the presence of the rubber producers' proprietary silicone additives, should be examined. Furthermore, we have not explored the optimum concentration of silica in these flame-resistant silicone rubbers that should be introduced by the reinforced stocks, and this remains to be studied.

Knowing that the purity and particle size of the flame retardant is very significant, the purification and pulverization of decabromodiphenyl under different conditions should be explored more fully to achieve the optimum.

Much of the information gathered during this investigation should be useful in improving the flame resistance of other elastomers. In particular, our results may be helpful in preparing silicone-rubber potting compounds with improved flame resistance. A limited investigation of this area should soon reveal whether the approach developed in this program has any promise with potting compounds.

APPENDIX

CALCULATION OF APPARENT MODULUS OF RIGIDITY

$$G = \frac{917TL}{ab^3\mu\phi} = \frac{\text{sample constant}}{\phi}$$

where G = apparent modulus of rigidity

T = torque

L = length of specimen

a = width of specimen

b = thickness of specimen

ϕ = angle of deflection

μ = structural factor depending upon ratio of a/b

Sample Calculation

$T = 0.022$ lb-in., $L = 2.0$ in., $a = 0.25$ in., $b = 0.099$ in., $\mu = 2.52$

$$G = \frac{917 \times 0.022 \times 2}{0.25 \times [0.099]^3 \times 2.52\phi} = \frac{6.58 \times 10^4}{\phi}$$

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