228
4/13/81
T.S.

①

DR 2514

R-3479

UCRL-53105

Effect of vinyl and phenyl contents of silicone gum on the properties of the elastomers and cellular silicone cushions

W. E. Cady

E. S. Jessup

A. T. Buckner

MASTER

December 2, 1980

Lawrence
Livermore
National
Laboratory

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

UCRL-53105
Distribution Category UC-25

Effect of vinyl and phenyl contents of silicone gum on the properties of the elastomers and cellular silicone cushions

W. E. Cady

E. S. Jessup

A. T. Buckner

Manuscript date: December 2, 1980

LAWRENCE LIVERMORE LABORATORY
University of California • Livermore, California • 94550

Available from: National Technical Information Service • U.S. Department of Commerce
5285 Port Royal Road • Springfield, VA 22161 • $5.00 per copy • (Microfiche $3.50)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

GLOSSARY

Banbury intensive mixer	Mixer produced by Farrel-Birmingham Co., Inc., Ansonia-Derby, Conn.
Bendix	The Bendix Corporation, Kansas City Division, Kansas City, Mo.
Cab-O-Sil MS7	Specific grade of silicon dioxide made by the Cabot Corporation, Boston, Mass.
Cadox TS50	2.4-dichloro-benzoylperoxide as a 50% paste in dimethylsilicone oil produced by the Chemical Department, McKesson and Robbins, Inc., N.Y., N.Y.
DC200 fluid	A trimethylsilyl-terminated, 10 cSt, polydimethylsiloxane endcapping fluid produced by Dow Corning Corporation, Midland, Mich.
DMS	Dimethylsiloxane repeating unit in our silicone polymers.
DPS	Diphenylsiloxane repeating unit in our silicone polymers.
DSC	Differential scanning calorimetry.
EEMCO rubber mill	Two-roll mill produced by Erie Engine and Mfg. Co., Erie, Pa.
GPC	Gel-permeation chromatography.
HiSil 233	Specific grade silicon dioxide produced by Pittsburgh Plate Glass Industries, Inc., Chemical Division, Pittsburgh, Pa.
Instron test machine	Universal testing machine produced by the Instron Corp, Canton, Mass.
L97K	Equilibrium polymerized silicone gum produced by LLNL.
LLNL	Lawrence Livermore National Laboratory, Livermore, Calif.
Luperco 101XL	2,5-dimethyl 2,5-bis(t-butyl peroxyl) hexane at 50% concentration is a curing agent produced by Lucidol Division, Pennwalt Corp., Buffalo, N.Y.
M_{IV}	Molecular weight calculated from intrinsic viscosity measurements.
M_N	Number average molecular weight from GPC measurements based on polystyrene equivalents.
MVS	Methylvinylsiloxane repeating unit in our silicon polymers.
M_W	Weight-average molecular weight from GPC measurements based on polystyrene equivalents.
MWD	Ratio of M_W/M_N. A measure of molecular weight distribution.
OMCTS	Octamethyl-cylotetrasiloxane. The cyclic tetramer of DMS used in our synthesis.
OPCTS	Octaphenyl-cyclotetrasiloxane. The cyclic tetramer of DPS used in our synthesis.
pph	Parts per hundred.
Pasadena Hydraulic press	Molding press made by Pasadena Hydraulics, Inc., El Monte, Calif.
Rex O	Durometer Hardness Tester, Type O made by Rex Gage Co., Glenville, Ill.
Shore A	Durometer Hardness Tester, Type A made by Shore Instrument and Mfg. Co., Jamaica, N.Y.
T_g	Glass transition temperatures.
TJ104	Code for a specific lot of L97K gum and the products made from it.

TMTVCTS	Tetramethyl-tetravinyl-cyclotetrasiloxane. The cyclic tetramer of MVS used in our synthesis.
UCC	Union Carbide Corporation Silicone Rubber, N.Y., N.Y.
V/V_0	Ratio of swollen polymer volume to the original volume. An indication of the degree of crosslinking.
W97	Specific grade of silicone gum produced by UCC.
Y1587	Triethoxy-end-blocked dimethylsilicone fluid produced by UCC.
Y or L1668	Intermediate reinforced silicone gum produced by UCC (Y) or LLNL (L).
Y or L3219	Heat stripped Y or L 1668.
Y or L3223	Molding compound of Y or L3219, temporary filler and curing agent or cellular silicone cushion produced from the molding compound. Nominal density of 0.63 - 0.65 Mg/m^3.

Effect of vinyl and phenyl contents of silicone gum on the properties of the elastomers and cellular silicone cushions

ABSTRACT

LLNL has an active interest in the synthesis and evaluation of siloxane polymers with properties tailored to meet specific design needs. We have synthesized two series of random terpolymers of dimethyl-diphenyl-methylvinylsiloxane. In one series, the amount of methylvinylsiloxane was varied from 0 to 5 wt% and diphenylsiloxane was maintained at a nominal 12 wt%. In the other series, diphenylsiloxane was varied from 0 to 18 wt% and methylvinylsiloxane was maintained at a nominal 1 wt%. Molecular weights were maintained around 500 000 as best we could. These gums were filled with about 26 wt% silicon dioxide and then converted to the intermediate elastomers, temporarily filled molding compounds, and cellular silicone cushions. The intermediate elastomers and cellular silicones were cured with a vinyl specific catalyst and tested. Increasing vinyl content increases the stiffness of the cushion but decreases its resiliency. Compression set reaches a minimum of about 5% at a methylvinylsiloxane content of about 0.9 wt%. Phenyl content has only a slight effect on cushion properties. Compression set is a minimum in a range of 7 to 14 wt% diphenylsiloxane.

INTRODUCTION

Lawrence Livermore National Laboratory has utilized cellular silicones as support materials and space fillers for almost two decades. Until recently these materials were supplied solely by Union Carbide Corporation (UCC) to the weapons complex, which was the only major customer. Union Carbide discontinued the production of both the filled molding compounds that it supplied to the Bendix Corporation and the silicone gum (W97) that it processed into the molding compounds. Because of the disappearance of W97-type products and the lack of proven commercial replacements, LLNL found it necessary to develop a silicone technology suited to its needs. We have developed both the capability to synthesize gums and to compound gums to cellular materials.

W97 gum was a random-equilibration terpolymer composed of approximately 88 wt% dimethylsiloxane units (DMS), 12% diphenylsiloxane units (DPS), and 0.2 wt% methylvinylsiloxane units (MVS), and had an M_W of around 500 000. The DPS reduced elastomer crystallinity, and the MVS provided means of crosslinking with a peroxide catalyst. By a series of compounding and processing steps, W97 was reinforced with silicon dioxides (Y1668), aged and heat stripped to a base gum (Y3219), filled with temporary filler (urea), and catalyzed with dichloro-benzoylperoxide (Cadox TS50) to give a molding compound (e.g. Y3223).

The molding compound was compression die molded and cured, water washed to remove the urea, dried, and post cured to form the shaped part that was the product of interest to us.

A good cellular silicone cushion should have low compression set, a high degree of load retention with time, and compatibility with adjacent components. These properties seem to be improved with a switch from urea to ammonium chloride as the temporary filler and from Cadox TS50 to a vinyl-specific catalyst such as 2,5-dimethyl 2,5-bis(t-butylperoxyl) hexane (Luperco 101XL). W97 did not seem to be the best composition to utilize these changes, so we decided to systematically vary the phenyl and vinyl contents of our random polymers to see what effect this would have on the properties of the gum; intermediate rubbers, both cured and uncured; and the cellular silicones. In this report we describe the effect of silicone polymer structure on the properties of interest.

SYNTHESIS AND CHARACTERIZATION OF THE SILICONE GUMS

Two studies were undertaken: in one, the vinyl content was the independent variable; in the other, the phenyl content was varied. In both series the gums were synthesized in 400-g batches. The materials employed were octamethylcyclotetrasiloxane (OMCTS or DMS), octaphenylcyclotetrasiloxane (OPCTS or DPS), tetramethyltetravinyl-cyclotetrasiloxane (TMTVCTS or MVS), trimethylsilyl-terminated polydimethylsiloxane, and potassium silanolate. For the vinyl series, we held DPS constant at 12 wt% and varied MVS from 0 to 5 wt%. For the phenyl series, we held MVS at 1 wt% and varied DPS from 0 to 18 wt%. Gum molecular weights were controlled at ~500 000 by the addition of the DC200 endblocker. Gums were stabilized by killing the catalyst with the addition of 1 wt% of silicon dioxide. Identification and data for the various gums are listed in Table 1.

In run TJ104, the temperature exceeded the desired limit of 160°C to dissolve the OPCTS, so the experiment was repeated in TJ107. Except for this minor variation in technique, TJ104 and TJ107 should be duplicates. They are similar in composition but different in weight-average molecular weight and molecular-weight distribution.

In the series TJ120 to TJ124, molecular weight seemed to climb with higher phenyl; so the series TJ129-TJ131 was run to achieve lower molecular weights. Thus TJ120 and TJ129 should be duplicates and so should TJ123 and TJ130 except

TABLE 1. Properties of experimental L97K silicone gums.

	DPS, wt%		MVS, wt%		Molecular Weight (10^{-5})				T_g[c]
ID	Nominal	Analysis	Nominal	Analysis	M_{IV}[a]	M_W[b]	M_N[b]	MWD[b]	C
TJ101	12	—	0	—	5.58	5.62	2.53	2.22	-107
102	12	13.67	0.2	0.23	5.60	5.29	2.30	2.30	-107
103	12	12.94	0.5	0.47	4.48	4.84	2.17	2.23	-108
104[d]	12	13.14	1.0	0.92	4.93	6.24	2.53	2.47	-109
105	12	12.66	2.0	1.85	5.37	6.17	2.61	2.36	-108
106	12	14.14	5.0	4.91	5.52	6.53	2.55	2.56	-108
107[d]	12	13.62	1.0	0.93	5.69	5.06	2.37	2.14	-107
TJ120	0	0	1.0	0.94	4.35	3.97	1.97	2.03	-117
121	3	3.4	1.0	0.91	4.61	4.27	2.00	2.14	-116
122	6	6.3	1.0	0.92	5.20	5.22	2.29	2.28	-114
123	9	9.1	1.0	0.80	5.95	5.79	2.51	2.30	-111
124	18	17.1	1.0	0.90	5.88	6.58	2.61	2.52	-104
129	0	—	1.0	0.7[e]	5.00	4.59	1.91	2.38	-116
130	9	8.3	1.0	0.87	5.95	5.06	2.21	2.29	-112
131	15	13.1	1.0	0.80	6.44	6.01	2.58	2.33	-107

[a] By intrinsic viscosity measurements.

[b] By gel permeation chromatography.

[c] By differential scanning calorimetry.

[d] Part of the phenyl series also.

[e] Being rechecked.

perhaps for molecular weight. Based on composition by analysis, TJ131 should be included in the vinyl series at 0.8 wt% vinyl. Additional data on these gums may be found in Ref. 1.

In the vinyl series the analyzed phenyl content varies only from 13.1 to 14.1 wt% DPS, so the series is relatively constant in phenyl content. Molecular weight by GPC (M_W) varies from 4.84×10^5 to 6.53×10^5. Since M_W is not expected to be an important variable in this range, the series is acceptable in M_W range for evaluation of the effect of vinyl content on rubber and foam properties.

In the phenyl series, the analyzed vinyl contents vary from 0.7 to 0.9 wt% MVS. TJ129 with 0% DPS is suspect with 0.7 wt% MVS. Molecular weight by GPC (M_W) varies from 3.97×10^5 to 6.58×10^5, which is a large spread of 2.61×10^5. TJ120 with 0% DPS is lowest in M_W at 3.97×10^5. Both lots with no phenyl appear to be somewhat abnormal: TJ121 is low in M_W, and TJ129 is low in MVS. This series with DPS present is probably sufficiently constant in vinyl content and molecular weight to show any significant effects due to the phenyl content.

COMPOUNDING OF THE GUMS

The compounding sequence to convert L97K gums into L1668 reinforced gums was different for the two series, as will be described. The compounding sequence to convert L1668 reinforced gums into flat slabs of flexible silicone foam was the same for both series of gum. Also the composition of the first intermediate compound (L1668), as shown in Table 2, was the same for both. The purpose of the Cab-O-Sil MS7 silicon dioxide is to reinforce the gum. The purpose of the HiSil 233 silicon dioxide, presumably, is to provide thermal stability to the reinforced gum during the high temperature postcure. Y1587, an ethoxy-end-blocked dimethylsiloxane fluid with an average molecular weight of about 2000, acts as a processing aid and as an end blocker. It helps in the dispersion of the silicon dioxide in the gum and in the reaction of the silicon dioxide particulate with the silicone polymer chain to reinforce the gum.

Initial compounding of L97K to L1668 was done in our one-pound-size Banbury intensive mixer. For the vinyl series, the gum, HiSil 233, Y1587 fluid, and one-third of the MS7 were added to the Banbury and thoroughly mixed for about 2 min at a blade speed of 45 rpm. The other two-thirds of the MS7 was added and mixing resumed. For the phenyl series, the gum, one-half of the MS7, and one-half of the Y1587 were added to the Banbury and mixed for about 2 min at 40 rpm. Then the HiSil 233, the other half of the MS7 and the remaining Y1587 were added and mixing resumed. For both series, the compound was finally mixed for 2 min at full ram pressure. The total mixing time was nominally 10 min, but it varies from 8 to 14 min. The temperature of the mixes varied between 43 and 63°C.

TABLE 2. Composition of typical L1668 compounds.

Material	pph of gum by wt	wt%	Batch wt, g		
L97K gum	100	67.6	307.0	or	220
SiO_2, grade MS7	32	21.6	98.0		70
SiO_2, grade HiSil 233	6	4.0	18.2		13
Processing aid Y1587	10	6.8	30.9		22

The compound from the Banbury was further mixed on our EEMCO 2-roll rubber mill. This mill has 15-cm-diam by 35-cm-long rolls; a roll speed ratio of 1.4/1, and a fast rear-roll speed of 7.6 m/min. The rolls were heated to about 60°C by hot water. Mixing time for the vinyl series was 8 min and for the phenyl series it was 5 min. The purpose of the rubber-mill mixing was to achieve final blending of the compound and to form the compound into a sheet slightly thicker than 6 mm. The sheets were allowed to age at ambient conditions for a minimum of 28 days. A 6.5 cm^2 disk of L1668 was checked for weight loss as a function of aging time. Hardness was also checked with age. In many cases, chloroform extractables and swell ratio in chlorobenzene were measured after 1 day of aging and after about 1 month of aging.

We heat stripped the sheets of bin-aged L1668 to convert them to L3219. The purpose of the heat-stripping operation is to complete the interaction of silicone polymer with silicon dioxide particulate, to drive off residual Y1587, and to remove any light

TABLE 3. Compositions of L3223 molding compounds.

ID	MVS,[a] nominal wt%	pph L3219 by wt L3219	pph L3219 by wt 101XL	pph L3219 by wt NH_4Cl	wt% L3219	wt% 101XL	wt% NH_4Cl
TJ102	0.2	100	0.5	106	48.43	0.24	51.33
103	0.5	100	1.25	107	48.02	0.60	51.38
104	1.0	100	2.5	108	47.51	1.19	51.31
107	1.0	100	2.5	108	47.51	1.19	51.31
105	2.0	100	5.0	111	46.30	2.31	51.39
TJ120–124 and 129–131	1.0	100	2.5	108	47.51	1.19	51.31

[a] Gum analysis.

ends such as traces of solvent, unreacted cyclic tetrameter, and low-molecular-weight polymerization products. For both series stripping was done in an air-circulating oven at 171 to 177°C for 18 h. Hardness of the sheet before and after stripping and weight loss on stripping were determined in many cases.

L3219s were converted into a molding compound by the addition of temporary filler and curing agent. The amount of filler added determines the final density of the cellular foam. We formulated our compounds to yield a density comparable to Y3223 (0.63-0.65 Mg/m^3). We filled them with ammonium chloride supplied to us by Bendix to meet the particle size requirements of 25 to 40 mesh size. We used the vinyl specific catalyst, Luperco 101XL, at the ratio of 0.5 part by weight per 100 parts by weight of L3219 for each nominal 0.2 wt% of MVS. For the vinyl series, both the amount of Luperco 101XL and the amount of ammonium chloride varied with the vinyl content; for the phenyl series, the composition was constant. These are listed in Table 3.

The Luperco 101XL was added to the L3219s by milling on the 2-roll mill for 5 min at 60°C. For both series the ammonium chloride was incorporated into the catalyzed L3219s by mixing in the Banbury at 40 rpm for 5 min at 60°C. For two additional minutes, the L3223s were rolled on the mill into sheets for molding. No tests were run on the uncured L3223 sheets.

L3223 molding compounds were converted into L3223 cellular silicones by die molding 20-cm by 20-cm by 0.25-cm sheets, washing, and post curing. The sheets were molded in a flat steel die in a Pasadena Hydraulics press at 20.7 MPa and 171°C for 10 min. The press-cured sheets were washed in about 90°C water in a washing machine programmed for the following cycles.

1. Soak for 30 min.
2. Seven cycles of 1-h agitation.
3. Two cycles of 2-h agitation.
4. One cycle of 5-h agitation.

Total wash time is about 20 h including filling and draining time.

The cushions were dried for at least 16 h at ambient and then oven dried at 149°C for 4 h. The dried cushions were post cured for 24 h at 251°C. The end product cellular-silicone cushions were tested for load-deflection properties, confined compression set, and their densities were measured.

EXPERIMENTAL RESULTS FOR THE VINYL SERIES

After L1668 was compounded from L97K, the two silicone dioxides, and the processing aid Y1587, it was allowed to sit for a period of time at ambient conditions. This bin aging presumably allows the silicone dioxides to interact with the silicone polymer to some steady-state condition. We have attempted to understand the bin-aging process by means of various measurements of uncured L1668

TABLE 4. Properties of uncured L1668s of the vinyl series.

		Hardness, Rex O Days aging						Weight loss, wt% Days aging					$CHCl_3$ extractables, wt% Days aging		V/V_0 Days aging	
ID	MVS,[a] wt%	0	1	7	21	28	35	1	7	21	28	35	1	35	1	35
TJ101	0	20	23	23	27	26	26	0.97	2.53	3.39	3.53	3.48	41.4	36.2	3.95	3.58
102	0.23	16	18	23	26	27	26	1.07	2.75	3.54	3.66	3.74	41.4	33.1	4.52	3.74
103	0.47	18	20	25	26	30	30	0.94	2.50	3.29	3.42	3.52	40.5	34.7	4.27	3.59
131	0.80	54	—	—	—	70[b]	—	—	—	—	—	5.5[b]	—	—	—	—
104	0.92	18	25	31	34	35	37	1.11	2.92	3.82	3.96	4.06	41.2	33.6	3.93	3.57
107	0.93	15	18	25	27	29	30	0.56	1.65	2.23	2.34	3.41	—	32.6	5.29	3.86
105	1.85	24	24	31	34	36	37	1.06	2.75	3.64	3.78	3.87	36.7[c]	35.3	3.98	3.47
106	4.91	18	23	27	30	31	31	1.09	2.85	3.67	3.81	3.90	38.5[c]	32.8	4.50	3.75

[a] Gum analysis.

[b] 29 days aging.

[c] 2 days aging.

as a function of time. These data are shown in Table 4. Small disks lose weight and harden under ambient conditions with time. It takes about 1 month for these values to stabilize. Both the quantity of chloroform extractables and the swell ratio in chlorobenzene decrease with time; this indicates some degree of bonding between the silicone dioxide and the gum.

The vinyl content seems to have no significant effect on the bin-aging process. It appears that TJ104 and TJ107 may not be alike, although the low weight loss of TJ107 is the only significant difference. Also TJ131 does not fit the pattern of the rest of the vinyl series as it should. At this point we do not know whether synthesis or compounding causes these differences. TJ104 and TJ107 have a known synthesis aberration, and TJ131 was mixed differently than the TJ101-107 series and also has a higher molecular weight.

L3219 is essentially a stabilized L1668 obtained by heat stripping the L1668. No data were collected on the uncured L3219s. The L3219s were catalyzed with Luperco 101XL at 0.5 part by weight for each nominal 0.2 wt% VMS as shown in Table 5. The catalyzed L3219s were molded into 15-cm by 15-cm × 0.2-cm slabs, which were press cured at 171°C for

TABLE 5. Properties of cured L3219 of the vinyl series.

			Hardness, Shore A					
ID	MVS,[a] wt%	101XL,[b] pph	After cure	Post cure	Loss on post cure, wt%	Density, Mg/m^3	V/V_0	$CHCl_3$ extractables, wt%
TJ101	0	0.5	0	0	3.3	1.18	7.813	—
102	0.23	0.5	48	51	2.7	1.184	3.397	2.35
103	0.47	1.25	57	61	2.8	1.188	2.664	1.74
131	0.80	2.5	68	72	—	1.206	2.301	1.59
104	0.92	2.5	68	72	3.2	1.194	2.295	1.28
107	0.93	2.5	70	74	3.0	1.203	2.214	1.18
105	1.85	5.0	76	80	3.1	1.201	1.967	0.93
106	4.91	12.5	87	89	3.6	1.237	1.617	—

[a] Gum analysis.

[b] Per hundred parts of L3219 on a weight basis.

15 min and post cured at 249°C for 16 h. All data except for hardness after cure were obtained on post-cured samples. Results are in Table 5.

The L3219 with no vinyl content was cured with 0.5 part of 101XL in order to compare with the 0.2% vinyl L3219 also cured with 0.5 part of 101XL. The zero hardness and high swell ratio of TJ101 compared to TJ102 indicate little or no crosslinking in the 0% vinyl L3219. This confirms that Luperco 101XL is vinyl specific, as advertised. TJ104 and TJ107 are similar except for swell ratio. TJ131 is similar to TJ104 in all respects except in chloroform extractables.

Weight loss on post-cure does not vary with vinyl content. Hardness and density increase with increasing vinyl content. Swell ratio and extractables decrease with increasing vinyl content.

The L3223 cellular silicones were tested to 40% deflection at room temperature for load-deflection properties on an Instron test machine with a cross-head spread of 1.25 mm/min. The 6.5 cm^2 disks for load deflections were weighed and measured and their densities calculated. Data are reported in Table 6; these are 3rd cycle data unless otherwise indicated. Samples TJ104 and TJ1107 are not alike, and TJ104 does not fit the pattern as shown in Fig. 1. TJ131 is like TJ107. This may imply that synthesis control is more important than compounding control or molecular weight. The load, unload, and unload-to-load ratio at any deflection increase as vinyl content increases. The load-unload hysteresis and the change in thickness from first to third cycle do not correlate with vinyl content. Density is higher than intended for L3223 and is somewhat erratic; TJ131 being the densest cushion.

Results of the confined compression-set test are summarized in Table 7. Samples TJ104, TJ107, and TJ131 are statistically alike in compression set. Compression set seems to reach a minimum value of about 5% at about 0.9 vinyl content. Ultimate recovery is very similar for all samples. For all but the 0.23% vinyl containing TJ102 recovery is about complete in 24 h.

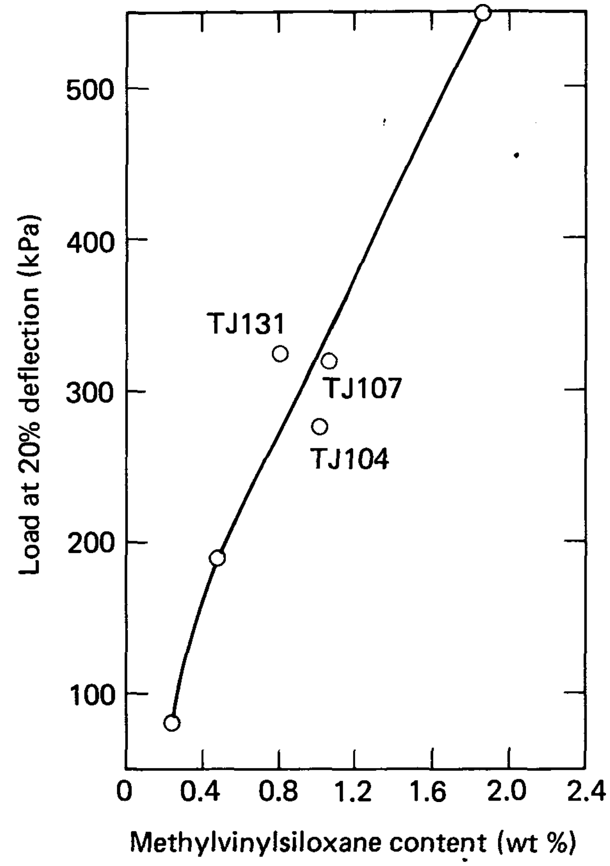

FIG. 1. Load at 20% deflection as a function of MVS content.

CONCLUSIONS FOR THE VINYL SERIES

Bin aging of L1668 at ambient conditions takes 3 to 4 weeks before a stable state is attained. There is bonding between the reinforcing silicon dioxide and the gum as indicated by the decrease in chloroform extractables and swell ratio of L1668. The vinyl content of the gum has no significant effect on the bin-aging process or on the final properties of the aged L1668. TJ131, made for the phenyl series, does not fit the vinyl series, and TJ104 and TJ107 are not close duplicates as they should be. It is not known if process variables or synthesis variables are the cause of these differences.

As expected, vinyl content is a significant variable in the properties of the cured L3219. As vinyl content and curing-agent content increase, the hardness and density of cured L3219 increase, and increased crosslinking causes the swell ratio and chloroform extractables to decrease. Luperco

TABLE 6. Load–deflection properties of L3223 cushions of the vinyl series.

		Load, kPa				
ID	MVS,[a] wt%	5% deflection	10%	20%	30%	40%
TJ102	0.23	27.9	48.1	81.7	138.3	368.3
103	0.47	60.8	108.7	188.0	313.8	791.6
131	0.80	100.7	180.2	326.9	599.4	—
104	0.92	Av 84.5	154.6	276.0	476.0	1298.2
		S 4.43	5.30	8.6	17.7	89.7
107	0.93	Av 97.7	177.8	320.4	567.2	1540.3
		S 4.88	6.89	11.9	30.3	64.8
105	1.85	145.0	281.1	550.1	1173.5	—

	Density, Mg/m^3	Unload, kPa		Unload/load		Load–unload hysteresis	Δt,[b] mm
		10%	30%	10%	30%		
TJ102	0.668	30.4	90.8	0.634	0.657	177.9	0.082
103	0.675	80.1	234.9	0.737	0.749	280.5	0.069
131	0.697	124.5	453.3	0.701	0.773	452.4	0.090
104	0.675	117.3	369.7	0.759	0.777	345.2	0.068
107	0.685	133.9	439.4	0.753	0.775	357.4	0.085
105	0.682	219.3	1062.0	0.780	0.901	311.2	0.104

[a] Gum analysis.

[b] Difference in starting thickness from 1st to 3rd cycle.

TABLE 7. Compression–set properties of L3223 cushions of the vinyl series.

				Recovery of original t, %				
ID	MVS,[a] wt%	Density, Mg/m^3	% set[b]	2 min	1 h	24 h	7 days	28 days
TJ102	0.23	0.6548	Av 10.80	93.30	96.23	96.73	97.31	97.99
			S 0.57					
103	0.47	0.6666	Av 6.26	97.09	97.81	98.34	98.34	98.58
			S 0.67					
131	0.80	0.6784	Av 5.68	97.59	98.01	98.22	97.98	98.08
			S 1.18					
104	0.92	0.6719	Av 4.51	97.91	98.42	98.76	98.50	98.83
			S 1.77					
107	0.93	0.6760	Av 5.31	97.68	98.14	98.51	98.34	98.58
			S 0.97					
105	1.85	0.6784	Av 6.39	97.31	97.76	98.27	98.20	98.20
			S 0.86					

[a] Gum analysis.

[b] Calculated after one hour recovery.

101XL is vinyl specific because there is little or no cure achieved with the vinyl free L3219. The discrepancies in TJ131, TJ104, and TJ107 data are still apparent but less pronounced in cured L3219.

Increasing vinyl content increases the stiffness of the L3223 cushion in both load and unload but also decreases its resiliency. Compression set reaches a minimum at about 0.9% MVS. TJ131 matches the load properties of the vinyl series but TJ104 does not. It may be that synthesis control is more important in cushion properties than is compounding control but that molecular weight is not a significant factor.

EXPERIMENTAL RESULTS FOR THE PHENYL SERIES

Unfortunately the phenyl series not only has an intentionally increasing phenyl content but also a concurrently increasing molecular weight. This complicates the interpretation of the results.

L1668s for the phenyl series were compounded and bin aged in the same manner as L1668s for the vinyl series, but less data were collected (see Table 8). TJ104 and TJ107 do not fit the phenyl series; probably because of differences in compounding procedures. Weight loss on bin aging decreases as phenyl content and molecular weight increases. Hardness is independent of both variables.

The L1668s were heat stripped to L3219s by the standard technique. Data for uncured L3219s are in Table 9. Hardness and weight loss on stripping are constant. All of the L3219s were catalyzed with 2.5 parts of Luperco 101XL per 100 parts of L3219 by weight and press-cured at 171°C for 15 min to a 15-cm by 15-cm × 0.2-cm slab. The slabs were post cured at 249°C for 16 h. All data except hardness after cure were obtained in post-cured samples. These data are listed in Table 10. Density and swell ratio of cured L3219 are plotted in Fig. 2 as a function of DPS content and in Fig. 3 on a function of molecular weight as measured by intrinsic viscosity. Hardness, wt% solubles, chloroform extractables, ultimate elongation, and modulus at 50% elongation are relatively constant. Ultimate tensile strength increases with increasing DPS content until 6% DPS and then remains constant. Both density and swell ratio increase with increasing phenyl content and with increasing molecular weight. The results are difficult to interpret. It is probable that molecular weight has a greater effect on density than phenyl content. The swell ratio correlates better with phenyl content, but the significance of this is not obvious. Again, TJ104 and TJ107 do not fit the phenyl series. Also, TJ129 is suspect perhaps because of its low vinyl content.

The L3223 molding compounds were all the same formulation; all were processed to cellular silicone in a like manner and tested in the same way. The results of the load-deflection testing are shown

TABLE 8. Properties of uncured L1668s of the phenyl series.

ID	DPS,[a] wt%	M_{IV} X10^{-5}	Hardness after aging, Rex O		Weight loss after aging 28–29 days, wt%
			0 days	28–29 days	
TJ120	0	4.35	50	65	7.2
129	0	5.00	56	68	7.2
121	3.4	4.61	53	67	7.5
122	6.3	5.20	52	67	6.7
130	8.3	5.95	56	69	6.5
123	9.1	5.95	50	65	6.3
104	13.1	4.93	18	35	4.0
131	13.1	6.44	54	70	5.5
107	13.6	5.69	15	29	2.3
124	17.1	5.88	56	68	5.1

[a] Gum analysis.

TABLE 9. Properties of uncured L3219s of the phenyl series.

ID	DPS,[a] wt%	M_{IV}[a] $X10^{-5}$	Hardness after stripping, Rex O	Weight loss on stripping, wt%
TJ120	0	4.35	71	9.2
129	0	5.00	74	9.7
121	3.4	4.61	72	10.3
122	6.3	5.20	72	9.5
130	8.3	5.95	74	9.7
123	9.1	5.95	72	9.8
104	13.1	4.93	—	—
131	13.1	6.44	74	9.9
107	13.6	5.69	—	—
124	17.1	5.88	74	10.1

[a] Gum analysis.

in Table 11a and b; these are third-cycle data unless otherwise noted. TJ120 and TJ129 are alike statistically. TJ104 is not like TJ107 or TJ131, but TJ107 and TJ131 are alike in load-deflection. Apparently the difference in compounding procedure for TJ107 and TJ131 had no significant effect on the L3223 cushion, but the synthesis variation in TJ104 and TJ107 did effect the cushion properties. Molecular weight does not seem to be a significant variable. There is a slight softening of the cushion as the phenyl content increases but the effect is not significant.

Results of the confined compression set test are shown in Table 12. It appears that compression set reaches a minimum of about 5% in the phenyl range of 7 to 14%, but that compression set is not very dependent on phenyl content or molecular weight. In most cases essentially maximum recovery is achieved in 24 h.

TABLE 10. Properties of cured L3219s of the phenyl series.

ID	DPS,[a] wt%	M_{IV}[a] $X10^{-5}$	Hardness, Shore A		Density, Mg/m^3	Chlorobenzene soak		$CHCl_3$ extractables, wt%	Ultimate tensile strength, kPa	Ultimate elongation, %	Modulus at 50% elongation
			Cured	Post cured		V/V_0	wt% sol.				
TJ120	0	4.35	69	74	1.180	1.990	1.6	3.29	3423	60	3003
129	0	5.00	70	75	1.185	1.929	1.5	1.25	3010	50	3010
121	3.4	4.61	68	72	1.182	2.074	1.5	1.21	3647	60	2920
122	6.3	5.20	68	73	1.190	2.127	1.5	1.40	4040	60	3116
130	8.3	5.95	70	74	1.196	2.185	1.6	1.51	4051	65	3230
123	9.1	5.95	69	73	1.196	2.194	1.6	1.27	2920	50	2920
104	13.1	4.93	68	72	1.194	2.295	—	—	—	—	—
131	13.1	6.44	68	72	1.206	2.301	1.7	1.59	3992	65	3134
107	13.6	5.69	70	74	1.203	2.214	—	—	—	—	—
124	17.1	5.88	70	74	1.216	2.304	1.6	1.49	4289	65	3320

[a] Gum analysis.

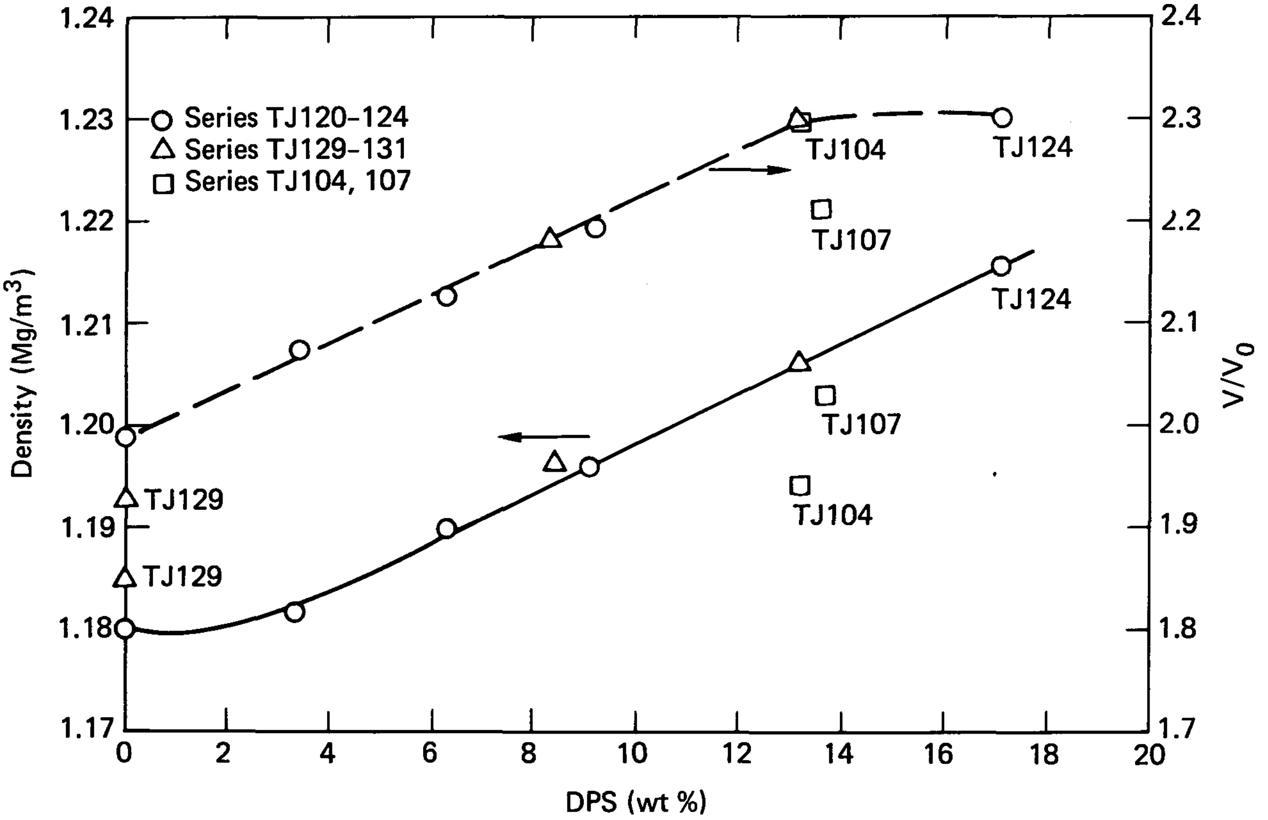

FIG. 2. Correlation of density and swell ratio of cured L3219 with phenyl content of the gum.

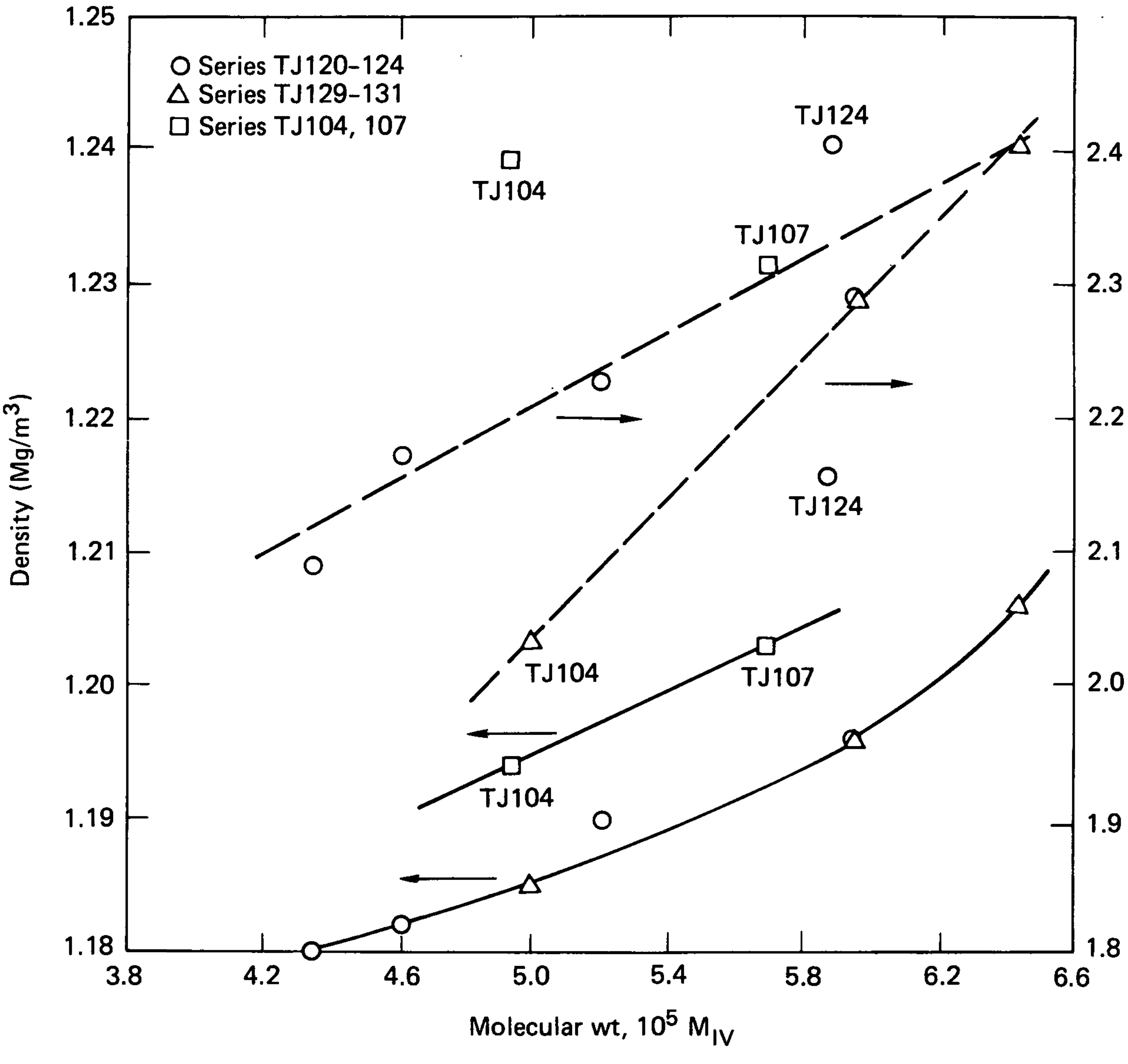

FIG. 3. Correlation of density and swell ratio of cured L3219 with molecular weight of the gum.

TABLE 11a. Load-deflection properties of L3223 cushions of the phenyl series.

ID	DPS,[a] wt%	M_{IV}[a] X10^{-5}	Load, kPa 5% deflection	10%	20%	30%	40%
TJ120	0	4.35	Av 98.9	177.1	317.1	570.2	—
			S 1.9	2.6	4.8	10.8	—
129	0	5.00	Av 96.1	173.8	310.9	550.7	—
			S 4.0	5.2	8.3	16.6	—
121	3.4	4.61	90.4	165.3	298.0	533.5	—
122	6.3	5.20	92.7	165.2	291.4	505.2	1400.6
130	8.3	5.95	Av 92.3	165.0	293.9	517.8	—
			S 0.5	0.9	2.5	7.4	—
123	9.1	5.95	Av 95.7	170.3	302.5	534.0	—
			S 3.0	4.5	7.7	16.9	—
104	13.1	4.93	Av 84.5	154.6	276.0	476.0	1298.2
			S 4.4	5.3	8.6	17.7	89.7
131	13.1	6.44	Av 100.7	180.2	326.9	599.4	—
			S 5.7	8.1	15.2	39.8	—
107	13.6	5.69	Av 97.7	177.8	320.4	567.2	1540.3
			S 4.9	6.9	11.9	30.3	64.8
124	17.1	5.88	90.1	161.1	285.4	493.3	1447.5

[a]Gum analysis.

TABLE 11b. Load-deflection properties of L3223 cushions of the phenyl series.

ID	DPS,[a] wt%	M_{IV}[a] X10^{-5}	Density, Mg/m^3	Unload, kPa 10%	Unload, kPa 30%	Unload/load 10%	Unload/load 30%	Load-unload hysteresis	Δt,[b] mm
TJ120	0	4.35	0.688	126.2	437.9	0.713	0.768	420.8	0.077
129	0	5.00	0.6702	123.6	424.6	0.711	0.771	412.8	0.076
121	3.4	4.61	0.6795	122.6	421.8	0.741	0.791	363.9	0.072
122	6.3	5.20	0.683	119.9	386.1	0.726	0.765	415.3	0.074
130	8.3	5.95	0.6782	114.9	387.1	0.697	0.748	460.3	0.081
123	9.1	5.95	0.6750	123.2	409.2	0.723	0.766	412.0	0.069
104	13.1	4.93	0.675	117.3	369.7	0.759	0.777	345.2	0.068
131	13.1	6.44	0.6784	124.5	453.3	0.701	0.773	452.4	0.090
107	13.6	5.69	0.685	133.9	439.4	0.753	0.775	357.4	0.085
124	17.1	5.88	0.6758	115.2	372.4	0.716	0.755	444.6	0.078

[a]Gum analysis.

[b]Difference in starting thickness from 1st to 3rd cycle.

TABLE 12. Compression set properties of L3223 cushions of the phenyl series.

ID	DPS,[a] wt%	M_{IV}^{a} X10^{-5}	Density, Mg/m^3	% set[b]	Recovery of orginal t, %				
					2 min	1 h	24 h	7 days	28 days
TJ120	0	4.35	—	— — — —	—	—	—	—	—
129	0	5.00	0.6702	Av 6.73 S 0.80	96.93	97.65	97.64	97.64	97.96
121	3.4	4.61	0.6795	Av 7.85 S 1.78	96.55	97.25	97.41	97.41	97.64
122	6.3	5.20	—	— — — —	—	—	—	—	—
130	8.3	5.95	0.6782	Av 4.82 S 0.68	97.84	98.37	98.57	98.19	98.31
123	9.1	5.95	0.6750	Av 6.37 S 0.83	97.17	97.77	97.65	97.71	97.84
104	13.1	4.93	0.6719	Av 4.51 S 1.77	97.91	98.42	98.76	98.50	98.83
131	13.1	6.44	0.6784	Av 5.68 S 1.10	97.59	98.01	98.22	97.98	98.08
107	13.6	5.69	0.6760	Av 5.31 S 0.97	97.68	98.14	98.51	98.34	98.58
124	17.1	5.88	0.6758	Av 7.27 S 1.58	96.98	97.45	97.48	97.89	98.11

[a] *Gum analysis.*

[b] Calculated after 1 h recovery.

CONCLUSIONS FOR THE PHENYL SERIES

Variation in phenyl content of L97K gum has little effect on the properties of L1668 after bin aging. There is a decrease in weight loss on bin aging as phenyl content and molecular weight are increased. This reduction in weight loss may be due to either molecular weight or to phenyl content.

Also phenyl content and molecular weight have no effect on the properties of the uncured L3219. For cured L3219, hardness, wt% solubles, chloroform extractables, ultimate elongation, and modulus at 50% elongation are constant. Ultimate tensile strength increases to 6% DPS and then is constant and doesn't correlate at all with molecular weight. Density and swell rates seem to correlate with both phenyl content and molecular weight, so no firm conclusions can be drawn.

There is no significant change in the load-deflection properties of L3223 with either phenyl content or molecular weight. There appears to be a minimum of about 5% compression set in the phenyl range of 7 to 14%. Compression set is not significantly dependent on either phenyl content or molecular weight.

RECOMMENDATIONS

In order to improve and and control the properties of cellular silicone cushions made from a random-equilibration terpolymer and in order to effectively use a vinyl-specific curing agent along with ammonium chloride as the temporary filler, we should alter the composition of the methyl-phenyl-vinylsiloxane terpolymer to contain 9 wt% diphenyl siloxane and 0.7 wt% methylvinylsiloxane. Molecular weight should remain in the 500 000 to 600 000 range.

SUMMARY

We have separately evaluated the effects of varying vinyl and phenyl content of random-equilibration silicone gums on the properties of the intermediate compounds (L1668, uncured and L3219, both uncured and cured) and of the cellular-silicone cushions (L3223). Vinyl content has a great effect on the cushion properties. Increasing vinyl content increases the stiffness of the cushion but decreases its resiliency. Compression set reaches a minimum at about 0.9% MVS. Phenyl content has a very slight effect on cushion properties. Compression set is a minimum in the range 7 to 14% DPS. From this study we have inferred an improved silicone gum containing 9% DPS and 0.7% MVS.

REFERENCES

1. H. G. Hammon, D. M. Hoffman, E. S. Jessup, J. R. Kolb, and M. O. Riley, *Structure-Property Relationships of Linear Methyl-Phenyl-Vinyl Siloxane Terpolymer*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-84303 (1980).

HLL/ml

Technical Information Department · Lawrence Livermore National Laboratory
University of California · Livermore, California 94550

First Class Mail