ADHESIVES, FILLERS & POTTING COMPOUNDS

A program for the development of and improvements in HE septa. The principal present aim is minimization of set and cure times toward maximum production capacity with a minimum of construction for new weapons.

Second Progress Report; December 1, 1967 to April 1, 1968

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ABSTRACT

Progress in the development program whose immediate purpose is to reduce set time of a silicone compound is described. Data are presented showing that a formulation of a current RTV silicone rubber with dibutyltin diacetate has a profitably lower set time than the same rubber in the present formulation which uses dibutyltin dilaurate, without increase in probability of either reversion or penalty to other weapons components. Time to set sufficiently to allow the next assembly step is 2 to 4 hours, compared to the 16 to 24 hours presently allowed or the 8 to 12 hours minimum attainable with the present formulation. The reduction is of the magnitude set as a goal, the attainment of which would increase production capacity enough to reduce the amount of new construction planned to accommodate weapons assembly programs.
INTRODUCTION

The overall development program is described in the First Progress Report, to December 1, 1967. That report also describes the initial work.

To reiterate the primary aim of the program, it is to yield better adhesives and filling or potting—"solid-pack"—compounds and processes for the assembly of weapons components, especially HE systems; these materials and operations are of special importance to the assembly plants in that they can affect production methods, equipment and capacities. "Better" at the present time primarily means faster set of the room temperature vulcanizing (RTV) silicone rubber solid-pack applications to two specific HE systems. The reason is that significant reductions in the set time can pay immediate dividends by obviating some of the construction planned to augment plant capacities to the level required for the programs in production during the next few years. The present capacity is in large measure circumscribed by adhesives and solid-pack set times, especially in "Gravel Gerties" but also in standard assembly areas, as described in USAEC Memo, December 20, 1967, H. Jack Blackwell to John C. Drummond.

The approach to solutions was divided into three major categories:

1. The use of present materials but with improved application processes.
2. Bringing into use extant materials not presently applied to weapons, using present processes or those developed in 1 above.
3. New materials and/or processes.
The work to the beginning of this period was in all three categories, with interesting possibilities in Categories 1 and 3. In particular, dibutyltin diacetate (DBTDA) indicated reduction in set times. This compound as a possible catalyst (to use the term for what should really be called a reactant loosely, as seems to have become common) for some RTV systems was selected as a result of explorations for new materials. In September, 1967, during an extensive tour (H. Lichte, most of it with F. Walker of LRL) Lichtenwalner at the G.E. Waterford, N.Y. plant suggested dimethyltin diacetate, among others; and Picatinny Arsenal suggested some possible tin, lead, zinc and iron compounds. Upon return, some of the materials suggested, plus DBTDA—which was chosen locally from standard chemical listings because it seemed to offer compositional and valency advantages—were ordered for screening experiments. G.E. later sent samples of two materials, one of them being DBTDA, to us and to LRL. The screening tests, described in the first report, quickly sorted out the inapplicable materials and indicated the hoped-for advantage in the DBTDA.
DISCUSSION

Dibutyltin Diacetate (DBTDA)

Catalyst Selection

A number of catalysts are known and have been studied in room temperature vulcanizing silicone rubber systems like the 93-009/93-029\(^1\) of present major interest. DBTDA apparently is now among those studied. As related in the Introduction, DBTDA was selected from available pure chemicals supplied as off-the-shelf items by major chemical suppliers.

The function of the DBTDA in a two-part silicone system (two-part meaning base resin plus cross-linking agent pre-formulated as one part with the catalyst added as the second part) is complicated and perhaps not fully understood; its apparent action is described in the Appendix. But one might reasonably estimate in advance that DBTDA would be more active than dibutyltin dilaurate (DBTDL) because of the origin acid and because the tin content is 34% in DBTDA compared to 18% in DBTDL; this may be compared to 28% in stannous octoate and 2% in 93-009 catalyst. These figures were verified by atomic absorption. One should note that the ratio of catalyst to base is not the same for all conventional formulations: to 100 parts by weight (pbw) one might use 4 pbw DBTDL, 4 pbw 93-009 catalyst, 0.5 pbw stannous octoate, and 0.5 pbw DBTDA.

\(^1\)"Silastics", Dow Corning, Midland, Michigan, dimethyl siloxane, etc. The catalyst sold with it is called 93-009 catalyst; it is approximately 30% dibutyltin dilaurate (DBTDL), 2% water. The usual present formulations are variations of 93-009/93-029, with 4 parts by weight DBTDL.
The recipe of 0.5 pbw DBTDA and 0.16 pbw water was selected from hardness versus time tests as giving a possible optimum formulation\(^2\), balancing cure time against possible deleterious effects of going too far with either catalyst or water. Varying the ratios of 93-009 to 93-029 for viscosity purpose, two formulations called "A" (75/25 93-009/93-029) and "B" (50/50) will be mentioned throughout this report. The DBTDA was kept low to minimize acetic acid formation, since in large quantities the acid could break the linear polymer "backbone", and to eliminate the secretion of a by-product which appears to be dibutyltin oxide at mold interfaces (See Fig. 1) when concentration of DBTDA was greater than 4 pbw.

The water content must also be low to minimize possibility of reversion of the cured system. Even at the low water level of 0.16 pbw reversion is possible under severe conditions, but very unlikely under the weapon storage and STS conditions. The water content of the standard 93-009 catalyst incidentally is 2% which in the normal formulation with it gives 0.08 pbw in the cured silicone system.

**Cure Variations**

Figs. 2 through 13 illustrate the effect of 0.5 to 5.0 pbw DBTDA, 0 to 0.32 pbw water, various ratios of 93-009 to 93-029 resin, and batch differences. These curves are plots of hardness (Shore A Durometer) versus time and thus indicate

\(^2\) Some variations, e.g., 0.5 pbw DBTDA and 0.08 pbw water, or 1.0 pbw DBTDA and 0.08 pbw water, may be the most stable configuration but with a set time penalty. See Appendix.
1 pbw DBTDA Catalyzed System
10 pbw DBTDA Catalyzed System

1 mm graduations

Fig. 1
100 pbw 50/50 93-009/93-029
cure time for the various formulations.

The time when cure has been accomplished of course may be selected at either an arbitrary level of hardness, or, better, at some meaningful level. The meaningful level of interest here is that at which movement or subsequent operations can be performed with little risk of displacement of assembly parts. For conservatism, we considered that to be Shore A 15 for some time; but LRL Weapons Engineering has stated that Shore A 10 is acceptable. In fact it can no doubt be lower, the minimum being at a level where the viscosity has increased rapidly, fluidity has disappeared and "rubberiness" has set in. For a measure of this, see "Snap Time" below.

The quickest curing formulation is not recommended because of higher reversion potential and secretion of a by-product as described earlier, as well as indications of loss of strength. Should these characteristics have a wider acceptability range than we have considered—e.g. strength is of little consequence in this application, and the secreted products may be harmless—then one might select a still faster formulation.

Figs. 2, 3, 4 and 5 show the DBTDA and water variations in a 50/50 mix of 93-009/93-029, from which the optimum formulation was selected. Variability between lots is indicated by comparing Fig. 2 with Fig. 3 and Fig. 5 with Fig. 8. (Lots A, B, C, and D are designations assigned for this study to separate 6 digit lot numbers assigned by manufacturer to raw material.) Lot "B" is clearly faster. In subsequent series of 12 tests each on Formulations A and B, variability within-lot is quantitated by the standard deviation $\sigma$, shown in Figs. 12 and 13. These curves also indicate the between-lot differences by the somewhat longer set time
Fig. 2
100 pbw 50/50 93-009/93-029
0.5 pbw DBTDA
Lot "A" Mixture

Fig. 3
100 pbw 50/50 93-009/93-029
0.5 pbw DBTDA
Lot "B" Mixture
Fig. 4
100 pbw 50/50 93-009/93-029
1.0 pbw DBTDA
Lot "A" Mixture

Fig. 5
100 pbw 50/50 93-009/93-029
5.0 pbw DBTDA
Lot "A" Mixture
Fig. 6
100 pbw 50/50 93-009/93-029
1 pbw DBTDA

Hardness, Shore A Durometer

Distilled Water, pbw
Fig. 7
100 pbw 50/50 93-009/93-029 Mixture
4 pbw DBTDA Catalyst
Lot "B" Mixture

Fig. 8
100 pbw 50/50 93-009/93-029
5 pbw 3BTDA
Lot "E" Mixture
Fig. 9

100 pbw 75/25 93-009/93-029
Lot "D" Mixture

Hardness, Shore A Durometer

Time, Hours
Fig. 10
100 pbw 50/50 93-009/93-029 Resins

Fig. 11
100 pbw 50/50 93-009/93-029
4 pbw 93-009 Catalyst Resins
Fig. 11-A
100 pbw 93-029 Resin
0.5 pbw DBTDA
Lot "D" Mixture

Fig. 11-B
100 pbw 93-029 Resin
1.0 pbw DBTDA
Lot "D" Mixture
Fig. 12
100 pbw 75/25 93-009/93-029
0.5 pbw DBTDA
0.16 pbw Distilled Water
Lot "C" Mixture
Error Bands are ± 0

Fig. 13
100 pbw 50/50 93-009/93-029
0.5 pbw DBTDA
0.16 pbw Distilled Water
Lot "C" Mixture
Error Bands are ± 0
than those obtained earlier in other lots "A" and "B".

Variability of the incoming material is noticeable in its viscosity. The specifications allow a range of 50 to 200 poise in the 93-009, 18 to 24 in the 93-029. Age of the raw material can cause viscosity to increase because of moisture, changes in dispersion of the filler particles, and chemical reactions.

The high molecular weight of the 93-009 base resin requires careful mixing techniques, (See the next section on Tensile Strength) but the material is useful because it gives the engineer a means of adjusting the mixture viscosity to the process application.

Tensile Strength

A parametric study of tensile strength and elongation was made using tests per ASTM D-412. Although strength is not important for most solid-pack applications—indeed for many applications it should either be weaker than the HE or be low in adhesion or both—nevertheless tensile strength is an indicator of the integrity of the silicone system and the state of cure; strength must also have some minimum value to assure ability to move, handle, and operate on the assembly. These tests were also conducted for comparison with the existing formulation and 4 pbw 93-009 catalyst.

Two resin mixes were tested, both with 0.5 pbw DBTDA and 0.16 pbw water: 75/25 and 50/50 ratios of 93-009/93-029. These are the Formulations A and B. The results, in Table I and Table II, indicate ultimate tensile strength is of the order of 310 psi in the 75/25 mix, and somewhat weaker—about 230 psi—in the
<table>
<thead>
<tr>
<th>Test Number</th>
<th>Thickness, Mils</th>
<th>Speed</th>
<th>Cure</th>
<th>Die</th>
<th>Ultimate, psi Mean</th>
<th>σ Mean</th>
<th>Elongation, % Mean</th>
<th>σ</th>
<th>Remarks</th>
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<td>075</td>
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<td>C</td>
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<td>35&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>Lengthen cure time before test&lt;sup&gt;4&lt;/sup&gt;</td>
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<td>C</td>
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<td>66&lt;sup&gt;5&lt;/sup&gt;</td>
<td>140&lt;sup&gt;5&lt;/sup&gt;</td>
<td>35&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>9</td>
<td>075</td>
<td>2</td>
<td>1</td>
<td>C</td>
<td>273</td>
<td>12</td>
<td>144</td>
<td>17</td>
<td>Decrease crosshead speed&lt;sup&gt;4&lt;/sup&gt;</td>
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<tr>
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<td>075</td>
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<td>1</td>
<td>C</td>
<td>294</td>
<td>16</td>
<td>146</td>
<td>15</td>
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<td>11</td>
<td>100</td>
<td>2</td>
<td>2</td>
<td>C</td>
<td>337</td>
<td>33</td>
<td>143</td>
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<td>100</td>
<td>2</td>
<td>2</td>
<td>C</td>
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<td>2</td>
<td>D</td>
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<td>Increase cure time, decrease specimen cross-sectional area&lt;sup&gt;7&lt;/sup&gt;</td>
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<td>2</td>
<td>C</td>
<td>377</td>
<td>12</td>
<td>140</td>
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<td>Increase cure time and area&lt;sup&gt;8&lt;/sup&gt;</td>
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<td>2</td>
<td>C</td>
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<td>146</td>
<td>6</td>
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<td>038</td>
<td>2</td>
<td>2</td>
<td>D</td>
<td>385</td>
<td>34</td>
<td>163</td>
<td>12</td>
<td>Decrease crosshead speed and area, increase cure time&lt;sup&gt;8&lt;/sup&gt;</td>
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<td>14</td>
<td>038</td>
<td>2</td>
<td>2</td>
<td>D</td>
<td>358</td>
<td>21</td>
<td>143</td>
<td>15</td>
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<tr>
<td>Combine slabs 1 to 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>310</td>
<td>29</td>
<td>152</td>
<td>13</td>
<td>Assumes slab population</td>
</tr>
</tbody>
</table>

1 1 = 20"/minute; 2 = 2"/minute
2 1 = 24 hours; 2 = 200 hours
3 C = ASTM D-412 die C; D = die D
4 Samples 1 through 5 in slab
5 Sample 3 odd failure and low U<sub>ts</sub>
6 Sample 3 omitted
7 Samples 1, 2, and 3 in slab
8 Samples 4, 5, and 6 in slab

Each test number consists of 6 samples. Resin paint shaker mixing 15 minutes; formulation mixed 5 minutes under vacuum.
### TABLE II

**Tensile Strength of 50/50 93-009/93-029 with 0.5 pbw DBTDA and 0.16 pbw Water**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness Mils</th>
<th>Speed</th>
<th>Cure</th>
<th>Die</th>
<th>Ultimate psi Mean</th>
<th>Elongation % Mean</th>
<th>Remarks</th>
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<td>1</td>
<td>075</td>
<td>1</td>
<td>1</td>
<td>C</td>
<td>236</td>
<td>138</td>
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<td>1</td>
<td>1</td>
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<td>240</td>
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<td>1</td>
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<td>2</td>
<td>D</td>
<td>296</td>
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</table>

**Remarks**

- Increase crosshead speed, increase cure time
- Decrease specimen cross-sectional area, increase cure time
- Increase cure time and area
- Decrease crosshead speed
- Increase specimen cross-sectional area, decrease crosshead speed, increase cure time
- Decrease specimen cross-sectional area, increase cure time
- Increase cure time and area

Combine slabs 1 to 6

1 = 20"/minute; 2 = 2"/minute
1 = 24 hours; 2 = 200 hours
C = ASTM D-412 die C; D = die D
Samples 1 through 5 in slab
Samples 1, 2, and 3 in slab
Samples 4, 5, and 6 in slab
Assumes slab population
50/50 mix. Elongations were about equal, being in the vicinity of 150%. The present standard formulation with 4 pbw 93-009 catalyst and 50/50 ratio base resins averages about 160 psi ultimate and 120% elongation, in production quality assurance tests.

For comparison to some HE's, the tensile strength is about 350 psi in LX-04-1, 120 psi in a formulation close to the eventual RX-09-AG, and 300 psi in 9404; elongations of course are small, being of the order of 2000 µin/in. Comparison to strengths of the HE is of limited interest, since normally there is no adhesion between the silicone rubber and the HE.

The 1 pound containers of silicone base resin were put in a paint shaker for 15 minutes before mixing, and mixing of the formulation was done under vacuum. The effect of forcing the materials back into uniform suspension and avoiding air entrainment during mixing are evident in the dispersion (standard deviation σ) of test data, although the comparison may be confounded by the difference in catalysts (DBTDA versus 93-009), and by differences in personnel and the time over which tests were carried out. The coefficient of variation (100 σ/mean) is about 6, versus 20 in older tests which include the production tests.
Viscosity

Viscosity measurements were made on the silicone rubber system as it proceeded through the cure cycle, as a measure of working time or pot life. Figs. 14 and 15 are plots of viscosity using the 75/25 ratio of 93-009/93-029 and from 0 to 0.35 pbw water; in Fig. 14 the formulation used 0.5 pbw DBTDA; in Fig. 15 it is 1.0. Each curve represents an average of three tests. Figs. 16 and 17 are similar plots with a 50/50 mixture of 93-009/93-029. The Brookfield RVF model viscometer was used at 10 rpm with spindles 4 through 7 as required.

Sound Velocity

Sound velocity was measured with a Budds Immerscope Model 424D with 0.5 megacycle crystals. It was measured for its value in shock hydrodynamics and for the possibility of detecting the change in the degree of polymerization.

The initial measurements (Table IIIA) have some uncertainty caused by fixture design and sample fabrication. Improvements were made, and the data appear in Table IIIB.

Sound velocity in Formulation "A"—75/25 93-009/93-029, 0.5 pbw DBTDA, 0.16 pbw water—was 940 meters per second at 24 hours cure, with little or no change after 200 hours cure. Formulation "B"—50/50 resin mix—averaged 980 meters per second, also with little or no change between 24 and 200 hours cure.

The two formulations are clearly distinguishable (940 versus 980 m/sec) but the indicated slight change with cure time (about 4 m/sec) between 24 and 200 hours
is not statistically proved and is probably near the resolution of the measurement. However, differences earlier in the cure, when the system is changing from liquid to rubbery, might be more easily measured and useful to indicate state of cure.
Fig. 14

100 pbw 75/25 93-009/93-029
0.5 pbw DBTDA
25°C

Time, Minutes

Brookfield Viscosity, Poise

.35 pbw Distilled Water
.18 pbw
.09 pbw
No Water
Fig. 15

100 pbw 75/25 93-009/93-029
1 pbw DBTDA
25°C
Fig. 16

100 pbw 50/50 93-009/93-029
0.5 pbw DBTDA
25°C
Fig. 17

100 pbw 50/50 93-009/93-029
1 pbw DBTDA
25°C

Brookfield Viscosity, Poise

Time, Minutes
TABLE III-A

Sound Velocity of 50/50 93-009/93-029 Silicone

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Thickness*</th>
<th>Mix or Cure Time</th>
<th>11:00</th>
<th>11:30</th>
<th>12:45</th>
<th>14:00</th>
<th>15:15</th>
<th>pbw DBTDA</th>
<th>pbw H₂O</th>
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<tr>
<td>1</td>
<td>.973</td>
<td>24 Hrs.</td>
<td>918</td>
<td>925</td>
<td>930</td>
<td>927</td>
<td>927</td>
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<td>0.1</td>
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<tr>
<td>2</td>
<td>.988</td>
<td>9:35</td>
<td>948</td>
<td>950</td>
<td>961</td>
<td>957</td>
<td>956</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>.975</td>
<td>9:55</td>
<td>945</td>
<td>954</td>
<td>960</td>
<td>955</td>
<td>956</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>.995</td>
<td>10:10</td>
<td>958</td>
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<td>978</td>
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<td>973</td>
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<td>0.4</td>
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<td>5</td>
<td>.993</td>
<td>10:20</td>
<td>958</td>
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<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>.980</td>
<td>24 Hrs.</td>
<td>943</td>
<td>956</td>
<td>963</td>
<td>957</td>
<td>957</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*This is the thickness of the silicone plus the 2 Plexiglas covers. The Plexiglas is 0.477 inch thick.

Note: Each sample varied in thickness, some as much as 0.020. Therefore, an average thickness for each sample was chosen.

TABLE III-B

Sound Velocity of Silicone Samples

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Sample No.</th>
<th>Sound Velocity After 24 Hour Cure (m/sec)</th>
<th>Sound Velocity After 200 Hour Cure (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;A&quot;</td>
<td>1</td>
<td>940</td>
<td>942</td>
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<tr>
<td>75/25 93-009/93-029 with 0.5 pbw DBTDA and 0.16 pbw H₂O</td>
<td>2</td>
<td>939</td>
<td>943</td>
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<tr>
<td>&quot;B&quot;</td>
<td>3</td>
<td>937</td>
<td>941</td>
</tr>
<tr>
<td>50/50 93-009/93-029 with 0.5 pbw DBTDA and 0.16 pbw H₂O</td>
<td>4</td>
<td>988</td>
<td>992</td>
</tr>
<tr>
<td></td>
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<td>980</td>
<td>984</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>982</td>
<td>985</td>
</tr>
</tbody>
</table>

Note: The Plexiglas total thickness in these tests was ~ 0.120". The silicone rubber remained ~ .5".
Snap Time

"Snap time" is a term sometimes used by others, including a manufacturer, as one definition of working time or pot life. Our definition of pot life has been derived from viscosity-time curves, described earlier, with 4000 poise often being taken as a limit. Since snap time is rather an easier measurement to make than viscosity and might serve to predict pot life of various batches, tests were performed with Formulations A and B. Snap time might also be a useful measure of state of cure insofar as it can indicate a change from liquid to rubbery and thus signal when work on assemblies can continue.

The snap test consists of pouring a quantity of the mixed formulation into an open container and dipping a spatula into the material periodically. The flat part of the spatula is brought in contact with the surface of the material and depressed below the surface. It is then brought out, with the material clinging to and stringing from it. At first, of course, the silicone rubber will flow from the spatula. The length of time that it takes for the strings to first break—thus showing first signs of rubberiness—is recorded and taken as the snap time. Several spots or trials are made at each time period.

The results were perhaps surprisingly consistent: In 12 tests the times for the A Formulation (75/25) were from 105 minutes to 130 minutes; times for the B Formulation (50/50) were 140 to 190 minutes. Another test using the B Formulation except with twice as much and half as much water gave 135 and 220 minutes, respectively.
Stability and Compatibility

Studies are well along to determine the resistance of this silicone rubber to reversion or depolymerization, to measure its physical stability and to evaluate compatibility of the rubber and any effluent, with weapon components.

The solid-pack weapon design is not ideal for many silicone rubbers because of the confinement and inherent pressure, if reversion effects are not acceptable. The most favorable conditions for reversion are heat, confinement and pressure. The confined silicone rubber does not have an opportunity to slough off excess catalyst, products of the chemical cure reactions or water. Since some of these can cause depolymerization as well as polymerization, reversion may be brought about when heat and pressure are applied. The effect of reversion is easily seen in the release of fluids, loss of some mechanical properties, and presence of decomposition products, which themselves may be unacceptable in the presence of other weapon components. Analysis of the chemistry involved is difficult because of the incompleteness of published data and proprietary factors. See, however, the Appendix.

Some silicone rubber systems can be pre-treated, compounded with different additives or filler, or induced by chemistry to inhibit reversion. Some suggestions for the 93-009/93-029/DBTDA/water system are in the Appendix. Reversion-resistant silicone systems are available and are used for other applications (e.g. Dow Corning 93-022, Sylgard 182, etc.) to reduce reversion. Their application to a variety of operations has not been fully studied.
Several techniques have been used during this study to determine the relative resistance of the 93-009/93-029, DBTDA, and water formulation.

Blotter tests have been performed to visually observe low molecular weight materials or liquids that may be secreted when the silicone rubber slabs are confined under 30 psi pressure and 180°F for several months. The fixture is a modification of the Ludwig (LRL) design as seen in Fig. 18. The sample consists of silicone rubber/filter paper stacks. The rubber samples are a 1" dia. and .020" thick. The tight fitting sleeve surrounding the sample stacks is intended to enhance the confinement simulation of the test. The approximate confinement ratio to be simulated is 450/1 (non-exposed to exposed area).

Formulation A samples have been observed after 7 days at 30 psi and 180°F; there were no apparent fatty acids, oils, or liquids present on the filter paper. The period of 7 days is too short to give a clear enough idea of likelihood of survival for the lifetime desired. The 30/60/90 day samples will be recovered and inspected for mechanical properties, and the filter paper chemically analyzed.

Slit tests have been performed to observe changes in configuration and mechanical properties when the silicone rubber slabs are under 30 psi and 180°F for several months. The fixture is a modification of the Woods (LRL) design as seen in Fig. 19. The sample consists of a silicone rubber slab (1.5" dia. x .020" thick) under mechanical 30 psi force, positioned over 2 slits in the base plate; one slit is .030" wide, the other 0.015". If the material depolymerizes or reverts under these conditions, it should flow more readily into the slots or crumble. The phenomenon may be observed by looking into the bottom of the fixture. After
Fig. 18

Blotter Test Fixture
Fig. 19
Slit Test Fixture
8 weeks at 30 psi and 180°F the DBTDA/water system has not shown signs of failure. Other 30/60/90 day samples will be recovered and inspected for mechanical properties.

A third test was conducted, which does not simulate the rubber application (because of absence of high pressure and confinement) to observe the relative resistance of the materials at much higher temperatures. This test was conducted at 260°C (another non-simulation factor) for 6½ hours. The rationale is to drive the material to the destruction threshold. Samples were cast in 2" x 2" x ½" slabs and placed on an aluminum panel. Hardness and weight were taken before and after the 260°C heat soak in the oven atmosphere.

The 0.5 pbw DBTDA/0.16 pbw water in 50/50 93-009/93-029 had a drop from Shore A 31 to 16. The 5 pbw DBTDA/2 pbw water in 50/50 indicated a breakdown condition after 45 minutes (See Fig. 20). The durometer was then recorded as 7. The silicone system 93-024 (a reversion resistant material similar to 93-022) had an increase in durometer from 30 to 50 after 6½ hours; extensive cross-link was evidenced by the sample brittleness and fracture with bending. The Shore A gage needle would puncture the material after several seconds. The 93-024 is supposed to be very reversion resistant, with good anti-softening characteristics.

One 4 pbw 93-009 catalyst in 50/50 93-009/93-029 slab indicated a drop from 31 durometer to 7.

The order of the materials based on their resistance to decrease in hardness during the heat soak is thus: (1) 93-024 with 10 pbw 93-024 catalyst; (2) 50/50
Fig. 20

100 pbw 50/50 93-009/93-029
5 pbw DBTDA
2 pbw Distilled Water
260°C for 45 Minutes
93-009/93-029 with 0.5 pbw DBTDA and 0.16 pbw water (Formulation "B"); (3) 50/50 93-009/93-029 with 4 pbw 93-009 catalyst.

Fig. 21 illustrated the effects of too much water or catalyst at extreme temperatures, 260°C for 6½ hours. The three samples were formulated with a 50/50 93-009/93-029 using good mixing techniques. The most swollen sample (on the left) had 2 pbw of DBTDA and .4 pbw of water. The before/after hardness (durometer) ratio was ~3.2. The second or center sample had 1 pbw of DBTDA and .4 pbw of water. The before/after hardness ratio was ~2.7. The third sample (on the right) had .5 pbw DBTDA and .16 pbw water. The before/after hardness ratio was 2.6. A fourth sample, not shown, using 4 pbw 93-009 in place of DBTDA, appeared similar to the .5 pbw DBTDA sample but with a 3.0 before/after hardness ratio.

A fourth test was conducted to specifically measure reversion resistance by hardness change (although hardness/reversion relationship is not necessarily valid: hardness might fall off for other reasons not connected with reversion, and without mechanical disadvantage for this application) due to temperature, pressure, cure time, and heat soak time. Round samples ½" thick by 1½" diameter were cured in a closed Plexiglas mold (< .005 sq. in. exposed to atmosphere). The Formulation "B" of 50/50 93-009/93-029, .5 pbw DBTDA, and .16 pbw distilled water was used. The experiment matrix, shown in Table IV, includes cure time 1, 5, and 10 days, temperature 130°F and 180°F, mechanical pressure 3 and 30 psi, and soak time of 0.1, 1.0, and 10 days.

The samples after the confined cure were immediately put in the slit fixtures
Fig. 21

100 pbw 50/50 93-009/93-029
Left - 2 pbw DBTDA/.4 pbw Water
Center - 1 pbw DBTDA/.4 pbw Water
Right - .5 pbw DBTDA/.16 pbw Water
260°C for 6½ Hours
(Fig. 19), pressure applied, and then put in an oven for soak time. After the samples were removed from the oven and had cooled the hardness was measured by a Shore A durometer test. The filter paper discs added on each end of the sample were visually examined for absorption of liquids.

The results to date of the hardness measurements are shown in Figs. 22, 23, 24 and 25. They indicate the expected trends plus a greater effect of cure time than anticipated: reversion as measured by softening was much less when cure time was longer (5 days versus 1 day, e.g.). It would seem that confinement was too close, time too short, and temperature too stable to allow escape of the products which Carmichael shows might cause reversion (see Appendix). Therefore, this finding is interesting, inasmuch as it indicates there may be an advantage in weapons not being immersed in antagonistic environments immediately. By the nature of production, this is the usual case.
TABLE IV
Reversion Test Sample Matrix

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cure, Days</th>
<th>Pressure, psi</th>
<th>Temp., °F</th>
<th>Heat Soak, Days</th>
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</tbody>
</table>
Hardness Decrease vs. Temperature & Pressure
100 pbw 50/50 93-009/93-029 Mixture
0.5 pbw DBTDA
0.16 pbw Water

Fig. 22

Normalized Durometer, D2/D1

Temperature, °F
Fig. 23

Hardness Decrease vs. Environment Soak for 130°F

Normalized Durometer, $D_2/D_1$

Soak Time, Days

3 psi (samples 1 & 13)

30 psi (samples 3 & 15)
Fig. 24

Hardness Decrease vs. Environment Soak for 180°F

Normalized Durometer, \( \frac{D_2}{D_1} \)

Soak Time, Days

- 3 psi (samples 6 & 18)
- 30 psi (samples 8 & 20)
- 30 psi (samples 4 & 16)
Fig. 25
Hardness Decrease vs. Environment Soak for 3 psi
Compatibility

System compatibility tests were begun concurrently with other LRL tests for similar materials. The test begins with a fixture similar to that shown in Fig. 18. The sample consists of a stack of 1" diameter discs representing a design cross-section in order of the material interfaces, e.g. metal, metal, silicone rubber (.003" thick), pad, silicone rubber (.008" thick), HE, silicone rubber (.025" thick), and metal. Again the stainless steel cylinder was used to enhance the confinement. The fixture loaded with the sample (under 30 psi mechanical) was then inserted into a small chamber and helium atmosphere. The chamber was then put into an oven at 180°F. The assembly will stay in the oven for several months before analyzing the gas present in the small chamber. There have not been any gas samples analyzed in this configuration during this reporting period.

Chemical reactivity test data on RX-09's with the silicone formulations (See Table V) were obtained. The RX-09-CB contains HMX, dinitropropyl acrylate polymer (PDNPA) and 2-fluoro-2,2-dinitroethyl formal (FEFO). RX-09-BJ contains a nitroplasticizer replacement for the FEFO. A gas chromatograph is used to measure the reaction between explosives and other materials and for thermal stability, often in place of the vacuum thermal stability test because not only the total gases but the kinds can be identified. Samples of the explosives, the test material, (½ gram each) and a 50/50 mixture of the two are heated at 120°C

---

3 L. C. Myers, First 1968 Quarterly Progress Report to LRL.
<table>
<thead>
<tr>
<th></th>
<th>N₂+O₂</th>
<th>NO</th>
<th>N₂O</th>
<th>CO₂</th>
<th>Total</th>
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<td>44.0</td>
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<td>39.1</td>
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<td>34.3</td>
<td>38.0</td>
<td>38.4</td>
<td>36.6</td>
<td>147.3</td>
</tr>
<tr>
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<td>21.8</td>
<td>-</td>
<td>-</td>
<td>5.6</td>
<td>27.4</td>
</tr>
<tr>
<td>+ 5% DBTDL + .16% H₂O</td>
<td>25.0</td>
<td>-</td>
<td>T</td>
<td>1.2</td>
<td>25.0</td>
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<tr>
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<td>21.8</td>
<td>16.2</td>
<td>26.4</td>
<td>103.6</td>
</tr>
<tr>
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<td>34.4</td>
<td>27.1</td>
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<td>22.4</td>
<td>100.2</td>
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<td>RX-09-BJ</td>
<td>23.6</td>
<td>13.4</td>
<td>8.1</td>
<td>17.1</td>
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<tr>
<td></td>
<td>33.0</td>
<td>7.0</td>
<td>6.9</td>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>+ 5% DBTDL</td>
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<td>-</td>
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<td>30.2</td>
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<tr>
<td>93-009/93-029 (50/50)</td>
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<td>-</td>
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<td>25.4</td>
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<tr>
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<td>-</td>
<td>-</td>
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<td>29.4</td>
<td>12.5</td>
<td>12.4</td>
<td>71.7</td>
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<td>-</td>
<td>-</td>
<td>5.6</td>
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</tr>
<tr>
<td>+ 5% DBTDL + .16% H₂O</td>
<td>25.0</td>
<td>-</td>
<td>T</td>
<td>25.0</td>
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<td>5.7</td>
<td>3.1</td>
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<td>34.9</td>
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<tr>
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<td>5.2</td>
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<td>46.9</td>
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<td>20.2</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td>22.6</td>
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<tr>
<td>+ 16.6% 93-009 Catalyst</td>
<td>18.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.5</td>
</tr>
<tr>
<td>RX-09-BJ + 93-009/93-029 (50/50)</td>
<td>32.0</td>
<td>4.7</td>
<td>5.0</td>
<td>6.9</td>
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<td>15.3</td>
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<td>114.2</td>
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<tr>
<td>+ 16.6% 93-009 Catalyst</td>
<td>43.4</td>
<td>30.9</td>
<td>15.4</td>
<td>32.0</td>
<td>121.7</td>
</tr>
</tbody>
</table>
for 22 hours and evolved gases are analyzed in the GC. The volumes of the various gas evolved by the components are compared to the volumes of the 50/50 mixture.

The results do not indicate any serious incompatibility.

DTA, pyrolysis, and isothermal weight loss data are still being obtained.\(^4\) Cursory review of the data, which is not in final form does not indicate large departures from the expected.

Less sophisticated compatibility tests were made to insure that the DBTDA catalyzed system would cure in contact with the various materials necessary. It has been reported by others\(^5\) that a stannous octoate catalyzed silicone system would not cure in confinement with an HE formulation containing FEFO. The tin in the plus two state, as in the stannous octoate, seemed to be the problem. Due to such reports, and as a matter of course with new materials, silicone rubbers had to be tested to insure there was no poisoning by the HE formulations or other contact materials.

Thin films of the 50/50 93-009/93-029 using DBTDA and water were allowed to cure with the various contact materials to observe the cure in the rubber system visually. There were no cases of failure to set. Physical property measurement will be made later.

\(^4\) G. L. Clink, Pantex; report in progress.
\(^5\) K. T. Pierce, Pantex; D. L. Seaton, LRL.
On two assemblies cured over a weekend, there was evidence that spots of adhesion had occurred, causing failure of the RX-09-CB explosive. These spots were approximately 1/8" diameter, with .006" deep craters in the RX-09-CB. The failure was on the equator of the HE below a relief slot for exuding silicone rubber (93-029 catalyzed with DBTDA). The relief slot was machined in the steel flange of the assembly mandrel and thus was in an area on the fixture in which no pressure was on the silicone rubber. To date it has not been determined what caused the failure. However, there was a possibility of alcohol and/or talcum powder at the interface. Alcohol can soften the HE and talcum powder contains boric acid which may soften the silicone rubber (it has been reported by others). The spots of failure represented ~ 2% of the total area.
Analysis of Testing Techniques

Analysis was made of the data produced by the several physical tests used, to compare the tests. The data—including some from tests made especially for this purpose—form a matrix with varying amount of water and DBTDA, and ratio of 93-009 to 93-029. An interesting example, shown in Fig. 26, indicates the relationship for a 50/50 mixture of 93-009/93-029 using 1.0 pbw DBTDA catalyst. The ordinate is the proportion of water; the abscissa is the time from mixing the formulation to the time at which the property was measured. Each property—viscosity, hardness, snap time, and tensile strength—is represented by a curve at one or more of the values of that property, e.g. 1000 and 4000 poise for viscosity.

In the curves, slope indicates the sensitivity of the testing techniques to the variables; for example, viscosity changes much more rapidly with small changes in the water content than, say, tensile strength. Position of the curve along the abscissa indicates sensitivity to the magnitude of the testing technique variable. For example, there is little difference between 1000 and 4000 poise, but considerable difference between Shore A15 and A30 hardnesses: the slope of the hardness curves are somewhat different, and the 15 curve occurs earlier, thus incurring less waiting time in the testing.

<table>
<thead>
<tr>
<th>Test Value:</th>
<th>1000 poise</th>
<th>4000 poise</th>
<th>A15</th>
<th>A30</th>
<th>Snap</th>
<th>psi</th>
</tr>
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<tbody>
<tr>
<td>Index:</td>
<td>11</td>
<td>10</td>
<td>5</td>
<td>2.8</td>
<td>3.5</td>
<td>.22</td>
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</table>

The curves and indices are useful in making decisions as to what tests and test levels to use. Using them, it is clear that hardness by durometer is a good
Fig. 26

100 pbw 50/50 93-009/93-029
1 pbw DBTDA

Ultimate Tensile Strength 190 psi

*Different lot from other tests.
measure, and the A15 is better than A30 because the sensitivity is greater and the curve occurs earlier on the time scale. Other factors of course influence decisions as to tests: whether to measure on the solid or the liquid, whether to make a laboratory type test which may be slower and more expensive but more precise, or a simple assurance test, of which many more can be made.

**Process Control**

Evidence was given above regarding variation in 93-009 and 93-029 base materials. There was only one batch of catalyst used throughout. Several small excursions were made to observe new techniques for monitoring variations. There is an advantage of measuring the viscosity of each can of raw material in the production areas: it would allow assembly people to predict its behavior in use and during the cure cycle. Obviously, a viscometer such as a Brookfield or Stormer would be expensive, time consuming, and possibly not appropriate to a production area.

Several tests were run attempting to correlate Zahn viscosity with the Brookfield viscosities measured. This technique would allow an operator to dip into each can with little material waste and no laboratory time. The following measurements (12 on each batch) were made using a No. 5 cup:
<table>
<thead>
<tr>
<th></th>
<th>Zahn Viscosity, Seconds</th>
<th>Brookfield Viscosity, Poise</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. Dev. σ</td>
</tr>
<tr>
<td>93-009</td>
<td>254</td>
<td>9</td>
</tr>
<tr>
<td>93-029</td>
<td>127</td>
<td>7</td>
</tr>
<tr>
<td>93-009/93-029 (50/50)</td>
<td>166</td>
<td>23</td>
</tr>
<tr>
<td>93-009/93-029 (75/25)</td>
<td>193</td>
<td>17</td>
</tr>
</tbody>
</table>

A nomograph could be made from more extensive test data to correlate Zahn/Brookfield satisfactorily to predict behavior.

Another process control technique investigated was a catalyst and water dispenser. A 5cc Kenics dispenser (Model 101) as shown in Fig. 27 was filled with water or stannous octoate and charged with 80 psi of air. The control tip is depressed to eject a drop of fluid as desired. The weights of the drops were recorded to determine the mass of fluid dispensed and accuracy. There was no apparent difference from holding the device in a horizontal versus a vertical position. The water dispensed averaged 12.6 mg per drop (σ = 0.8 mg) through the .020" tip, and 18.8 mg per drop (σ = 1.1 mg) from the .032" tip. The stannous octoate (ρ = 1.3) was dispensed at 9.8 mg per drop (σ = 1.1) from the .020" tip, and 12 mg per drop (σ = 0.9) from the .032" tip. In addition to the repeatability advantage, the dispenser could be easily prepackaged with approved material, and thus prevent possible accidental compromising of the material quality. The present system of using "eye-droppers" requires the operator to open the catalyst container many times, which makes it vulnerable to contamination, etc. Eye droppers presently used with water may dispense a 10 mg range
Fig. 27
Catalyst or Water Dispenser
in one model and 4 mg in another model, with still greater variability if horizontal and vertical positions are intermixed: the average drop weight was 36 mg when horizontally dispensed versus 18 mg when vertical. LRL has suggested a graduated pipette in place of eye droppers; this will be investigated. Whichever device is used must be controlled closely because of the small proportions required with the DBTDA and water formulations.

Other New Materials

Other materials were analyzed tentatively and cursorily (to the present; more will be done) but not directly compared to 93-009/93-029 base materials. An extant silicone rubber system (92-007) was reevaluated for use with RX-Og-CB. It offers the advantage of lower viscosity. The 92-007 is a one-part system that requires moisture for cure (usually from the atmosphere). It has been used for spray process applications at Pantex, being supplied by the manufacturer with a designation of 92-009 (and with a lower solids content than 92-007). Since it has low viscosity and can set rapidly, with adhesion to HE, the prospective use would be as a detonator seating material; it will be so investigated.

Several experimental materials were investigated, which are similar to 93-009/93-029, designated 93-094/93-095 by the manufacturer. These also seem to be condensation systems. The initial cure tests indicate 93-094/93-095 catalyzed

6 Dow Corning; Midland, Michigan
7 Ibid.
with DBTDL is comparable in cure time to the 93-009/93-029/DBTDA/water system. The chemical reactivity analysis is given in Table VI. This material will also be investigated as a detonator adhesive. This material has potential as a future substitute for the 93-009/93-029 system.

Chemistry & Consultant Services

To help us in the understanding of the basic chemistry of silicone RTV rubbers and to obtain an independent judgment of findings (independent of AEC agencies and manufacturers), as well as to provide another source of new information and potential materials, a number of people and institutions were interviewed for consultative services. Jack B. Carmichael, Assistant Professor of Chemistry at the University of Massachusetts, Amherst, was selected for his knowledge of and contributions to both the general and specific fields. This report, in draft form, the data generated and the methods used were then discussed with him toward the end of the present period. The result is his first report, "The Chemistry & Physical Properties of Silicone Rubbers: Phase I", which appears as an appendix to this report. In it will be found descriptions of the DBTDA mechanism, reversion process, proposed formulations, testing procedures at elevated temperatures, determination of extractible materials, possible special specifications in raw materials, and other information.

George L. Clink, Pantex, has also contributed to the research on the chemistry, particularly in work toward determining the nature of the white solid by-product formed when a surplus of DBTDA is used.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{N}_2+\text{O}_2$</th>
<th>NO</th>
<th>$\text{N}_2\text{O}$</th>
<th>CO$_2$</th>
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<td>93-094</td>
<td>10.4</td>
<td>0.5</td>
<td>-</td>
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<td>93-094</td>
<td>26.9</td>
<td>T</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>93-095</td>
<td>23.6</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
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<tr>
<td></td>
<td>21.3</td>
<td>15.3</td>
<td>7.1</td>
<td>22.0</td>
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</table>
COMMENTS; CONCLUSIONS; FUTURE WORK

The following conclusions are drawn and recommendations made:

1. Formulations using 93-009/93-029 with 0.5 parts by weight of DBTDA and 0.16 parts by weight of water provide acceptable RTV silicone rubbers in thin sections for some solid-pack applications. These applications include those currently using the same base materials with a DBTDL/water catalyst (the catalyst supplied by the manufacturer for 93-009 and 93-029 resins).

2. These formulations set profitably faster than the DBTDL system, curing to the point where next handling or operations can be carried on in 2 to 6 hours. Good specifications and material control will assure reduction of the range of time: it is considered to have been demonstrated that the probability of set time under such controlled conditions being 3 ± 1 hours is sufficiently high to warrant stating that number for planning production rates.

3. The experimental indications are that the DBTDA/water system does not have importantly greater incipient stability or compatibility difficulties than the DBTDL/water system it replaces. This finding does not seem to be contra-indicated by the theoretical chemistry.

4. One of the principal purposes or goals of this project was to increase production plant capacity by reduction of set times. (Indeed, that is the main justification for ALO sponsorship of this program, since weapon parameters are the province of and well taken care of by the design
laboratories. Our concern with those parameters is that they be not transgressed. LRL has signified that the formulation is acceptable for the principal present application in the Mk 62 and Mk 68). The amount of set time reduction brought about by the new material DBTDA and the formulations containing it satisfies the goal to a profitable degree, in that it greatly reduces or removes a stated capacity limiting factor involved in the size of planned assembly facilities.

5. Other new materials, especially the 93-094 and 93-095 system are beginning to indicate utility.

6. The outlines of better specifications for and control of raw materials have been drawn. Some areas include limits on cyclic dimethyl siloxane content, water limits in the catalyst, dispersion pre-mixing, and testing of raw materials.

7. Methods to aid processing uniformity, predictive testing, and acceptance testing have been described. These include a simple measure of viscosity of the raw material, a catalyst dispenser for accuracy in formulating, and simple hardness and "snap time" tests both to predict behavior of batches and to signal cure time.

8. Contributions to the understanding of the chemistry of the silicone system were obtained through consultative service. This service also resulted in many raw material specification details and analytical techniques which can be applied to material control.

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The present 93-009/93-029 93-009 or DBTDL/water system in use is allowed 16 to 24 hours to cure; in informal tests the time does not seem to be reducible below about 8 to 12 hours.
The future work includes searches for very fast setting materials for detonator seating applications, a widening of the range of moderately fast-setting materials (so that viscosity, etc. can be tailored better to the process applications) and continuing testing of the new formulation, including long-term testing. It also includes searches for other entirely new materials and methods, and studies of the advantages and means of formulating complete silicone systems from basic resin stocks. Specific goals for the next period include detailing of specifications for the raw material and improvement of monitoring techniques for raw material and the finished product.
REFERENCES


APPENDIX
THE CHEMISTRY AND PHYSICAL PROPERTIES OF SILICONE RUBBERS:

PHASE I

An assessment of room temperature vulcanizing silicone rubber cured by dibutyltin diacetate plus water.

First Progress Report, to April 10, 1968

Jack B. Carmichael

Consultant to the

MASON & HANGER - SILAS MASON CO., INC.
Pantex Plant
Amarillo, Texas
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<td>3. Analysis of the hydrolysis product of</td>
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<tr>
<td>[(C₄H₉)₂ Sn (O - C = CH₃)₂]</td>
<td></td>
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<tr>
<td>4. Test for compatibility of the hydrolysis product with FEFO</td>
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<td>5. Test for possible malfunction of the black box containing electronic equipment in the presence of a saturated atmosphere of low molecular weight dimethylsilicone</td>
<td></td>
</tr>
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H. Possible Special Specifications for Quality Control of Incoming Lots of Manufacturer's Materials................................. 22

1. H₂O content in dibutyltin diacetate
2. Extractibles level allowed in a fully cured RTV silicone rubber
3. Alkali metals content in base rubber
4. General suggestions regarding purchase of manufacturer's materials
A. Description of the Problem

A dibutyltin diacetate-cured RTV silicone rubber formulation is required which meets two primary and several secondary considerations.

Primary considerations:
1. Cure time must be sufficiently rapid to allow assembly of 2 devices per day.
2. After being cured in relative confinement, the rubber must exhibit excellent stability and resistance to reversion in a confined application at temperatures up to 180°F for a period of several years.

Secondary considerations:
1. No cure inhibition should result from the FEFO substrate used in the device.
2. No materials from the rubber during or after cure should react in any way with the FEFO.
3. Volatile materials from the rubber should not inhibit in any way the functioning of the black box containing electrical components.
B. Chemistry of the Water-Dibutyltin-Diacetate Catalyzed Curing Mechanism

Step 1

\[
\begin{align*}
CH_3 C - O - Sn - O C CH_3 + HO Si - O - (Si - O)_x Si - OH & \xrightarrow{H_2O} \\
& C_4H_9 CH_3 CH_3 CH_3 CH_3 \\
& C_4H_9 CH_3 CH_3 CH_3 CH_3
\end{align*}
\]

Step 1 can be viewed as a condensation type of reaction somewhat analogous to the condensation of a bifunctional amine with a bifunctional alcohol (glycol) to form a nylon polymer (ex. of Nylon 66) with the elimination of a molecule of water in each step. Here a molecule of acetic acid is eliminated in each step. In their second progress report, Lichte and Akst clearly demonstrated that the addition of small amounts of water (0.08 to 0.32 parts by weight) greatly accelerates the rate of cure of the rubber. The role of water in accelerating the rate of Step 1 is not clear to the present author. However, the addition of excess dibutyltin diacetate and/or water greatly accelerates the undesirable reversion reaction, discussed in the next section (Section C).
Step 2

\[ \text{Step 2} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{C} & \quad \text{O} & \quad \text{Sn} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad (\text{Si} - \text{O})_x & \quad \text{Si} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{C} & \quad \text{O} & \quad \text{Sn} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{OH} \\
\text{C}_4\text{H}_9 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{C}_4\text{H}_9 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

(Cross-linking agent)

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{OH} & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{OH} & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

\[ \begin{align*}
\text{CH}_3 & \quad \text{Si} & \quad \text{O} & \quad \text{Sn} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad (\text{Si} - \text{O})_x & \quad \text{Si} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{Si} & \quad \text{O} & \quad \text{Sn} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{OH} \\
\text{C}_4\text{H}_9 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{C}_4\text{H}_9 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

Step 2 represents the condensation of the intermediate produced in Step 1 with a trifunctional (3 OH groups) silicone to begin the formation of the cross-linked rubber network. Another molecule of dibutyltin diacetate is now capable of reacting with any of the three Si-OH groups present in the reaction product formed in Step 2.
The trifunctional cross-linking agent shown in Step 2 was chosen for purposes of illustration and does not duplicate the structure of the cross-linker present in a manufacturer's RTV base formulation. A commercial cross-linker is quite likely to be a polyfunctional three dimensional structure with many active Si OH groups per molecule.
C. Chemistry of the Reversion Process of the Rubber under Confinement

Step 1

\[ \text{HOH} + \text{CH}_3\text{C} - \text{OH} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{C} - \text{O}^- \]

The author views water taking part in the reversion reaction by reacting with acetic acid to form hydronium ion. The hydronium ion is viewed as the active species which catalyzes reversion. The amount of water initially added to the formulation should therefore be the least amount which yields an acceptably rapid cure rate.

Step 2

[Chemical structure diagram]

\[ + \text{H}_3\text{O}^+ + \text{CH}_3\text{C} - \text{O}^- \]
In Step 2, reversion occurs through the acid catalyzed hydrolysis of the Si – O – Sn linkage. One molecule of water is consumed but the acetic acid is regenerated. Continued reactions reduce the molecular weight of the network and thereby decrease the durometer and tensile strength. Ultimately, the strength of the rubber is entirely lost and the durometer is scarcely measurable.
D. Three Proposed Formulations to Meet the Application Requirements

Base: Mixture of RTV base numbers 93-009 and 93-029. The author suggests a mixture in the proportions which will yield the highest possible viscosity consistent with processing requirements. The highest viscosity mixture will develop the best physical properties on curing and will be less susceptible to reversion under confinement under elevated temperatures and pressure.

Catalyst: Three combinations of amounts of dibutyltin diacetate and water are suggested.

<table>
<thead>
<tr>
<th>Catalyst Formulation</th>
<th>Dibutyltin Diacetate, Parts by Weight Added</th>
<th>Water, Parts by Weight Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.16</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Some data on cure rate have been gathered by Akst and Lichte for each of these formulations (see Figs. 2 and 3, Second Progress Report). Catalyst formulation No. 2 received the preliminary recommendation in their report. Catalyst formulation No. 1 may yield a more reversion resistant rubber with slightly longer cure rate. The decrease in cure rate will be more pronounced using catalyst formulation No. 3 but the improvement in reversion resistance may be so substantial that the slower cure rate can be accepted.
E-1. Differential Thermal Analysis of Confined Rubber Samples

DTA data on confined rubber samples may allow rapid screening of the order of magnitude of reversion resistance characteristic of a given formulation.

One key to obtaining DTA data which will be indicative of rubber behavior in the actual confined application, is to use a sample container which can be hermetically sealed under a pressure of 30 psi or there about. Such a sample holder will contain all by-products of the curing mechanism and subsequent products formed during reversion reactions.

E-2. Thermal Gravimetric Analysis of Open Samples under an Inert Gas Atmosphere

A rubber sample analyzed by TGA in a He or N₂ atmosphere will appear to be serviceable at substantially higher temperatures than a confined sample of the same material.

The initially observed weight loss during the TGA analysis will be due to two kinds of materials in the sample.

1. Material in the rubber sample which were not affected by the cross-linking reactions. Such materials are all cyclo-dimethyl siloxanes \( [(\text{CH}_3)_2 \text{SiO}]_x \), \( x = 3, 4, 5, 6, 7, \ldots \) and linear dimethyl siloxanes end-blocked at both ends by trimethyl siloxy—or other non-reactive groups

\[
\left( (\text{CH}_3)_3 \text{SiO(SiO)}_y \text{Si(\text{CH}_3)}_3 \right)
\]
2. Volatile materials formed during the stages of the curing mechanism

\[
\begin{align*}
\text{O} & \\
\text{H}_2\text{O}, \text{CH}_3\text{-OH} & \\
\end{align*}
\]

Subsequent weight losses will be due to materials produced during the thermally induced rearrangement (thermally accelerated rearranged catalyzed by traces of either acid or basic materials in the rubber) or materials formed by thermal degradation of the rubber sample at still higher temperatures.

The TGA analysis in an inert gas atmosphere thus measures the inherent thermal stability of the network chains and the amount of nonvolatile catalytic material present.

The initially observed sample weight loss during TGA should correlate reasonably well with the percent materials extracted from the same fully cured sample in the Soxhlet extractor.

The rubber sample studied by TGA in H2 will obviously be much less subject to reversion than a confined sample since much of the acetic acid is removed in initial stages of analysis and all volatile materials are removed soon after they are formed.

E-3. Prediction of Rubber Life Expectancy at the Maximum Specification Temperature by Testing of Accelerated Reversion at Higher Temperatures

Procedure:

1. Find some convenient empirical relation between a macroscopic parameter and time which holds well over a range of temperatures. Lichte has indicated
in a private conversation that the relation: \( D = k \log t + c \) may be appropriate. \( D \) = durometer, \( k \) is a temperature-dependent rate constant for the reversion process, \( t \) represents time, \( c \) is an empirically determined constant. Times obtained by Lichte thus far are: 0.1, 1, and 10 days, respectively.

2. Approximate the temperature variation of the rate constant \( k \) by the Arrhenius expression,
\[
k = A e^{-\Delta E/RT}
\]
\( A \) = frequency factor, determined by intercept of plot of \( \log k \) as \( \frac{1}{T} \).
\( \Delta E \) = activation energy for the reversion process, determined by the slope of \( \log k \) versus \( \frac{1}{T} \).
\( R = 1.987 \text{ Cal/Mole} \)
\( T = \text{Temperature in degrees Kelvin} \)

**Sample Plot #1**

- \( C \)
- \( D \)
- Slope = \( k \)

Obtain such plots at several temperatures and calculate values of \( k \).

**Sample Plot #2**

- \( \log A \)
- \( \log k \)
- Slope = \( -\frac{\Delta E}{2.3R} \)

\( \frac{1}{T} \)
The durometer drop for any long period of time at any temperature (say, 180°F) can now be approximated by the expression:

\[ D = A e^{-\Delta E/RT} \log t + c \]

where \( A \) and \( \Delta E \) were obtained from Sample Plot #2 and \( c \) was obtained from Sample Plot #1.
F. Determination of Rubber Cure Time Using Increase of Viscosity and Durometer versus Time

The author suggests continuation of both Brookfield viscosity and Shore A durometer measurements versus time to measure cure rate. Akst and Lichte have shown that differences in initial rates of cure of various formulations can be monitored by Brookfield viscosity measurements on the curing mass. Rates of cure in the latter stages are conveniently measured by Shore A durometer. Both of these tests should be run by the control laboratory on each lot of material prior to its use in production (See also Section H-4 for other information regarding purchase of manufacturer's materials).
G-1. Determination of Quantity and Constitution of Extractible Material in RTV-Cured Silicone Rubber

Experimental Procedure

1. Dice a sample of cured silicone rubber into small cubes using a solvent-cleaned razor blade.

2. Weigh a small Soxhlet extractor thimble. Place approximately 2.5 g of the diced rubber into the thimble and reweigh.

3. Place the thimble into a Soxhlet extractor containing sufficient benzene to allow a good reflux of solvent in contact with the thimble (approximately 50 - 75 cc). Be sure to use reagent grade, thiophene-free benzene. After extraction, the solvent will be evaporated and the extract analyzed. Thus, any nonvolatile impurities in the benzene will be concentrated in the extract. Carry out the extraction for 24 hours.

4. When the extraction is completed, remove the thimble and allow the benzene to evaporate from the rubber cubes. Carry out all evaporations in a hood. Benzene fumes are quite toxic. Re-weigh the thimble plus rubber cubes. Compute the percent material extracted as:

\[
\text{\% material extracted} = 100 - \left( \frac{\text{Wt. of rubber after extraction}}{\text{Wt. of rubber prior to extraction}} \right) \times 100
\]

5. Filter the benzene solution of extracted material through a fine grade of filter paper. Save the solid material collected on the filter for analysis.
of tin, silicon, potassium, and other alkali metals. The filtrate from this step is handled subsequently in Step 6.

6. Allow the benzene to evaporate from the filtrate in the hood. After complete evaporation (which should occur in 24-48 hours at room temperature), a low viscosity oil should remain. The oil may not be clear due to extraction of some highly colored additives from the original rubber sample. Analyze this oil by infrared to confirm the presence of siloxane. Analyze the constituents of the oil using programmed-temperature dual column gas chromatography with dual thermal conductivity detection. See J. B. Carmichael, D. J. Gordon, and C. E. Ferguson, "Journal of Gas Chromatography 4, 347 (1966)" for a typical experimental procedure which one follows for the gas chromatography analysis.

G-2. Determination of Materials Absorbed during Blotter Test

**Experimental Procedure**

1. Remove the sample configuration from the oven and allow to cool to room temperature. Remove and weigh the filter paper.

2. Place the filter paper in a small (½ oz.) vial and fill the vial with reagent grade hexane. The use of pure solvent is essential since any nonvolatile impurities in the solvent will later be present in the concentrated extract of materials absorbed by the blotter.
3. Shake, or otherwise agitate, the vial for a few hours at room temperature to dissolve materials absorbed on the filter paper.

4. Remove the filter paper, pat dry with a Kimwipe and allow the remainder of the solvent to evaporate at room temperature for 30 minutes.

5. Reweigh filter paper.

\[
\% \text{ materials from rubber absorbed by filter paper} = \left( \frac{\text{Wt. of filter paper in Step 1} - \text{Wt. of paper in Step 5}}{\text{Wt. of rubber sample}} \right) \times 100
\]

6. Place the solution of absorbed materials in hexane from Step 3 into the hood and allow the solvent to evaporate at room temperature.

7. Filter the hexane solution which contains dissolved material from the filter paper through a fine grade of filter paper. Save the solid material collected on the filter for analysis of tin, alkali metals, and any other desirable analyses (such as silicon). The filtrate from this step is handled further in Step 8.

8. Allow the hexane to evaporate from the filtrate in the hood. After 24 hours, a small amount of clear, low viscosity oil should remain. Analyze this oil by infrared to confirm the presence of silicon linkages. Analyze the constituents of this oil using programmed-temperature dual column gas chromatography with dual thermal conductivity detection. See J. B. Carmichael, D. J. Gordon, and C. E. Ferguson, "Journal of Gas Chromatography 4, 347 (1966)" for a typical experimental procedure which one can follow for the gas chromatography analysis.
Calibration Standard Preparation Using Silicone Fluid

If desired, a calibration standard can be prepared and analyzed prior to analyzing the constituents from blotter test for reversion resistance.

1. Proceed by weighing a small circle of filter paper.

2. Saturate this paper with SF-96 silicone fluid, 20 cts. Pat off excess silicone fluid using a Kimwipe.

3. Reweigh the filter paper.

4. Proceed identically through Steps 2 through 8 above, with the exception of Step 5.

G-3. Analysis of the Hydrolysis Product(s) of \((C_4H_9)_2 Sn (O-C-CH_3)_2\)

The hydrolysis of \((C_4H_9)_2 Sn (O-C-CH_3)_2\) has been observed by Mr. George Clink to yield a gelatinous material which, upon vacuum drying, is converted to a white solid whose structure appears to be identical with that of the white solid observed by Mr. Lichte on the surface of RTV silicone rubber samples cured with a large excess (5 to 10 parts by weight) of dibutyltin diacetate. The present author postulates that the gelatinous material is a low molecular weight stannoxane formed by the condensation of \((C_4H_9)_2 Sn (OH)_2\) with itself. Vacuum drying under mild heat probably causes further condensation to yield a material of the empirical composition \((C_4H_9)_2 Sn 0\) but possessing a linear polymer structure:
The chemistry of these suggested reactions follows:

**Step 1**

\[ (C_4H_9)_2 Sn \cdot (O C - CH_3)_2 \cdot H_2O \rightarrow CH_3 C - OH \]

**Step 2**

\[ (C_4H_9)_2 Sn - O C - CH_3 + H_2O \rightarrow CH_3 C - OH \]

\[ + (C_4H_9)_2 Sn \cdot (OH)_2 \]

(Intermediate stable only at quite low temperatures)

**Step 3**

\[ (C_4H_9)_2 Sn \cdot (OH)_2 + HO - Sn - O Sn - OH \]

\[ + H_2O \]
Step 4

Further consideration of products such as the distannoxane appearing on the right hand side of Step 3 to yield low molecular stannoxane polymer. Such a mixture of low polymer and water would likely have a gelatinous appearance.

Step 5

\[
\begin{align*}
\text{C}_4\text{H}_9 & \quad \text{HO} - (\text{Sn} - \text{O})_x \quad \text{H} \xrightarrow{\text{Vacuum drying}} \quad \text{HO} - (\text{Sn} - \text{O})_2x \quad \text{H} \\
\text{C}_4\text{H}_9 & + \quad \text{H}_2\text{O}
\end{align*}
\]

Step 5 represents the further condensation of the low polymer previously formed in Step 4 and the removal by vacuum drying of the water formed in reactions discussed in Steps 3 and 4. When the water is removed, the high molecular weight stannoxane shown on the right hand side of Step 5 would have the approximate empirical formula

\[
\begin{align*}
\text{C}_4\text{H}_9 & \quad \text{Sn} \quad \text{O} \\
\text{C}_4\text{H}_9
\end{align*}
\]

and could appear as a white solid.

The simplest way to determine the validity of the mechanism proposed is to check the molecular weight of the gelatinous material and the subsequent
white solid produced during the vacuum drying step. The vapor phase osmometer is the recommended instrument. If the molecular weight of the gelatinous material is several times that calculated for \((\text{C}_4\text{H}_9)_2\text{Sn(OH)}_2\) and if a further three to tenfold increase in molecular weight is observed for the white powder found during vacuum drying, the postulated mechanism is likely correct as given.

G-4. Test for Compatibility of the Hydrolysis Product of Dibutyltin Diacetate with FEFO

The gelatinous hydrolysis product of dibutyltin diacetate should be tested for compatibility with the FEFO. Mr. George Clink suggested the importance of such a test. Ground up FEFO could be mixed with the gelatinous material in weight ratios of 100/10, 100/1, and 100/0.1. The mixtures could then be heated and tested for the evolution of gaseous by-products. Perhaps the conditions required for explosion of these mixtures should also be determined.

The tests outlined above should be repeated using the solid dibutyltin derivative obtained by vacuum drying.

The author hopes that neither material shows any tendency to accelerate the decomposition. Such tests as discussed above must be run to be sure that reaction with FEFO does not occur below the maximum specification temperature.
G-5. Test for Possible Malfunction of the Black Box Containing Electronic Equipment in an Atmosphere Containing Low Molecular Weight Silicones

In Section G-1 of this report a method was suggested for determining the amount and constitution of extractible materials in a fully cured RTV silicone rubber. These materials will include cyclo-dimethyl siloxanes and possibly low molecular weight homologues of the constituents of SF-96 dimethyl silicone fluid.

It is well known (J. Carmichael and R. Wisger, "Journal of Polymer Science" A-3 971, 1964) that an equilibrium polymerization to yield high molecular weight linear poly dimethyl siloxane yields approximately 16% by weight of low molecular weight cyclo-dimethyl siloxanes as well \( \left( \left[ (\text{CH}_3)\text{SiO} \right]_x \right) \), \( x = 3, 4, 5, 6, 7, 8, \ldots \). These cyclo-siloxanes are nearly certain to be present in varying amounts in all commercial silicone rubber base formulations. Since the cyclo-siloxanes are not affected by the dibutyltin diacetate curing mechanism, they will not be incorporated into the network. Therefore, if the cured rubber is not completely confined in the application, some of these cyclo-siloxanes will diffuse from the rubber over long periods of time. Since the cyclo-siloxanes may also be present in the atmosphere surrounding the black box containing electronic equipment, it is important to test a priori the compatibility of the silicone vapors with the electronic equipment.

One might place the black box in a dry box containing a shallow pan filled with 5 cts. SF-96 silicone fluid. If, after several days exposure to the
silicone vapors, the black box will continue to function properly while in
the dry box, then many years of life expectancy could be predicted in the
application. The actual concentration of silicone vapors present in the
atmosphere surrounding the box in the application will no doubt be $10^4$ times
less than the exposure during the dry box test discussed above.

Since acetic acid is released during the cure of the formulations catalyzed
with dibutyltin diacetate, the dry box compatibility test should also be
run in an atmosphere containing some acetic acid vapor.
H-1. Specification of Water Content in Dibutyltin Diacetate

Any substantial variability in the water content of lots of dibutyltin diacetate will clearly markedly alter the curing rate. (See Progress Report No. 2 by Akst and Licht showing the accelerating effect of increasing levels of added water on cure rates).

To minimize cure time variations and consequent disruptions of production schedules, the present author suggests that anhydrous dibutyltin diacetate be purchased from the manufacturer. Probably Mason & Hanger should ask for an analysis certificate showing parts per million H₂O in each lot of catalyst shipped. Suggested packaging and storing procedures for the catalyst are discussed in Section H-4.

H-2. Specification on the Amount of Extractibles Allowed in a Fully Cured RTV Silicone Rubber

If any of the materials extracted from an RTV silicone rubber (using the procedure described in Section G-1) show a reaction with the FEFO or inhibit the proper functioning of the black box containing electrical equipment, Mason & Hanger must require the manufacturer to eliminate these materials from the base formulations.

Establishing a maximum acceptable limit of extractible material in the cured rubber is the most realistic specification to place upon the manufacturer. All incoming lots can then be tested according to Section G-1 and base material showing an unacceptable level of extractible materials can be rejected.
(See Section H-4, part b, for further discussion of the purchasing variables of the RTV base).


The present author believes that the presence of alkali metal ions in the base rubber plays a vital role in determining the extent of reversion resistance. A few parts per million of K⁺ in the rubber may improve reversion resistance by reacting with some of the CH₃ COH to form KOOC-CH₃ (which, however, acts itself as a rearranging catalyst at sufficiently high temperatures). The role played by K⁺ or other alkali metal ions in improving reversion resistance must be marginal since these ions are undoubtedly already present in the base rubber in salts with weak acids.

A careful plot of the appropriate measure of lifetime of the confined rubber at an elevated temperature (See Sections E-1, E-2, and E-3) versus total alkali and alkaline earth metal ion concentrations, in parts per million, will probably show a maximum in lifetime for some finite concentration of alkali plus alkaline earth metal ions.

Probably flame photometry is the easiest and most sensitive way of measuring the amounts of individual alkali and alkaline earth metal ions present in the manufacturer's base rubber.
Postulated dependence of lifetime of the confined rubber (as measured by durometer, tensile strength, or other macroscopic physical properties) versus the total concentration of alkali plus alkaline earth metal ions.

If these postulates by the author are proven to be correct and the amounts of alkali and alkaline earth metal ions providing maximum lifetime under confinement are experimentally established, such levels should be incorporated into a specification on incoming lots of RTV base material from the manufacturer.
H-4. General Suggestions Regarding Purchase of Manufacturer's Materials

a. Catalyst

The dibutyltin diacetate should be purchased in lots of small, moisture tight containers containing sufficient catalyst for one day of production operation. The containers of catalyst and the catalyst dispenser (described in Fig. 18 by H. W. Lichte and I. B. Akst in their second progress report on this project) should be stored in a dry box. Prior to a day's production run, the operator can go to the dry box, dump one container of catalyst into the dispenser, seal the dispenser tightly, and proceed to the normal production operation. These procedures will assure that fresh catalyst is used to catalyze production material each day, and will insure that moisture contamination of the catalyst does not occur during storage or during the filling of the dispenser.

b. RTV Base

The RTV base should be purchased from the manufacturer in containers which contain sufficient material for one day of production operation. If the base is purchased in containers of this size, each container can be tested in the control laboratory for cure rate and physical properties, and for other variables described elsewhere in this report.

If the base is purchased in small (1 pound) containers, thorough testing by the control laboratory of the material in each can is probably impossible. The unsettling possibility of using one or more clearly
inferior 1 pound cans of base in the production operation cannot be allowed. The suggestion outlined in the preceding paragraph eliminates this possibility.

In progress report No. 2, Lichte showed that a considerable reduction in variability of physical properties of the RTV silicone rubber could be achieved by thoroughly mixing the RTV base material on a paint shaker prior to catalyzing to form the rubber. The present author suggests that this mixing process be adopted as a standard procedure before quality control tests are run on any can of base from the manufacturer. If a particular can of base is not used in production for a period of one month or longer after testing in the quality control laboratory, the mixing procedure should be repeated before that base is used in the production of devices.
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