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HYDROGEN GAS FROM CURED RTV SILICONES

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DEVELOPMENT DIVISION

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MASTER

Process Development
Endeavor No. 101

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RTV

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ABSTRACT

Eight different RTV silicones were sealed in containers and after preselected times the amount of hydrogen in the containers was determined. The silicone samples were conditioned at 80 C in a 100% RH air atmosphere and at 23 C in a dry air atmosphere.

The amount of gas from duplicate samples varied considerably. The cause of these variations was investigated and it was determined that humidity in a helium atmosphere produced the maximum hydrogen, and the amount of hydrogen is less if oxygen is present in the atmosphere.

INTRODUCTION

Los Alamos Scientific Laboratory (LASL) requested that Mason & Hanger investigate the hydrogen gas from cured RTV silicone potting material.

The materials investigated were:

1. Dow Corning 93-119
2. Dow Corning 93-120
3. Dow Corning 95-077
4. Sylgard 184
5. Sylgard 186
6. General Electric 664
7. General Electric 6153
8. General Electric 6152

These materials are classed as addition curing silicones and they normally consist of a two part kit. The "resin" part contains a linear dimethylpolysiloxane (DMPS) with reactive vinyl groups and some form of a platinum catalyst. The second "catalyst" part contains a crosslinker such as polymethylhydrosiloxane (PMHS)

with active hydrogen sites (see Fig. 1).

Fig. 1. The Crosslinking Reaction Between a Vinyl Group and an Active Hydrogen of a Two Component Silicone Rubber System

If a portion of the active hydrogen sites do not react with vinyl groups these sites would then be subject to hydrolysis and hydrogen would be produced.

EXPERIMENTAL

A standard test was developed to determine the amount of hydrogen produced and the approximate rate of hydrogen evolution. This was accomplished by sealing silicone samples in a container with an air atmosphere and a supply of water.

Three 44.5 mm diameter by 3.17 mm thick disks (~ 15 grams) were placed in each container. These disks were placed on an aluminum cylinder in the container with stainless steel screen wire between the samples to allow good air circulation around the samples (see Fig. 2).

Three containers of each silicone sample were prepared and one gram of water was added to two of the containers. The three containers were sealed and the two containing water were cooled with liquid nitrogen to freeze the water while being evacuated and leak checked. The containers were backfilled with air to 26.6 kPa and the two containers with water were stored at 80 C. The "dry" container was stored at 23 C.

At the end of 7, 50, 125 and 200 days, the two containers with water were removed from storage, cooled with liquid nitrogen and their atmosphere removed and fractionated to separate the hydrogen from the air. The volume of hydrogen was measured and each sample analyzed by a mass spectrometer to assure that the hydrogen was fractionated from the air. After analysis at 7, 50 and 125 day periods the containers were refilled with air and returned to the 80 C storage. The 23 C

Fig. 2. Test Assembly used to Measure the Hydrogen Gas for Various Silicone Rubbers

samples were analyzed for hydrogen after 200 days. The data are given in Table I and plots of the 80 C results are shown in Figs. 3 through 10. These data show a considerable amount of variation in the volume of hydrogen evolved by supposedly duplicate samples. The plots indicate an initial rate (in the first 7 to 10 days) followed by a much slower rate. If hydrolysis of the active hydrogen is the only mechanism for hydrogen evolution the rate should approach zero but this does not appear to be the case at least over the time period studied.

Table I. Hydrogen Gas from RTV Silicones

Material	Container No.	Temperature (C)	Sample Weight (g)	Time (Days)	H ₂ (mL)	H ₂ (mL/g)	Material	Container No.	Temperature (C)	Sample Weight (g)	Time (Days)	H ₂ (mL)	H ₂ (mL/g)
93-119	115	80	13.69	7	9.40	0.687	Sylgard 186	16	80	19.47	7	5.70	0.293
				49	0.029	0.002					42	34.78	1.79
				119	0.315	0.023					142	3.27	0.168
				231	2.53	0.185					236	4.06	0.208
	129	80	13.20	7	9.36	0.709		117	80	18.73	8	9.56	0.510
				49	12.87	0.975					44	18.18	0.971
				120	0.914	0.069					146	0.98	0.052
				232	2.50	0.189					236	3.12	0.167
	127	23	13.40	230	Trace	Trace		134	23	19.70	237	0.178	0.009
93-120	71	80	15.75	7	2.27	0.144	GE 664	37	80	18.94	12	54.99	2.90
				62	23.45	1.49					67	15.20	0.803
				136	3.28	0.208					123	8.46	0.447
				225	5.608	0.356					202	7.285	0.385
	116	80	15.74	9	1.95	0.124		11	80	18.9	13	49.89	2.63
				62	1.69	0.107					68	5.75	0.304
				139	1.56	0.099					124	0.55	0.029
				226	9.313	0.592							
	130	23	16.74	226	0.760	0.045		1	23	19.99	203	2.530	0.133
95-077	49	80	19.54	6	21.38	1.09	GE 6153	93	80	16.65	6	Leak	
				48	1.97	0.101					48	9.41	0.565
				144	0.511	0.026					147	0.622	0.037
				231	1.99	0.102					228	3.95	0.237
	111	80	19.43	7	16.71	0.860		167	80	16.5	7	8.82	0.534
				48	0.82	0.042					49	2.04	0.123
				146	0.378	0.019					148	0.584	0.035
				232	3.28	0.169					229	1.345	0.081
	3	23	19.57	232	0.664	0.034		74	23	16.23	230	0.512	0.032
Sylgard 184	6	80	12.33	6	33.59	2.72	GE 6152	38	80	13.37	8	10.65	0.797
				48	11.33	0.919					46	1.97	0.147
				146	0.907	0.074					85	0.242	0.181
				234	3.573	0.290					232	2.080	0.156
	2	80	13.38	7	41.31	3.09		19	80	12.61	6	10.10	0.801
				49	0.483	0.036					47	12.25	1.01
				152	0.532	0.040					86	0.418	0.033
				235	2.115	0.158					233	1.702	0.135
	133	23	13.98	235	2.16	0.155		126	23	15.41	233	0.727	0.048

- ⊙ TS No. 115 at 80 C
- TS No. 129 at 80 C

Fig. 3. Hydrogen Gas from Dow Corning 93-119

Fig. 4. Hydrogen Gas From Dow Corning 93-120

- TS No. 49 at 80 C
- TS No. 111 at 80 C

Fig. 5. Hydrogen Gas from Dow Corning 95-075

- TS No. 6 at 80 C
- TS No. 2 at 80 C

Fig. 6. Hydrogen Gas from Sylgard 184

- TS No. 16 at 80 C
- TS No. 117 at 80 C

Fig. 7. Hydrogen Gas from Dow Corning Sylgard 186

- TS No. 37 at 80 C
- TS No. 11 at 80 C

Fig. 8. Hydrogen Gas from General Electric 664

- TS No. 32 at 80 C
- TS No. 167 at 80 C

Fig. 9. Hydrogen Gas from General Electric 6153

- TS No. 38 at 80 C
- TS No. 19 at 80 C

Fig. 10. Hydrogen Gas from General Electric 6152

The maximum quantity of hydrogen evolved for each material is shown in Table II.

Table II. Total Hydrogen Evolved from Several Silicones

(Hydrogen Evolved at 80 C in ml/g Corrected to STP)

Sample	Time Days	H ₂ (ml/g)
DC 93-119	232	1.94
DC 93-120	225	2.20
DC 95-077	231	1.32
Sylgard 184	234	4.00
Sylgard 186	236	2.45
GE 664	202	4.54
GE 6153	228	1.37
GE 6152	232	2.36

The reason for variations between samples was investigated and the following determinations were made.

1. Analysis of the atmosphere in the containers showed no oxygen. The oxygen had been consumed by the sample.
2. The free volume of the containers were different so the samples contained different amounts of oxygen.

A preliminary investigation was made to determine the effect of both oxygen and water on Sylgard 184.

Duplicate assemblies were made with each of the following atmospheres:

1. Helium
2. Helium and Water
3. Helium/Oxygen/Neon
4. Helium/Oxygen/Neon and Water

Since it was not possible to match the free volumes of the containers, a special mixture of helium, oxygen, and neon (73/17/10) was prepared. By determining the amount of neon at the end of the test, the amount of oxygen originally in the container could be calculated.

These samples were analyzed after 40 days at 70 C for oxygen and hydrogen. These data are given in Table III.

Table III. Hydrogen Gas from Sylgard 184 that was Backfilled with Different Atmosphere

Atmosphere	Container No.	H ₂ (ml/g)	Consumed Oxygen (ml/g)
He + H ₂ O	191	12.7	*
	192	11.0	*
He (dry)	193	0.22	*
	194	0.20	*
He/O ₂ /Ne + H ₂ O	195	4.6	23.1
	196	5.4	12.4
He/O ₂ /Ne (dry)	197	0.39	6.8
	198	0.50	6.5

*Contained only helium.

Comparison of the helium and helium/water samples shows that water increased the amount of hydrogen. Comparison of the helium/water and helium/oxygen/neon/water samples shows that oxygen reduces the amount of hydrogen gas.

Essentially all of the oxygen was consumed in the samples containing the helium/oxygen/neon mixture.

An additional test was conducted to determine if water was consumed with atmospheres of helium and helium/oxygen/neon by sealing a sample of Sylgard 184 in a container

with a hydrometer probe. The samples were conditioned at 70 C for approximately one month and in both cases the dew point decreased with time.

CONCLUSIONS

There are at least two mechanisms that effect the amount of hydrogen

gas present in the containers. Tests are planned to determine rates for:

1. Water Consumption
2. Oxygen Consumption
3. Hydrogen Evolution

With these data it should be possible to define the parameters for a standard test which will give reproducible results.

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