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ORGANIC MATERIALS DIVISION QUARTERLY REPORT

January Through March 1978

J. K. Lepper

June 29, 1978

Work performed under the auspices of the U.S. Department of Energy by the UCLLL under contract number W-7405-ENG-48.

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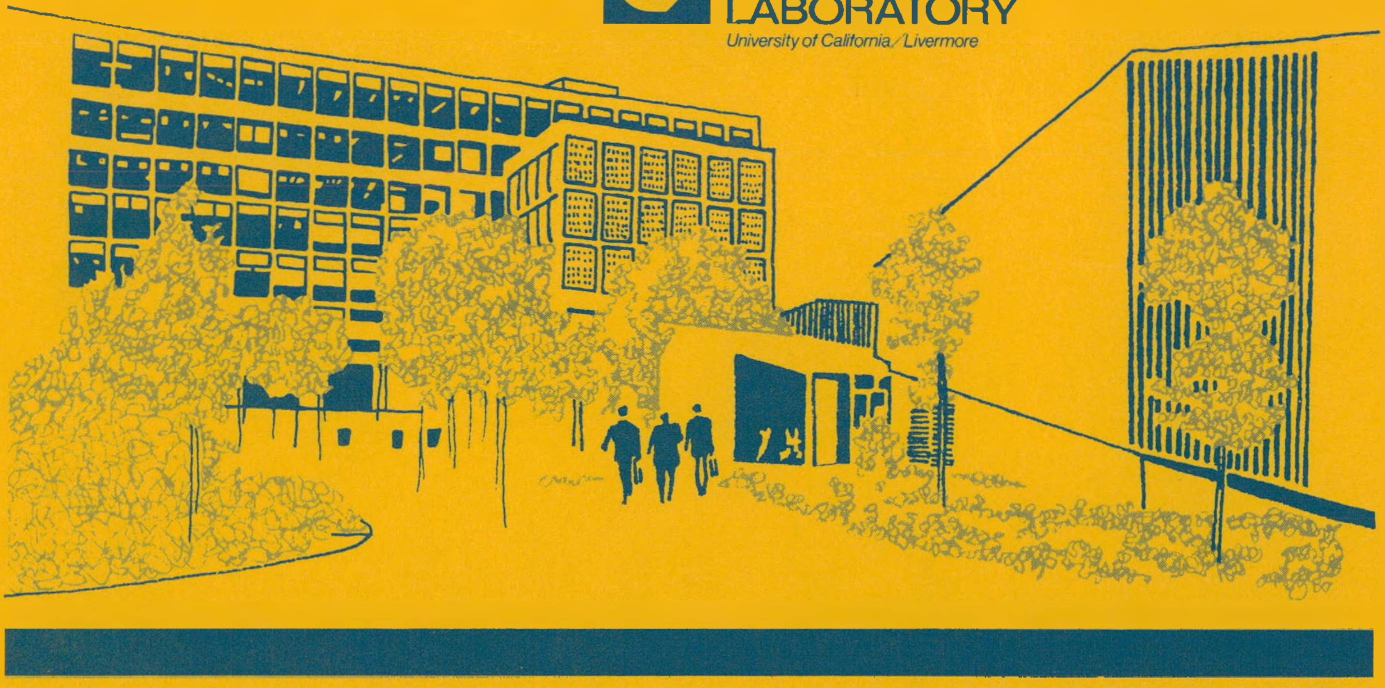

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FOREWORD

This document describes research and development work in the Organic Materials Division. It contains brief articles summarizing the current status of research and development projects. The articles are intended to give interested readers a concise statement of the Division's activities; hence, the experimental details are kept to a minimum. However, principal investigators are identified and our readers are encouraged to contact these workers directly if more information is desired.

CONTENTS

Production/Stockpile

We have synthesized silicone gum of molecular weight 500 000, which is suitable for making cellular silicone cushions.

LLL and Pantex are engaged in a cooperative program to develop potting compounds to replace those discontinued by Dow Corning.

The new substitute potting compounds developed at LLL for the W68 retrofit have higher shear moduli and dynamic viscosity than the discontinued DC-93 polymers.

Energy

We have modified the ZnSe cycle to improve the efficiency and process design.

Abstracts

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*Argonne National Laboratory, Argonne, Illinois

ORGANIC MATERIALS DIVISION QUARTERLY REPORT

PRODUCTION/STOCKPILE

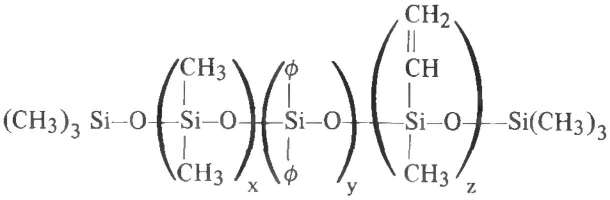
Synthesis of W97 Silicone Gum for Use in Cellular Silicone Cushions

Introduction

Union Carbide has discontinued making cellular silicone (from which we make cushions) and W97 gum from which the cellular silicone is made. The processing characteristics as well as mechanical, compatibility, and aging behavior are well known for cushions based on W97 gum. We are working to develop the capability to synthesize W97, rather than seeking new commercial gums, which would have to be fully certified in the cushion application.

Progress

We desire to synthesize a silicone gum identical to the W97 gum produced by Union Carbide. We are looking for a molecular weight of 5 to 8 × 10^5 and a vinyl content of 0.18%. The structure of the W97 polymer is shown below:



$$(CH_3)_3\,Si{-}O\left(\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right)_x\left(\overset{\phi}{\underset{\phi}{Si}}{-}O\right)_y\left(\overset{CH_2=CH}{\underset{CH_3}{Si}}{-}O\right)_z{-}Si(CH_3)_3$$

where

$x = 6500$
$y = 120$
$z = 10$.

We have synthesized this polymer by reacting octamethylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane, and polymethylsiloxane in the presence of a base catalyst. The amounts of initiator (potassium silanolate) or end blocker (polymethylsiloxane) required for a given molecular weight can be calculated from the following equation:

$$\text{Degree of polymerization} = \frac{\text{Tetramer concentration}}{\text{Probability of initiation} \cdot \text{Initiator concentration}} .$$

We first held end blocker constant and varied the catalyst concentration until a 90% conversion was achieved. The catalyst concentration was then held constant and the end-block concentration varied to obtain the required molecular weight (Fig. 1). Finally, knowing the end-blocker concentration and the required degree of polymerization, the minimum amount of catalyst could be calculated. We are now able to produce W97 silicone gums of the 5 to 8 × 10^5 molecular weight desired. In a recent experiment in which the target molecular weight was 5.5 × 10^5, we actually obtained a molecular weight of 5.33 × 10^5 (see Table 1).

Future work includes scaling up the polymerization. A large batch (3 kg) of W97 will be synthesized. The gum will then be processed through the Y1668 and Y3219 stages and finally X3333 or Y3260 cellular silicone cushions will be made. Further, we will snythesize the block polymer Y3976, which is made of the same tetramers.

Development of Alternate Silicone Potting Compounds

Introduction

Because Dow Corning Corporation has discontinued production of the entire series of silicone potting compounds that the DOE now uses in WR production, we must develop alternate materials for future needs, and especially for the W68 retrofit. With LASL's help, LLL and Pantex have begun a cooperative program to develop such materials for both LLL and LASL.

Progress

Dow Corning has discontinued production of silicone potting compounds 93-119, 93-120, and 93-122. We are developing a series of substitute compounds based on Dow Corning's Sylgards 184 and 186, Dielectric Gel Q3-6527, Accelerator XCF3-6559, and Dow Corning 1107 fluid. We are also using Cabot's Cab-O-Sil MS 75 as a thickening agent. These materials are similar in chemistry to the discontinued products, and are commerically available products used in relatively large volumes for electronic encapsulation.

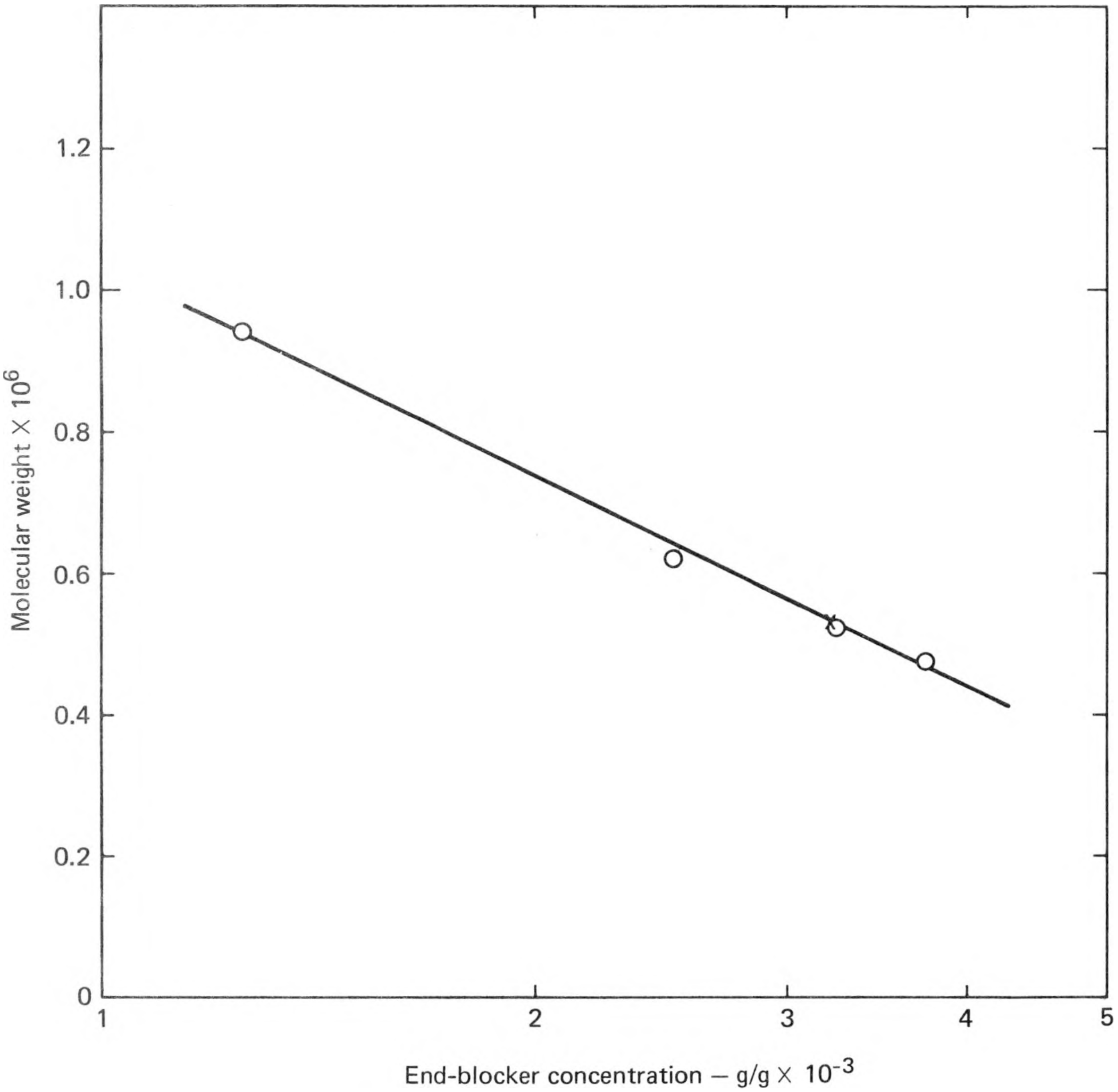


Fig. 1. Molecular weight vs. end-blocker concentration for W97 gum.

Table 1. Polymerization runs aimed at synthesizing W97 silicone gum.

Batch number	TJ-29	TJ-31	TJ-32	TJ-30	TJ-33	TJ-34
End-blocker concentration, g/g × 10^{-3}	1.25	2.50	3.08	3.75	3.08	3.08
Potassium silanoate concentration, g/g × 10^{-3}	5.00	5.00	5.40	5.08	2.51	1.65
Molecular weight (× 10^5)	9.4	6.2	5.3	4.7	5.5	2.9
Yield, %	88	90	90	90	89	60

The LLL and Pantex programs are parallel programs utilizing different lots of major compounds. LLL and Pantex are duplicating certain experiments to confirm the data and check on the equality of data from both organizations. The cooperative program we are undertaking is designed to generate only the basic information that we need to establish that we have suitable substitute potting compounds. Additional effort will be needed to compile all the information we should have for a thorough knowledge of the new materials. Details of the experimental program are in Ref. 1.

Most of the analyses and chemical characterizations of the starting materials have been completed. We have established that the following composition will substitute for potting compound 93-119:

	Parts by weight
Sylgard 184 resin	100
Sylgard 184 curing agent	10
Dielectric Gel Q3 resin	5
Dielectric Gel Q3 curing agent	5
Accelerator	8

We have also established a substitute composition for 93-120:

	Parts by weight
Sylgard 184 resin	40 to 43
Sylgard 184 curing agent	4 to 4.3
Sylgard 186 resin	60 to 57
Sylgard 186 curing agent	6 to 5.7
Accelerator	6

Representative cured formulations of both these formulations are being characterized.

The amount of accelerator required to give new compounds based on Sylgard 184 a snap time of 90 min. is 6 parts per 100 parts of 184 resin and 10 parts of 184 curing agent. This formulation is being characterized.

One of the compounds to be replaced is DC 93-120 resin cured with DC 93-122 curing agent to give a fast setting, relatively weak material. We have developed a substitute material based on the Dielectric Gel, Accelerator and DC 1107. Since the Dielectric Gel Q3 is very slow curing and could not be speeded up enough by the addition of accelerator, DC 1107 was added to further accelerate the cure. DC 1107 is a methyl hydrogen polysiloxane fluid, which liberates hydrogen to react with the vinyl groups in the Q3. We have developed formulations with a gel time of 15 to 20 min. A representative formulation is listed below:

Material	Parts by weight
Dielectric Gel Q3 Resin	50
Dielectric Gel Q3 Curing Agent	50
Accelerator	5-10
DC 1107 Fluid	0.9-1.0

Characterization of the substitute material is in progress. Work has begun on the DC 93-122 substitute.

Characterization of Silicone Potting Compounds

Introduction

Because Dow Corning Coporation has discontinued production of the entire series of silicone potting compounds that DOE now uses in WR production, we must develop alternate materials for future needs, and especially for the W68 retrofit. To replace the Dow Corning 93-119, 93-120, and 93-122 compounds, we are developing a series of substitute compounds based on Dow Corning's Sylgards 184 and 186, Dielectric Gel Q3-6527, Accelerator XCF3-6559, and DC 1107 fluid. We are also using Cabot's Cab-O-Sil MS 75 as a thickening agent. This study is a part of the characterization of these potting materials.

Progress

The eccentric rotating disk geometry can be used to measure dynamic mechanical properties of materials such as these silicone compounds. The storage (G') and loss (G'') moduli of the Sylgard series of crosslinked silicones are consistently higher than the DC 93 silicones: G' (Sylgards) $\cong 3.5 \times 10^5$ dynes/cm^2 as compared with G' (DC 93) $\cong 1.5 \times 10^6$ dynes/cm^2, and G'' (Sylgard) $= 5 \times 10^5$ dynes/cm^2 as compared with G'' (DC 93) $= 4 \times 10^4$ dynes/cm^2. The higher moduli probably correspond to the increased crosslink density of the Sylgard resins. Dynamic viscosities at 100 radians/s are 5×10^3 and 4×10^2 poise for Sylgards and DC 93 cured polymers, respectively.

By addition of filler or diluent it is possible to match mechanical properties at some temperature and frequency. However, because the Sylgard resins are chemically different from DC 93, the material properties will not be the same over a range of temperatures and frequencies. If the chemical structure of the crosslinking agent and copolymer composition can be identified, it should be possible by chemically altering the Sylgard to approximate the original material more closely. Details of this work are reported in Ref. 2.

The ZnSe Thermochemical Hydrogen Cycle

For the past 5 years we have been working to develop thermochemical cycles for the production of hydrogen. The cycle that we have concentrated most of our efforts on is based on zinc selenide. The initial stages of this cycle and the improvements we have made have been described elsewhere.[3]

A modified version of this ZnSe cycle, which shows significant advantages in efficiency and process design, has been developed. This modified version is described by the following major reaction steps:

$$(1)\quad ZnO + Se(l) + SO_2(g) \xrightarrow{800K} ZnSe + ZnSO_4$$

$$(2)\quad ZnSe + 2HCl(aq) \xrightarrow{350K} ZnCl_2(aq) + H_2Se(g)$$

$$(3)\quad ZnCl_2(l) + H_2O(g) \xrightarrow{900K} ZnO + 2HCl(g)$$

$$(4)\quad ZnSO_4 \xrightarrow{1200K} ZnO + SO_2(g) + 1/2\, O_2(g)$$

$$(5)\quad H_2Se(g) \xrightarrow{750K} Se(l) + H_2(g).$$

By converting $ZnCl_2$ directly to ZnO by steam hydrolysis, Reaction (3) improves the cycle by reducing the number of moles of $ZnSO_4$ decomposed (per mole of H_2 produced) from 2 to 1. This improvement allows us to spread the heat input over a 400 K range for Reactions (3) and (4) which are two endothermic reactions requiring heat input.

Thermodynamic calculations based upon literature data[4-6] indicate that reasonable yields of HCl(g) are to be expected from Reaction (3) at about 900-1000 K by reacting steam with molten $ZnCl_2$, i.e.

$$(pHCl)^2/pH_2O = 3 \text{ kPa } (0.03 \text{ atm}) \text{ at } 900K$$

$$\text{and } 13 \text{ kPa } (0.13 \text{ atm}) \text{ at } 1000K.$$

We have recently carried out exploratory transpiration experiments to obtain approximate rate and yield data. In these experiments, a carrier gas, N_2, saturated with $H_2O(g)$ near room temperature, was passed over molten $ZnCl_2$ with a surface area of about 2 cm^2 for a contact time of approximately 2 s. The unreacted H_2O (g) was absorbed in an in-line $Mg(ClO_4)_2$ trap. Product HCl was collected, its volume measured, and its purity determined by infrared analysis. Results of these experiments indicate that equilibrium is readily attained at temperatures above 800 K. Equilibrium data at 780 to 980 K are illustrated in Fig. 2. The experimentally measured equilibrium points lie about a factor of 1.8 above the calculated curve based on the literature, except at the lowest temperature where equilibrium probably has not been attained.

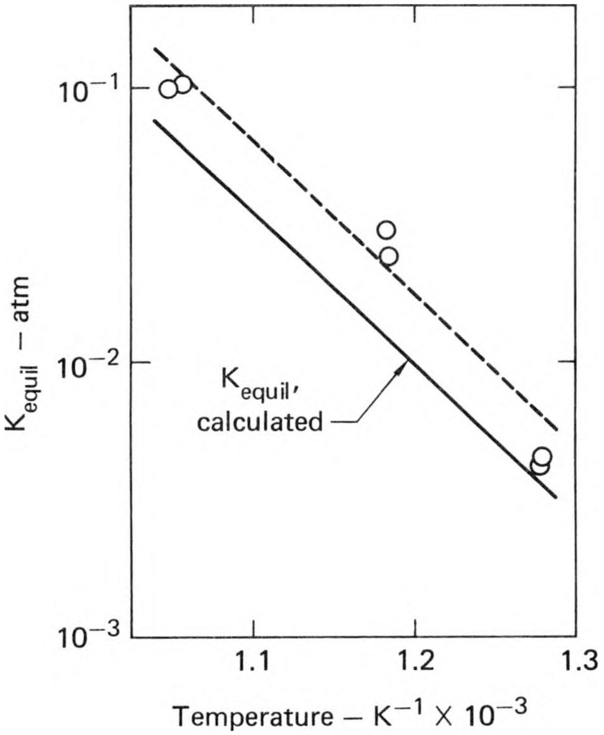


Fig. 2. Transpiration measurements of K_{equil} for Reaction (3).

ABSTRACTS

Investigation of the Safety of Explosives with Concrete (Grout)

In future Nevada Test Site (NTS) operations it is possible that grout (concrete) will come in direct contact with high explosive. The specific concern is that the alkalinity of the grout and/or the elevated temperature of curing grout may pose a safety or compatibility problem if the grout and explosive come into intimate contact.

We exposed a number of explosives to the conditions of alkalinity and temperature that may occur. In our experiments, we looked for any sign of reaction or incompatibility.

The current candidate grouts HPNS-II and LLL-IA have a PH of 12.0 and are mildly alkaline. The grouts present no safety or compatibility problems with LX-10-0, HMX, PETN, or PBX 9407 as either cured or uncured material. As long as the PH remains at 12 or below, no safety problems are anticipated. Details of this work are reported in Ref.7.

Infrared Single Photon Absorption Reaction Chemistry in the Solid State: The System SiH_4 and UF_6*

A Chemical reaction between SiH_4 and UF_6 has been induced with infrared photons of low flux density (< 25 mW cm^{-2}) at 12 K under matrix isolation conditions with products that are the same as the gas phase thermal reaction and with an activation energy about 15 × lower. This is another example of the single photon absorption reaction chemistry in the solid state (SPARCSS) process. For details see Ref. 8.

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