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CALLERY CHEMICAL COMPANY UNCLASSIFIED

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August 12, 1963

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MONTHLY PROGRESS REPORT NO. 5

to

Sandia Corporation

from

Callery Chemical Company

[redacted]

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MAR 1 1966
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Submitted by:

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1st Review Date: 10/22/97	UNCL
Authority: Name: R B Cranor	
2nd Review Date: 10/28/97	DECLASSIFY
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CALLERY CHEMICAL COMPANY

RESEARCH & DEVELOPMENT DIVISION · CALLERY, PA. · EVANS CITY 3510 · TWX-EVANS CITY 136

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Serial AB-5
Aug. 12, 1963
Page 1

Sandia Corporation
Post Office Box 5800
Albuquerque, New Mexico

Attn: Mr. E. B. Bergquist, 4321

Ref. Sym: 4333/142, P. O. 13-5966

Dear Mr. Bergquist:

The following constitutes the fifth monthly report for the period July 1 to July 31, 1963, as required under Purchase Order 13-5966:

Experimental investigation was continued on Phase I, Part 3 of the program. Presently our efforts have been devoted to selecting one of the various methods of preparing hydrazino bisborane, the alternate material for this program.

The results this month show that the pyrolysis of hydrazine monoborane is the most satisfactory method of preparing hydrazino bisborane. The purification procedure for obtaining hydrazino bisborane from the pyrolysis product requires more development.

BACKGROUND

Several methods of preparing hydrazino bisborane have been reported in the literature. These methods are shown by the following equations:

1) $2\ N_2H_4BH_3 \longrightarrow BH_2N_2H_2BH_2 + N_2H_4 + 2\ H_2$

2) $BH_3N_2H_4BH_3 \xrightarrow{\Delta} BH_2N_2H_2BH_2 + 2\ H_2$

3) $N_2H_5Cl + NaBH_4 \xrightarrow[\text{Ether}]{\text{Ethyl}} BH_2N_2H_2BH_2 + 2\ NaCl + N_2H_4 + 4\ H_2$

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The first method, i. e. the pyrolysis of hydrazine monoborane, was reported in detail by Goubeau and Ricker[1] and briefly by Esso[2]. In the work of Goubeau and Ricker, samples of hydrazine monoborane were pyrolyzed at 70°C, 85°C, 100°C and 200°C for various lengths of time. For example at 200°C, ninety seconds were required for complete reaction to hydrazino bisborane base on gas evolution measurements. (It is interesting to note the decomposition of $BH_2N_2H_2BH_2$ to BHNNBH occurs slowly, requiring five to eight days at 200°C to obtain eighty percent completion). After the pyrolysis was complete, the product was purified by extracting the pyrolysis residue with a solvent, such as ether, dioxane, tetrahydrofuran or water. Water was found to be the most successful. The hydrazino bisborane was then dried and analyzed. The biggest problem in drying was the removal of the occluded hydrazine produced by the reaction. The analytical results indicate that reasonably good hydrazino bisborane was prepared.

The second method of hydrazino bisborane preparation [2], i. e. the pyrolysis of hydrazine diborane, consists of heating a sample of hydrazine diborane for eight days at 100°C. The decomposition product was treated with twenty percent hydrochloric acid, filtered and the filter cake washed with cold water. The product was dried in vacuo for sixteen hours at 75°C followed by twenty four hours at 100°C. A recovery of seventy five percent was reported. No analytical data was reported.

The third method of preparation [3] was not reported in any detail. This is the method for preparing hydrazine monoborane except that tetrahydrofuran is used as the solvent. The use of ethyl ether is reported to give a product consisting of twenty five percent hydrazine monoborane and seventy five percent hydrazino bisborane.

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1. Goubeau, J. and Ricker, E. Hydrazine Borane and its Pyrolysis Products, Z. anorg. u. Allg. Chem. 310, 123-142 (1961), translated by Clayton, C. N., Oct. 17, 1962 for Callery Chemical Company.

2. Esso Research and Engineering Company, Quarterly Progress Report on Research on Advanced Solid Propellants, March 11, 1960 to June 10, 1960, Report No. 60-2, (Confidential).

3. Esso Research and Engineering Company, Quarterly Progress Report on Research on Advanced Solid Propellants, September 11 to December 10, 1960, Report No. 60-4, (Confidential).

EXPERIMENTAL

Two methods of preparing hydrazino bisborane were investigated this month. In the pyrolysis of hydrazine diborane, 45 grams of pilot plant hydrazine diborane (Lot No. 2, Jar No. 1) were heated in vacuo at 110°-115°C for seven days in a one liter flask on a Rinco Evaporator. The decomposition product was cooled to 0°C and 200 ml. of water were slowly added. The product foamed, filling the flask, condenser and addition funnel. The temperature rose to 20-25°C. After standing overnight, the foam was washed into the flask with additional water. The flask was cooled to 0°C and 20 ml of twenty percent hydrochloric acid was slowly added. The material foamed excessively for two to three hours. The product was filtered, washed with water then dried in vacuo for seven days at 60°C.

In the pyrolysis of hydrazine monoborane, difficulty was encountered in using a Rinco Evaporator. In the first attempt, 28 grams of hydrazine monoborane in a one liter flask was heated in vacuo at 60-65°C using a Rinco Evaporator. Within two hours, the reaction mixture foamed, plugging the evaporator. The decomposition product remaining in the flask was slurried in 300 ml of water and 30 ml of hydrochloric acid. The temperature rose to 50°C during this hydrolysis. The product was filtered, washed with water and dried in vacuo overnight.

In the second attempt using the Rinco Evaporator, 28.5 grams of hydrazine monoborane was charged to a five liter flask. The flask was heated to 110°C for about two hours, at 55°C for fifteen hours, then 110°C for three hours in vacuo in a Rinco Evaporator. At least half of the hydrazine monoborane charged was found as a sublimate into the head of the Rinco Evaporator.

Part of the product (3.2 grams) was slurried in 300 ml of C.P. methanol and refluxed for five hours, at which time half of the methanol was distilled off. The remaining material was cooled to 0°C, filtered and dried in vacuo overnight. About two grams of product was recovered.

The product remaining in the five liter flask was washed with water, filtered and dried in vacuo.

Because of the difficulty in the use of a Rinco Evaporator, 30 grams of hydrazine monoborane was pyrolyzed in a five liter flask

backed up with a three liter flask attached to a vacuum system. The three liter flask was used to contain the hydrazine monoborane sublimate. After heating at 105-110°C overnight, little foaming was observed and only a small amount of hydrazine monoborane sublimed from the five liter flask. The product is a fine white powder that is presently being treated with methanol.

RESULTS

The product from the pyrolysis of hydrazine diborane was a hard cake which powdered easily. The product analyzed: B, 24.6 mat/g; C, 1.23 mat/g; H, 70.7 mat/g; N, 19.2 mat/g; N-N bond, 9.3 mmole/g; Cl^-, 2.7 meq/g; $O^=$ (by difference), 18.3 mat/g. X-ray reports mostly boric acid and a faint line for hydrazino bisborane. Based on the elemental analysis, one possible product composition is:

Hydrazino bisborane	34.5%
Boric oxide	42.5%
Hydrazine hydrochloride	18.5%
Tetrahydrofuran	2.2%
Hydrazine	0.7%
TOTAL	98.4%

The hydrochloric acid treated product from the first attempt to pyrolyze hydrazine monoborane analyzed as follows:

	B mats/g	C mats/g	H mats/g	N mats/g	N-N mmole/g
Found	32.5	3.23	108	31.8	15.6
Theory for $BH_2N_2H_2BH_2$	35.9	0	108	35.9	18.0

X-ray analysis of this material indicates mainly the desired product, hydrazino bisborane.

DISCUSSION

The evaluation of hydrazino bisborane preparative methods indicates that the pyrolysis of hydrazine monoborane is the most

satisfactory method. The biggest problem at this point is the purification of the pyrolyzed product. The use of water and hydrochloric acid as reported in the literature appears to be undesirable based on boric acid (or oxide) and the Cl^- ion found in our product. The use of methanol has several advantages for this purification. All possible impurities (boric acid or oxide, hydrazine monoborane and hydrazine) are very soluble in methanol and should thus be removed from the product. The second advantage is the easier removal of methanol by drying in vacuo as compared to the removal of water.

The main advantage of the hydrazine diborane pyrolysis is the availability of quantities of hydrazine diborane. However, the purification of the pyrolyzed product is complicated by the excessive amount of foaming. In fact, the first run exploded during this operation. Also, the product obtained from the second pyrolysis contained only about thirty five percent hydrazino bisborane. No further work is planned on this method of preparation.

FUTURE WORK

1) Prepare the quantities of hydrazino bisborane required for thermal stability studies.

2) Determine if the thermal stability of hydrazino bisborane meets the requirements of this problem.

3) Search for other hydrogen-producing compounds which possess the necessary thermal stability.

Very truly yours,

CALLERY CHEMICAL COMPANY

R. B. Cruikshank/mb

R. B. Cruikshank
Project Leader

/mb