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CALLERY CHEMICAL COMPANY

SC-DC-3576X

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SANDIA SYSTEMATIC DECLASSIFICATION REVIEW	
1st Review Date: 10/21/97	Determination (Circle Numbers):
Authority: ADD	Classification Retained
Name: RB Cruikshank	Classification Changed to: U
2nd Review Date: 11-14-97	Contains No DOE Classified Information
Authority: ADD	Coordinate With:
Name: W Layne	Contains UCNI
	Comments:
	OK FOR OPENNET

Serial No. AB-8

Copy 4 of 6

September 13, 1963

RS 3427 43540

MONTELY PROGRESS REPORT NO. 6

to

Sandia Corporation

[redacted]

from

Callery Chemical Company

INVENTORIED MAR 8 '65 3422-3

SANDIA SYSTEMATIC DECLASSIFICATION REVIEW DOWNGRADING OR DECLASSIFICATION STAMP	
CLASSIFICATION CHANGED TO: U	AUTHORITY: W C Layne
Emelda Selph 11/19/97	
PERSON CHANGING MARKING & DATE	RECORD ID: 98SN0817
Willem Layne 12-15-97	
PERSON VERIFYING MARKING & DATE	DATED: 11/17/97

INVENTOR

MAR 1

3428-3

Submitted by:

R B Cruikshank

R. B. Cruikshank
Project Leader

Approved by:

H S Uchida

H. S. Uchida
Assistant Research Director

Wrote 19 Sept

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George F. Huff
3421-3

George F. Huff
Vice President
Research and Development

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

This document consists of 7 pages

Copy No. 4 of 6, Series A

Serial AB-8
September 13, 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 sixth monthly report for the period August 1 to August 31, 1963, as required under Purchase Order 13-5966:

Experimental investigation was continued on Phase I, Part C of the program. Presently our efforts have been devoted to the preparation and thermal stability of hydrazino bisborane and other alternate materials for this program.

The results of this month's work show that the rates of decomposition at 165°F of (1), hydrazino bisborane, (2), a mixture of tetramethylammonium hydrotriborate(1) and triaminoguanidinium hydrotriborate(1-), and (3) a mixture of lithium borohydride and ammonium chloride are orders of magnitude higher than the 2.5 standard cc H_2 evolved/gm-mole contained H_2/yr as specified in the purchase order. Although these systems did not meet the stability requirements at 165°C, it is very possible that the requirements could be met at a slightly lower temperature. Initial stability investigations indicate that lithium borohydride is stable at 165°F. Investigation

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of lithium borohydride systems will begin after the necessary lithium borohydride is prepared. Work has also started to prepare aminoborane decamer $[(BH_2NH_2)_{10}]$.

EXPERIMENTAL

Stability Determinations

The thermal stability determinations were conducted in the same type of metal bombs as used for the hydrazine diborane ($BH_3N_2H_4BH_3$) stability studies except no hydrogen back pressure was used. This procedure is described in detail in MPR No. 4.

Hydrazino Bisborane Preparation

Three batches of hydrazino bisborane ($BH_2N_2H_3BH_2$) were prepared by the pyrolysis of hydrazine borane ($N_2H_4BH_3$) followed by methanol purification. A summary of these runs is presented in Table I. In these runs, the hydrazine borane was charged to a five liter flask backed up with a three liter flask to stop hydrazine monoborane sublimate. After evacuation (through the three liter flask), the five liter flask was heated. Upon completion of the pyrolysis as indicated by the cessation of gassing and foaming, the crude hydrazine bisborane was added to methanol and heated to reflux temperature. After a given time at reflux temperature, the slurry was cooled and filtered. The hydrazino bisborane filter cake was washed with methanol then dried *in vacuo*.

Tetramethylammonium Hydrotriborate(1-)-Triaminoguanidinium Hydrotriborate(1-) System

A mixture consisting of 5.4270 grams of tetramethylammonium hydrotriborate(1-) and 4.5859 grams of triaminoguanidinium hydrotriborate(1-) was prepared for stability studies. The reaction to produce hydrogen should proceed in the following manner:

$$5\ (CH_3)_4NB_3H_8 + 2\ (N_2H_3)_3CB_3H_8 \longrightarrow 47\ H_2 + 15\ BN + 14\ C$$

The starting materials were produced at Callery Chemical Company under an ARPA sponsored program.

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TABLE I

RUN SUMMARY

HYDRAZINO BISBORANE PREPARATION

Run No.	$N_2H_4BH_3$ Charged Grams	Heating Time Hours	Heating Temp °C	Crude Product Grams	Crude Product B mat/g	Crude Product C mat/g	Crude Product H mat/g	Crude Product N mat/g	Crude Product N-N Bond mmole/g	Methanol Treatment Time Hours	Methanol Treatment Temp °C	Purified Product Grams	Purified Product B mat/g	Purified Product C mat/g	Purified Product H mat/g	Purified Product N mat/g	Purified Product N-N Bond mmole/g
1	30	2 18	70 110	18.7	34.8	1.4	116	35.7	17.4	2	25→64.7	17.5	35.2	1.4	118	35.2	17.6
2	29.7	2	75-80 110-115	18.2	----	---	---	----	----	3	64.7	16.1	35.3	1.7	116	35.1	17.5
3	59.1	3 2 4 20	25→66 69 95 105	38.5	34.4	1.3	116	36.6	17.9	15 6	25 64.7	34.7	35.2	1.0	110	37.5	18.0
4	Run 3 Purified Product			12.5						119	64.7	5.5	33.8	1	111	36.1	17.4
	Theory for $BH_2N_2H_2BH_2$				35.9	0	108	35.9	18.0				35.9	0	108	35.9	18.0

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Lithium Borohydride

The lithium borohydride was prepared previously at Callery Chemical Company. Only ten grams of this material was available. This sample was known to be about ninety-six percent pure with teflon being the major impurity.

Lithium Borohydride-Ammonium Chloride System

A mixture consisting of 2.9065 grams of the previously described lithium borohydride and 7.1337 grams of vacuum dried ammonium chloride was prepared for stability studies. The reaction to produce hydrogen should proceed in the following manner:

$$LiBH_4 + NH_4Cl \longrightarrow 4\,H_2 + BN + LiCl$$

RESULTS

A summary of the thermal stability studies is presented in Table II. The treatment of the data is the same as that for the hydrazine diborane thermal stability studies in metal bombs as discussed in MPR No. 4. The differences in the stability of the four hydrazino bisborane samples are probably due to small errors in pressure measurement, which are magnified when extrapolated to one year.

The methanol treatment to purify crude hydrazino bisborane was very satisfactory as indicated by the analytical results presented in Table I. These analytical results are also backed up by infrared spectra which in all cases indicated excellent hydrazino bisborane. The higher than theoretical hydrogen content of these samples as determined by analytical means is probably in error. The extensive treatment of these samples in terms of temperature and methanolysis leaves little chance for incomplete pyrolysis of the hydrazine borane.

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TABLE II

SUMMARY OF RESULTS

THERMAL STABILITY OF CANDIDATE SYSTEMS AT 165°F

System	Source of Material	Sample Weight Grams	Bomb Free Vol. cc.	Immersion Number	Time of Immersion Hours	Bomb Pressure PSIA	Cumulative Pressure Increase PSIA	Cumulative Time Hours	Decomposition Rate Over Constant Rate Period Std. cc H_2 Evolved / GM-mole contained H_2/yr.
$BH_2N_2H_2PH_2$	Run 1	7.01	82.7	1	49	11	11	49	2100
				2	477	12.7	23.7	526	
	Run 2	5.35	83.4	1	336	17.4	17.4	336	4400
	Run 3	5.38	88.4	1	249	12.3	12.3	249	6100
	Run 4	3.53	93.2	1	142	6.1	6.1	142	4800 (1)
2 $(N_2H_3)_3CB_3H_8$ / 3 $(CH_3)_4NB_3H_8$	CCC	0.34	90.5	1	21	13.7	13.7	21	
				2	161	4.7	18.4	182	
				3	337	2.0	20.4	519	10100
$LiBH_4$	CCC	3.02	90.4	1	384	(2)	(2)	384	(2)
$LiBH_4$ / NH_4Cl	CCC	10.04	87.8	1	87	(3)	---	---	---

1. Not quite levelled out during this period
2. Pressure fluctuations too small to be significant
3. Beyond limit of gage

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DISCUSSION

The rates of decomposition at 165°F of (1) hydrazino bisborane, (2) a mixture of tetramethylammonium hydrotriborate(1-) and triaminoguanidinium hydrotriborate(1-), and (3) a mixture of lithium borohydride and ammonium chloride are all orders of magnitude higher than the 2.5 standard cc H_2 evolved/gm-mole contained H_2/yr as specified in the purchase order (Table II column 10). Although these systems did not meet the stability requirements at 165°F, it is very possible that the requirements could be met at some lower temperature.

Other systems are available for this program. The use of lithium borohydride either by itself or with a second component as hydrogen generating systems, provide a possible means of meeting the stability requirements of this program. The use of materials containing methyl groups may not be satisfactory because of the possibility of forming methane and/or acetylene during the combustion. Aminoborane decamer $(NH_2BH_2)_{10}$ also offers a possibility. This material is purified by subliming at 302°F which indicates that the stability at 165°F should be satisfactory. Unfortunately, the method of preparing this material is not well described in the literature and preparative studies are required. A list of possible systems considered for this program is presented in Table III. All these systems are compared with the calcium hydride-molybdenum trioxide system on both a weight and volume basis.

FUTURE WORK

1) Prepare lithium borohydride for stability studies with sulfur and the various fluorine containing materials.

2) Study the preparation of aminoborane decamer to obtain enough material for stability studies.

3) Continue the investigation for other hydrogen generating systems.

Very truly yours,

CALLERY CHEMICAL COMPANY

R B Cruikshank

R. B. Cruikshank
Project Leader

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TABLE III

HYDROGEN GENERATING SYSTEMS

System	Sp. Gr.	Mole H_2 / g	Weight Improvement Factor	Mole H_2 / cc	Volume Improvement Factor
$3\ CaH_2 + MoO_3$	2.54	0.0111	1	0.0282	1
$BH_3N_2H_4BH_3$	0.91	0.0838	7.55	0.0762	2.70
$BH_2N_2H_2BH_2$	1.15	0.0539	4.86	0.0620	2.20
$LiBH_4 + NH_4Cl$	1.11	0.0531	4.78	0.0588	2.09
$(CH_3)_4NB_3H_8 + 4\ Li$	0.719	0.0647	5.83	0.0466	1.65
$2\ LiBH_4 + S$	0.926	0.0529	4.77	0.0490	1.74
$3\ (CH_3)_4NB_3H_8 + 2\ (N_2H_3)_3CB_3H_8$	0.879	0.0700	6.31	0.0615	2.18
$(BH_2NH_2)_{10}$	---- *	0.0693	6.24	------	----
$2\ LiBH_4 + MgF_2$	1.22	0.0378	3.41	0.0461	1.63
$2\ LiBH_4 + CF_2$	1.05	0.0427	3.85	0.0451	1.60
$2\ LiBH_4 + BeF_2$	1.01	0.0442	3.98	0.0445	1.58
$3\ LiBH_4 + AlF_3$	1.85	0.0257	2.32	0.0475	1.68
$LiBH_4$	0.66	0.0690	6.20	0.0455	1.61

* Not Reported