AD-787 303

DEVELOPMENT OF A SITE-MARKER BALLOON INFLATION SYSTEM

MSA Research Corporation

Prepared for:

Army Land Warfare Laboratory

June 1974

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AD 787 303

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Technical Report No. LWL-CR-03M73
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Development of a Site-Marker Balloon Inflation System
5. TYPE OF REPORT & PERIOD COVERED
6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)
8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Mine Safety Research Corporation, Division Mine Safety Appliances Co., R.D.#2, Evans City, Pa. 16033
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 03-M-73
11. CONTROLLING OFFICE NAME AND ADDRESS: Land Warfare Laboratory, Aberdeen Proving Grounds, Aberdeen, Maryland
12. REPORT DATE
13. NUMBER OF PAGES: 81
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
15. SECURITY CLASS. (of this report)
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Site Marker Balloon
Probability of Detection by Support Aircraft
Gas Generator - Solid Source
Helium Equivalent Gas Mixture
Sodium Borohydride
Dihydrazinium Sulfate
Lithium Hydride

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report presents the results of the development of a sodium borohydride-dihydrazine sulfate gas generator as a site marker balloon inflation system. This combination generated gas with an average molecular weight of 6.0 compared to 4.0 for helium. Nitrogen, water and hydrogen sulfide were the principle contaminants. The

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DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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20. addition of lithium hydride significantly reduced the water and hydrogen sulfide contents, lowering the molecular weight to approximately 4.3.

Studies on the charge demonstrated that the burning rate was primarily a function of pressed charged density. The balloon inflation gas was readily produced at the desired rate of approximately 5 SCFM.

The temperature of the gas generated by the solid charge was also shown to be a function of charge density and composition. Although tests on the final balloon material were not conducted it was felt that successful balloon inflations could be accomplisned with balloons constructed of polyester film.

Thermal stability tests on the final charge showed a premature gas release sufficient to consider it unsafe for storage. Reagent purification studies and microencapsulation of the basic ingredients failed to resolve this problem.

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SUMMARY

There is a need for a position marking device for use by ground units and individuals to mark positions under a heavily-forested canopy. A unit which is functionally acceptable has been developed by the U. S. Army Land Warfare Laboratory. The system is based on a tethered helium-filled balloon and flashing light. The helium is contained in a 40 cubic inch high-pressure helium bottle. The total weight of the system is 3 1/2 pounds.

Helium under pressure is considered unsafe for use under combat conditions, and a solid-source hydrogen generator system which has been developed by the Navy is considered to be too expensive for the present application. The objective of this program was to develop a site marker balloon inflation system that was reliable and light in weight, and one that could be economically produced under conventional mass production procedures.

A system based on sodium borohydride and dihydrazinium sulfate was studied which was potentially an economical gas generator system. The mixture generated a gas composition with buoyancy properties close to that of helium, met all of the operational requirements, but failed to meet military standards for storage stability.

A sodium borohydride-dihydrazinium sulfate charge generated a gaseous mixture of hydrogen, nitrogen, water and hydrogen sulfide with an average molecular weight of about 6.0, as compared to 4.0 for helium. The gas composition varied somewhat with the sodium borohydride-dihydrazinium sulfate ratio, but a stoichiometric ratio of 4:1 was found desirable. Added lithium hydride significantly reduced the water and hydrogen sulfide content, lowering the molecular weight of the buoyancy gas to approximately 4.3.

The gas generation rate, or burning rate of the charge was primarily a function of pellet density and available surface area. Free-standing pellets, pressed to densities above 1.1 g/cm^3, fractured upon release from the mold. Pellets with a density of about 1.1 g/cm^3 maintained integrity and produced gas at a rate above 5 SCFM.

Ignition of the charge was accomplished with an electric squib, heat paper, and a 5 gram sample of loose powder charge. Charge densities in the 1.1 g/cm^3 range ignited easily without delay. Charges with higher densities showed delays sometimes approaching 30 seconds.

Gas effluent temperatures were measured at the canister exit. Temperatures at this point ranged from 500 to 1000°F, but cooled quickly downstream. Slower gas generation rates were the primary method of lowering gas temperatures. Added lithium

hydride and sodium borohydride had similar effects, but to a lesser extent.

Thermal stability testing of the final gas generator formulation showed that with the dryest reagents, gas was released on standing at room temperature. Storage at 122°F, 43 degrees below mil spec, released 6.6 percent in only 10 hours. Obviously these conditions would rupture the inflation system in storage.

Microencapsulation or coating of the reagents, sodium borohydride and dihydrazinium sulfate, with a wall membrane of several polymeric materials produced a room temperature storable system; but storage at 165°F still caused excessive gas release.

The production of 50 units for evaluation by LWL was not considered since the system failed to satisfy the 165°F storage requirement.

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1. INTRODUCTION

1.1 Problem

The Land Warfare Laboratory has a requirement for a site marker unit for use by the military. Color-coded markers suspended above the tree canopy are needed to precisely locate positions of friendly troops for plane drops, pickup and assembly points, and when equipped with an aerial, to give assitance in radio transmissions.

Balloon systems have been tried as position markers on an experimental basis and have been found to be feasible and to have potential for meeting this requirement. A report covering the development of such a system, and the background of site markers in general, has been published by the U. S. Army Land Warfare Laboratory [1]. This system, designated as LWL's Elevated Site Marker, consisted of a spherical weather balloon filled from a 2 1/2 lb. high pressure bottle.

In most situations, the LWL system was adequate, but there were two serious shortcomings:

- The spherical balloon did not perform well in winds above 10 knots;
- The high pressure helium bottle was a heavy item and subject to explosive rupturing if hit by small arms fire or other velocity fragments.

LWL studied the balloon design and has shown that a V-shaped balloon, or a teardrop design, responds well in winds over 10 knots. There remained, therefore, the problem of finding a suitable replacement gas generator system for the helium bottle.

Studies at MSA Research Corporation had disclosed the production of hydrogen from solid chemical sources based on a mixture of sodium borohydride and dihydrazinium sulfate. This chemical mixture generates a blend of hydrogen and nitrogen approximating helium in buoyancy.

MSAR demonstrated a balloon inflation unit based on this system in 1970. The unit inflated an 8 cubic foot balloon in about 5 minutes with a hydrogen-nitrogen mixture consisting of about 85% hydrogen. Although incomplete and preliminary in construction, the unit weighed less than 2.5 pounds.

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1. Wood, Benjamin F., Improved Elevated Site Marker, Technical Rept. No. 74-07, December 1973, U. S. Army Land Warfare Laboratory, Aberdeen Proving Ground.

This program was for further development of this gas generation system to obtain properties compatible with military requirements. The contract specified that chemical charge studies be made in order to optimize the mix relative to the required gas generator characteristics which are as follows:

- buoyancy - The generated gases to have buoyancy at least equivalent to pure helium, compared at a temperature of 69 degrees Fahrenheit, and a pressure differential of 1 1/2 (1.5) inches of water at one atmosphere.

- rate of generation - The rate of generation is to nominally give five (5) SCF per minute.

- packaged weight - The packaged weight is not to exceed three (3) ounces per SCF of gas generated. This includes the igniter, filter screens, cooling tubes, etc.

- packaged volume - The packaged volume is to be the minimum compatible with other required characteristics.

- delivered gas temperature - The gas temperature delivered to the balloon should be the minimum compatible with other required characteristics, but shall not exceed 200 degrees Centigrade.

It further specified that filtration studies be conducted on the charge to insure that the delivered gas was sufficiently free from solid particles to maintain a safe pressure level in the charge container, and to insure that no particles contain sufficient heat to degrade the structural or gas-holding qualities of the balloon. In addition, thermal stability testing was to be conducted to insure that the final charge would meet military requirements. Two tests were to be conducted. They were: (1) an accelerated test at 165°F; and (2) a modified MIL-STD-304.

Finally, the program proposed a production of 50 generator cartridges with a capacity of 10 SCF to the characteristics outlined.

1.2 State of the Art

MSA Research Corporation has had a continuing interest in the problem of balloon inflation for the past several years, especially as related to the production of hydrogen from a solid chemical source. MSAR maintains an active development group in the production of gases such as O_2, H_2, N_2, CO_2, etc.

from solid sources, and with the knowledge of the need by the military, we were continually on alert for lighter weight and more economical systems that meet their needs.

Solid source hydrogen systems, in the past, have failed to meet one or more of the requirements for a balloon inflation unit. Sodium borohydride with either lithium hydroxide hydrate or oxalic acid failed to meet thermal stability requirements. Hydrazine bis-borane, on the other hand, is relatively expensive and extremely fast in its operation; the latter presenting both a heat and solids filter problem. A sodium borohydride-dihydrazinium sulfate system, the system proposed for this program, had been given a cursory examination on a past program, but its operational characteristics had not been fully evaluated. Later, while evaluating this system more completely, the total characteristics of the system were recognized as closely approximating the requirements for a balloon inflation unit, and the system was then specifically researched with the balloon application in mind.

The reaction is basically that represented by the equation:

$$4\ NaBH_4 + (N_2H_4)_2H_2SO_4 \longrightarrow Na_2S + Na_2O + 4\ BN + 10\ H_2 + 3\ H_2O$$

In actual practice only a negligible amount of water is produced. On the other hand, significant quantities of nitrogen are also produced which materially lower the average molecular weight of the gas to about 5.2, or somewhat less than that of pure helium.

This mixture, when pressed to a density of about 1.30 to 1.35 g/cm^3, burned at a rate of about 0.6 in./min. to deliver hydrogen at an efficiency of about 0.75 l/g. Thus, approximately 375 g of total charge is required to produce ten cubic feet of hydrogen, or about 325 g to produce ten cubic feet of a gaseous mixture of hydrogen and nitrogen containing about 65% hydrogen. At a density of 1.35 g/cm^3, the solid charge (375 g) occupies a volume of 278 cm^3 (17.0 in.^{3}).

The reaction is exothermic and is self-sustaining when initiated. Initiation can be accomplished by means of an electric squib or an M-42 military primer as the primary igniter, and a secondary booster charge (heat paper). The dissipation of the reaction heat is a major concern, but we demonstrated that 10 feet of aluminum tubing, weighing only 60 g, provides sufficient cooling to allow the inflation of even heat sensitive rubber weather balloons, as well as polyester plastic film balloons.

Some solids were produced in the gas stream but most of it remained behind as a clinker-like residue. It was not certain if filtration of the gas stream was necessary.

Figure 1 is a sketch of a prototype unit successfully demonstrated at LWL on April 9, 1970. Three units were tested. Two employed 3/8 inch aluminum tubing (0.035 in. wall thickness) as the cooling coils and weighed 2.46 pounds (without balloon and overpack). Both of these functioned successfully. One inflated a rubber weather balloon, which broke before full inflation after having been whipped by high winds onto a rough ground gravel. The second inflated an LWL-designed aerodynamic-lift 6 cu. ft. balloon, accomplishing the inflation in about five minutes. Excess gas was available and had to be allowed to escape. The balloon was flown and exhibited excellent lift properties. The third unit used 1/4 inch aluminum tubing (0.035 in. wall thickness) as the cooling coil and weighed 2.04 pounds (without balloon and overpack). This unit developed greater pressure than anticipated about a minute after ignition, and eventually blew a rupture disc (70-80 pounds). The generator charge burned quietly to extinguishment.

The following point deserves special emphasis. The sodium borohydride-dihydrazinium sulfate system is the most economical of the dry chemical hydride-based systems known to date. Sodium borohydride is a commercial commodity, and is the cheapest of the borohydrides. It is also considerably more economical than either of the more common complex metal hydrides, $LiAlH_4$ or $NaAlH_4$. Dihydrazinium sulfate, also a commercial commodity, sells for a fraction of the cost of the borohydride. This combination is potentially a basis for a truly economical solid chemical hydrogen source suitable for Site-Marker systems and, along with the several desirable characteristics of the system already demonstrated, was the basis for this effort.

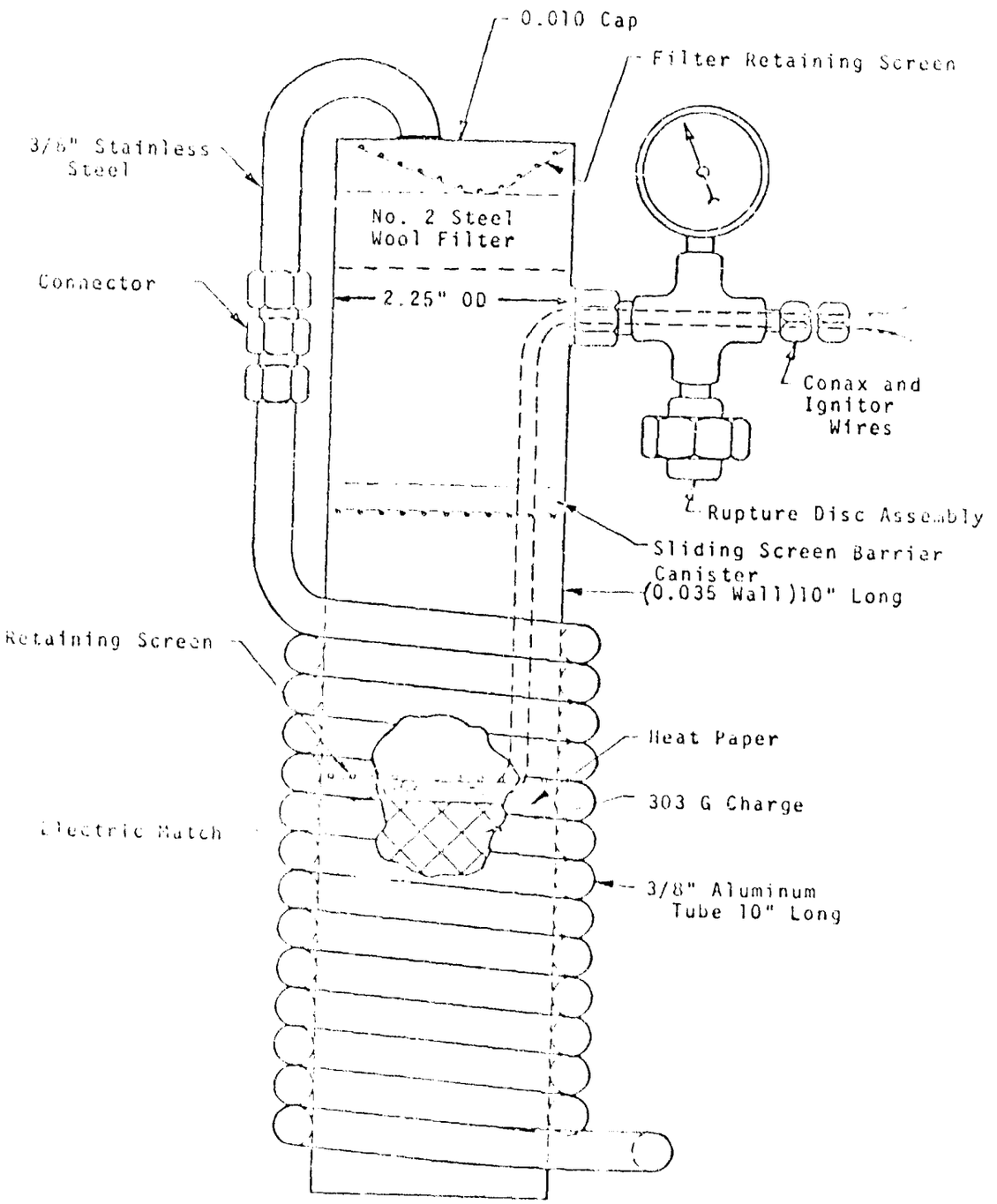

Figure 1 - Prototype Balloon Inflation Unit

2. DEVELOPMENT

The study was sub-divided into four tasks designed to give a logical development of a site-marker unit based on the sodium borohydride-dihydrazinium sulfate gas generator system. The program was designed to optimize the system for a period of performance, buoyancy, and temperature of produced gas; study the filtration requirements; and to check the storage stability. The tasks and a brief description of each are as follows:

Task 1 - Chemical charge studies - to optimize the gas composition for increased buoyancy, to study additives which may reduce the effluent gas temperature, and to study the burning rate of the charge as a function of the charge density and surface area.

Task 2 - Filtration requirements - to study filter materials and configuration to remove solids from the inflation gas stream.

Task 3 - Thermal stability testing - to conduct tests to insure that the charge and final system meet military requirements.

Task 4 - Production of 50 units - the production of gas generator cartridges to be supplied to the Land Warfare Laboratory for their evaluation.

This section summarizes the effort for the Tasks 1, 2 and 3. Further details are appended under appropriate headings. Task 4, the production of 50 units, was not conducted because of the failure of the charge to meet thermal stability requirements.

2.1 TASK 1 - Chemical Charge Studies

Task 1 had the objective of studying the sodium borohydride (SB)-dihydrazinium sulfate (HS) system under expected operational conditions to determine reaction characteristics and to modify these characteristics if necessary to achieve the desirable gas generator properties previously outlined.

Based on lab-scale experiments, the reaction expected was essentially that of the equation

$$4NaBH_4 + (N_2H_4)_2\ H_2SO_4 \rightarrow Na_2S + Na_2O + 4\ BN + 10\ H_2 + 3\ H_2O$$

However, the data do not support the presence of water in the expected quantities, nor the absence of nitrogen. Gaseous mixtures with little water and with an average molecular weight approximating helium have been obtained.

The available gas composition and burning rate data had previously been obtained on small charges confined in large massive die reactors. Thus, the rate measured was that of an end burning grain, and the products those of a reaction in which heat could be lost or absorbed by the surrounding metal reactor. In a practical balloon inflation system the ratio of the heat capacity of the delivery reactor to the total reaction heat will be small and the reactants will be subjected to a higher heat flux causing probable changes in products.

The chemical charge task was designed to study methods of altering the composition of the generated gas to raise the hydrogen content, methods of modifying the burning rate, and techniques for lowering the effluent gas temperature. In addition, it encompassed techniques for achieving smooth ignitions of the charge and for producing unbroken single pellet gas generator pellets.

The principal charge parameters studied were the ratio of sodium borohydride to dihydrazinium sulfate, charge density, available burning surface and the effect of additives.

2.1.1 Test Facility

A test facility was designed and constructed in a hood enclosure of 1/4 inch thick steel plate capable of withstanding violent explosions. The appropriate ignition, timing temperature measuring, pressure recording, gas sampling and total gas flow measuring devices were incorporated. A schematic of the facility is shown in Figure 2.

The test canister (Figure 3) was a 2 7/8 inch ID steel cylinder 8 inches in length. It was equipped with a Tri-Clover, Ladish Company flange which employs a silicone gasket to form a gas-tight, reusable seal. In the initial run a Snap-Tight quick connector was used to attach the canister to the system. This was replaced in subsequent runs with a simple 3/8 NPT nipple, 7 inches in length, to remove the restriction in the delivery line and to collect a small amount of white solids (1 to 2 g) that appeared to sublime from the reaction zone.

The temperature was measured just downstream of the canister, about 5 inches from the charge, and recorded with a Minneapolis-Honeywell Speedomax. Gas samples (4) were taken at desired intervals for subsequent mass spectrometer analysis by manually opening the evacuated glass sampling tubes.

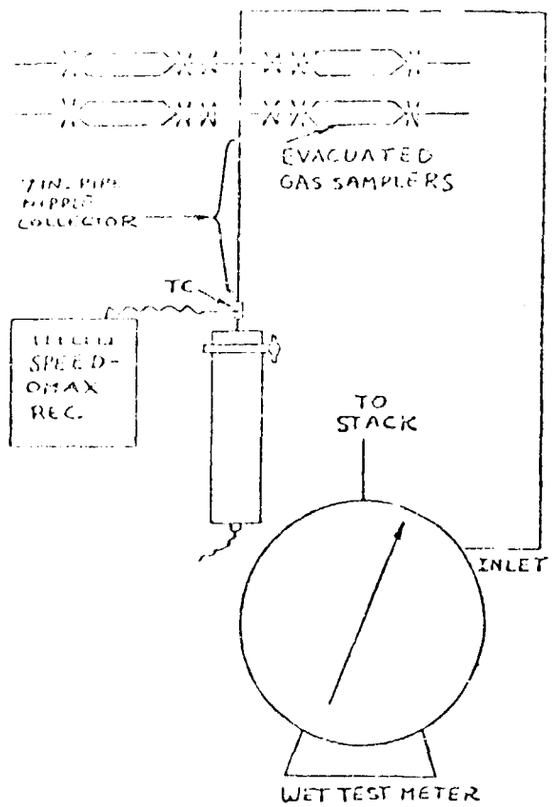

Figure 2
Schematic of Test Facility

The total gas produced and rate was followed with a 10 cfm wet test meter, taking 15 second readings on the meter during the burn period.

2.1.2 Procedure

The charge was prepared by grinding and mixing the components in a nitrogen-filled, dry-atmosphere glove box, and pressing them to the pellet form. Sodium borohydride is dry as received. Hydrazinium sulfate, on the other hand, contains approximately 1.5% water which is removed by vacuum drying at 122°F. Both components were hand-ground to a fine powder and blended by tumbling in a glass container on a roller mill.

The charge was pressed in a die mold to form a cylindrical pellet 2.25 inches in diameter and approximately 3 inches long. The pressing load varied from 2860 to 8060 psig on a 2.563 in. diameter ram-capacity hydraulic press.

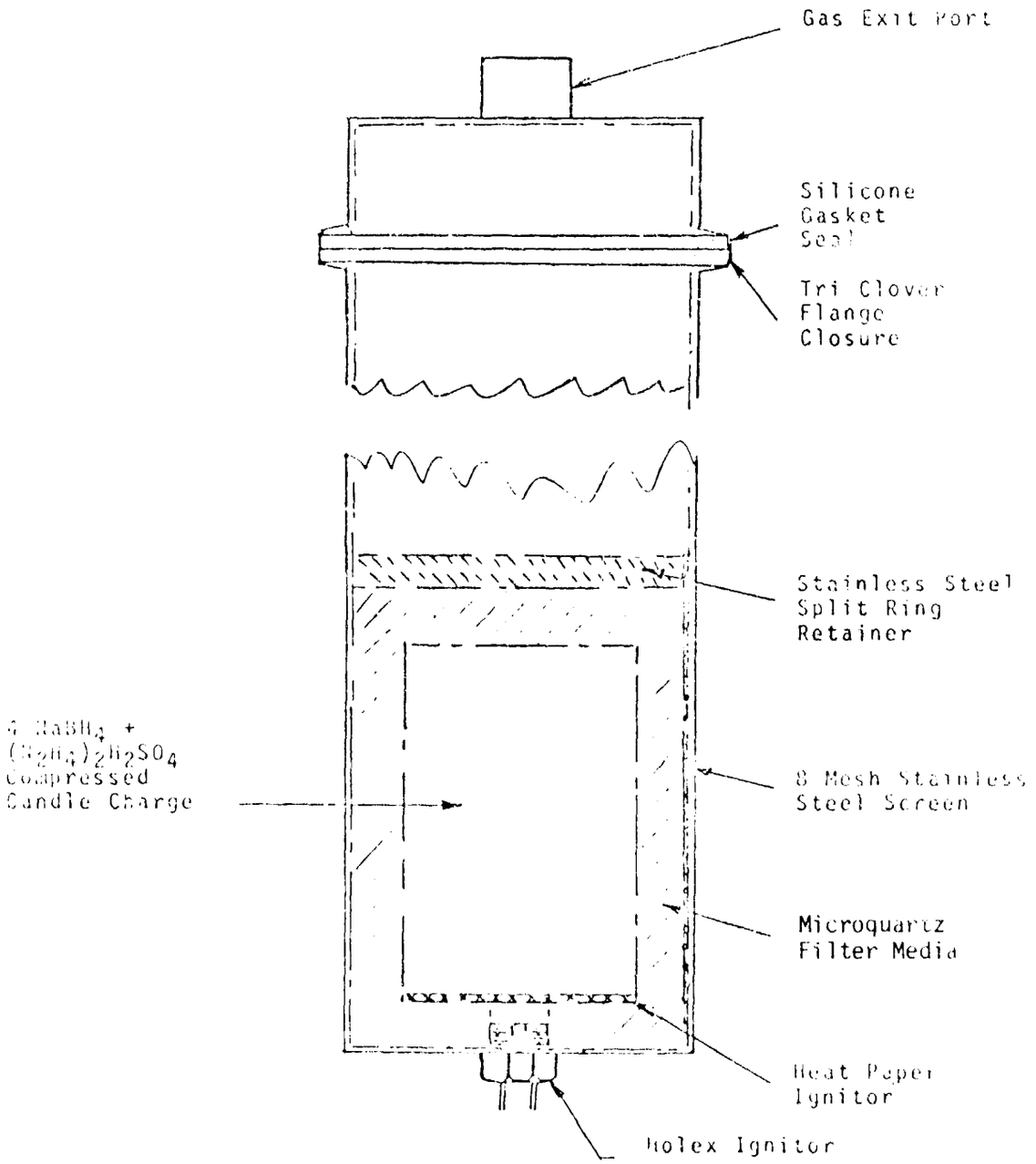

Figure No. 3 - Chemical Charge-Filtration Study Canister

After release from the die mold the resultant charge was examined for cracks and the length measured for a density determination. It was then wrapped with 1/2 in. thick Johns-Manville Microquartz felt and No. 8 mesh stainless steel screen. The felt served as an insulation on the bottom and sides of the canister as well as a filter medium. The filter will be discussed in greater detail in a later section.

The system was assembled as shown in Figure 3. The charge was inserted into the canister and covered with a 1/2 in. layer of felt and a metal plate perforated with 1/8 in. holes. This entire charge unit was then pushed down against the ignition system and held in place with a split ring. The installation of the closure completed the assembly.

The test canister was attached to the system and a dry-hydrogen gas sparge used to remove residual air. An electric squib ignitor was installed in the base of the test assembly and all electronic measurement systems started. The ignitor was fired and a time-lapse clock started simultaneously. The progress of the reaction was followed with the wet-test meter and registered by instantaneous temperature and flow rate traces on Speedomax recorders. Gas samples, as many as four, were generally taken at 1 cu. ft. intervals.

2.1.3 Ignition

Ignition of the charge was routinely initiated with an electric squib (Holex, inc., Part No. 1196A or B) as the primary ignitor and heat paper as the secondary. Heat paper is a product of Catalyst Research Corporation, a division of Mine Safety Appliances Company. It consists of a reactive metal-oxidizer mixture impregnated in a fiberglass mat. Type F, used in the application, releases 400 calories per gram at a rate of 4 to 5 inches per minute.

Delays up to 30 seconds from time of ignition to gas release were experienced initially in the test runs. A 5 gram loose powder charge in contact with the heat paper materially cut down on the delay. However, the problem was essentially eliminated when the density of the total charge was lowered to 1.1 gm/cm^3.

The ignition sequence used thereafter consisted of the Holex ignitor, heat paper and loose powder charge.

2.1.4 Gas Filtration

The filtration of the buoyancy gas was adequately handled throughout the test runs with a wrap of 1/2 inch Microquartz made by Johns-Manville Company. The felt also doubled as insulation. It completely encased the free-standing charge and provided sufficient surface area to prevent blinding of the filter. An outside wrap of No. 8 stainless steel screen helped

to hold the felt intact, and provided a free passage between the felt and the outside wall of the test canister for the escape of the gas. A plug of Microquartz and 1/2 inch of stainless-steel wool was placed on the top of the charge and held in place with a perforated steel disc and split ring retainer.

The reactor walls remained free of solids from the top of the charge to the gas exit port. Some solids, about 2 grams, were found downstream, but proved to be sublimate rather than unfiltered material. Solids thus appeared to be adequately handled.

A more detailed discussion of this area can be found in Section 2.2.

2.1.5 Gas Analyses

The effluent gas generated by the SB-HS system was collected by thief devices and analyzed for hydrogen, nitrogen, hydrogen sulfide and water content. All the gases except water were identified and measured on a Consolidated Engineering Corporation Mass Spectrometer Model 21-620.

Several methods were employed to measure the water content of the gas generated. The first method used a standard dew point apparatus (a Panametrics Model 1000) and a Minneapolis-Honeywell Dewpoint Sensor in the effluent gas stream from the product canister. This method had shortcomings; the sensor device responded too slowly to changes in gas composition.

A more reliable analysis by a Research Chromatograph Model 5750 from Hewlett Packard Company provided reproducible data. However, it was necessary to heat all samples prior to charging since the water concentration was above the room-temperature dew point. Changing chromatographic column characteristics due to trace impurities in the generated gas, necessitated conditioning of the column and complicated the analyses.

Infrared analysis was later used successfully (MSA LIRA) without interference problems associated with the gas chromatography analyses.

2.1.6 Discussion of Results

A complete tabulation of the run data is found in Tables 6-11 of the Appendix. This section summarizes the results, with a more detailed discussion appearing in Appendix A.

2.1.6.1 Altering Gas Composition - The composition of the gas produced, as compared by average molecular weight, varied little with the ratio of sodium borohydride to dihydrazinium sulfate in the mixtures of interest, but was

significantly affected by additives. The buoyancy, or lift on the balloon, is determined by the difference in weight between the buoyancy gas and the air it displaces, and thus is a function of the average molecular weight of the contained gas mixture. Air has an average molecular weight of about 29. Hydrogen with a molecular weight of 2 is the most efficient buoyancy gas, with helium (value of 4) ranking second. Our mixtures, containing hydrogen, nitrogen, water and negligible amounts of hydrogen sulfide, varied from a low of 4.2 to a high of 7.1. The low values, however, could not be obtained on stable compositions.

In our studies to raise the hydrogen content, and thus lower the molecular weight, we raised the sodium borohydride to dihydrazinium sulfate ratio over the stoichiometric 4:1 and included other chemicals as additives. Our theory was that there was excess heat available from the self-sustained exothermic reaction to decompose additional borohydride. With additives, we hoped to alter products, LiH, for example, hopefully would react to reduce the nitrogen or water content:

$$\text{(a)}\ 6LiH + N_2 \longrightarrow 2\ Li_3N + 3H_2$$

$$\text{(b)}\ LiH + H_2O \longrightarrow LiOH + H_2$$

Some typical runs for which complete gas analysis is available are summarized in Table 1.

Added sodium borohydride (5:1 ratio runs) may have had some minor effect, but lithium hydride was more effective at removing the trace quantities of hydrogen sulfide and reducing the water content. Larger quantities of lithium hydride had possibly some effect, but not significant. It was later established, unfortunately, that lithium hydride reacted slowly with the blend even at room temperature, causing a slow hydrogen release.

2.1.6.2 Altering Burning Rate - The burning rate of the gas generator charge was primarily a function of surface area, with some effect due to density and a significant effect with lithium hydride. End-grain burning as conducted in our in-house effort had established burning rates of about 0.7 inches per second, which for the gas produced (8 cubic feet) gave a release rate of about 1.6 cubic feet per minute. Table 2 shows representative data for typical mixtures using the free-standing charge as studied on this program, in which all surfaces were available for burning.

Data was tabulated only for those runs for which we had an unbroken pellet and no significant ignition delay. It is sufficient, however, to show the effect of the free-standing charge, and the pronounced effect of lithium hydride. It also demonstrates that the desired rate of 5 SCFM could readily be achieved.

TABLE 1 - COMPARISON OF GAS COMPOSITION AND AVERAGE MOLECULAR WEIGHT OF PRODUCED GAS

Run No.	SB/HS	Additive (Wt.%)	Gas Composition (Mole %) H_2	N_2	H_2O	H_2S	Average Mol.Wt.
1391-92	4:1	-	84.4	9.0	6.6	-	5.4
-96	4:1	-	81.9	12.7	5.4	-	6.2
-100	4:1	-	84.2	10.0	5.8	-	5.5
-104	4:1	-	88.2	8.4	3.4	-	4.7
-108	5:1	-	84.7	7.2	8.1	-	5.9
-111	5:1	-	87.8	5.9	6.3	-	5.2
-113	5:1	-					
		(NH_4Cl	88.0	Lost	7.5	-	5:1
-115	4:1	6.3	86.0	7.9	5.7	0.5	5.7
-118	4:1	6.3 (LiH)	84.8	8.9	5.7	0.7	6.0
-121	4:1	4.9	90.5	7.1	2.4	0.0	4.5
-125	4:1	4.9	87.8	8.8	3.4	0.0	5.2
-127	4:1	4.9	91.0	7.0	2.0	0.0	4.3
-129	4:1	4.9	91.0	7.2	1.8	0.0	4.3
-131	4:1	7.2	89.0	7.1	3.9	0.0	4.8
-133	4:1	4.9	86.9	8.8	4.3	0.0	5.4
-136	4:1	4.9	89.6	8.8	1.6	0.0	4.7
-143	4:1	4.9	89.3	7.3	3.4	0.0	4.8
-146	4:1	7.2	91.5	6.8	1.7	0.0	4.2
-155	4:1	-	82.5	6.5	11.0	0.0	6.6

TABLE 2 - BURNING RATES OF FREE STANDING CHARGES

Run No.	SB/HS	Additive	Density (g/cm^3)	Total Gas (Ft^3 STP)	Burn Time (Min.)	Burn Rate (Ft^3/min)
1391-100	4:1	-	1.2	6.1	1.3	4.7
-104	4:1	-	1.2	7.1	1.3	5.5
-108	5:1	-	1.1	6.4	1.0	6.4
-111	5:1	-	1.1	6.8	1.0	6.8
-113	5:1	-	1.1	6.9	1.0	6.9
-127	4:1	LiH	1.1	6.0	0.5	12.0
-129	4:1	LiH	1.1	6.0	0.5	12.0
-131	4:1	LiH	1.1	6.2	0.5	12.4

2.1.6.3 Altering Effluent Gas Temperature - Attempts to lower the temperature of the evolved gases by varying the reactant ratio or additives were unsuccessful. The burning rate was the principal factor.

Figure 4 is a plot of the maximum temperature recorded during a run versus duration of run. As expected, the maximum temperature is an inverse function of run time, and does not appear to be altered by either higher borohydride content or additives (LiH and NH_4Cl). Assuming that the reactions involved are not altered drastically, approximately the same reaction heat must be accounted for in all runs. Thus, a quicker reaction (higher burning rate) dictates a higher maximum temperature.

These temperatures were measured as the gas exited the canister. In all of our runs the heat dissipated quickly downstream similar to our demonstration experiments for LWL in 1970 when coiled aluminum tubing was used as the heat sink. We feel, therefore, that the heat is controllable in the 5 SCFM gas production rate, equivalent to a 2 minute inflation time.

2.1.7 Study of the Sodium Borohydride-Monohydrazinium Sulfate System

Monohydrazinium sulfate was studied as a substitute for dihydrazinium sulfate in the formulation with sodium borohydride, to attempt to obtain a charge with suitable thermal stability. Monohydrazinium sulfate can be made essentially anhydrous and free of excess hydrazine, both of which were suspected as contaminants in the dihydrazinium sulfate, and causing premature gas release.

The assumed reaction was:

$$2NaBH_4 + N_2H_4 \cdot H_2SO_4 \longrightarrow 2BN + Na_2SO_4 + 7H_2$$

Sodium sulfate reduction to give water should also be expected.

A half-scale run was conducted to determine the burn rate and gaseous products. The formulation consisted of 68 g $NaBH_4$ and 116.5 g of monohydrazinium sulfate. The pellet pressed to a density of 1.25 g/cm^3. Ignition was successful and instantaneous using the same ignition combination as the dihydrazinium system. The gas was delivered over a two-minute period with a large drop in flow after 80 seconds. The run data and gas analyses are tabulated in Table 3.

The gas mixture contained large quantities of water and hydrogen sulfide, calculating to an estimated molecular weight of 8.5 to 9. Data from three additional runs with 2.2, 2.0 and 1.8 mol ratios of sodium borohydride to monohydrazinium sulfate showed little effect on the course of the general reaction. The

TABLE NO. 3

SUMMARY OF SODIUM BOROHYDRIDE AND MONOHYDRAZINIUM SULFATE GAS GENERATION DATA

RUN NO.	SB-MHS RATIO	TIME MIN.	MAX. TEMP. °F	WT. CHARGE (g)	Ft^3 GAS	TOTAL GAS Ft^3/STP	H_2 (MOL%)	N_2 (MOL%)	H_2O (MOL%)	H_2S (MOL%)	(H_2N_2)	AVG. MOL WT.
1391-191	2.0	2.0	845°F	41.4		4.4	73.5	11.1	8.2	7.2	6.6	9.1
1494-43	2.0	2.0	1000°F+	41.4		4.4	70.7	13.7	12.4	3.1	5.2	9.8
1494-46	2.2	1.7	1000°F+	37.6		5.1	74.4	10.9	11.1	3.5	6.9	8.8
1494-49	1.8	1.2	900°F	41.6		4.3	70.2	12.4	11.7	5.7	5.7	9.9

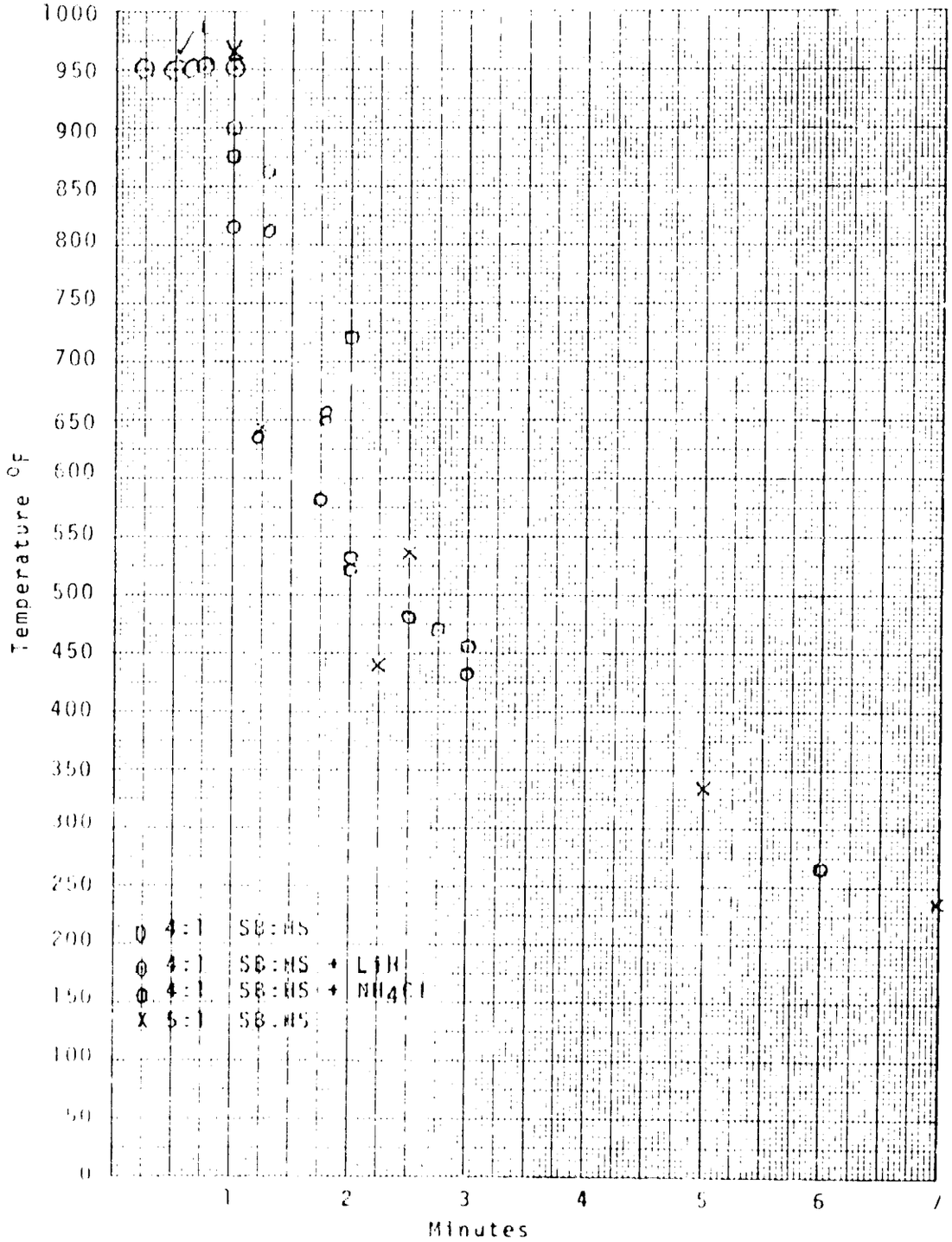

Figure 4 - Effect of Run Duration on Maximum Temperature of Effluent Gas

incorporation of LiH additive may have significantly reduced the H_2S and H_2O; however the product gas mixture as now constituted would not meet the lift requirement.

2.2 Task 2 - Filtration Studies

MSAR previously tested in-house prototype inflation units of the end-burning type which employed about 4 grams of No. 2 grade steel wool placed in approximately five layers as the filter medium. This material apparently entrapped coarse, but failed to trap fine solids. The fines were found in transfer cooling lines and the inflated balloons.

In the present studies an opportunity was afforded to study filter media and deployment. The most logical choice was to completely encase the free-standing charge with filter to significantly increase the surface area and thus decrease the pressure drop. Hopefully, the filter would also provide insulation.

A matted quartz felt with the trade name Microquartz from Johns Manville Company successfully serves as insulation and filter media in MSA's free-standing candle oxygen generators. It was tested and performed successfully in the test canister developed for this study (Figure 3).

Our first run used a 1/2 inch layer of felt on the bottom of the canister, on top of which rested the secondary ignitor (heat paper) and the hydrogen generator charge. The charge was wrapped first in a 1/2 inch of Microquartz and then a single layer of No. 8 stainless steel screen. The screen was to provide a passageway for gases released from the bottom and sides of the free-standing charge, up the inside walls of the canister. A 1/2 inch pad of felt and 1/2 inch of steel wool (No. 2 grade) were placed on top of the charge and covered by a perforated steel disc which was held in place by a split stainless steel tension retainer ring. The perforated disc and retaining ring were to hold the filter medium as well as to hold expansion of reaction residue to a minimum.

The reaction residue remained in place within the felt, with only negligible fines blowing downstream. The canister walls were relatively free of solids from the reaction residue surface to the exit point. A white solid sublimate collected in a Snap-Tight connector used to attach the canister to the transfer line, and caused erratic pressure surges as minor plugging and blow-out occurred.

In the second run, the steel wool and Snap-Tight connector were replaced by a pipe nipple connector. This eliminated the plugging, allowing a smooth delivery of gas, and served as a collector for the sublimed solids. The material, about 2 grams total, was very hygroscopic and tested high in sulfate.

The Microquartz felt served reasonably well as a filter media in the first 26 runs in the free-standing charge studies. However, as an insulator, 1/2 inch is inadequate. The walls of the canister glowed a dull red at the mid-point of the run, which

would surely melt rubber and most plastics, and probably set paper and leaves on fire. A larger diameter canister was designed that would allow a multiple layered thickness of felt to be placed around the free-standing charge, but fabrication was never completed.

After the first 26 runs, the burn rate of the free-standing charge increased to where most of the gas was evolved in a period of 30 seconds or less, and larger amounts of solids were found in transfer lines and even the we test meter. To study these, a very large packed filter was added to the external transfer line to determine if the quantity was sufficient to warrant their separation in the balloon inflation unit. A very cautious approach to collecting these solids was necessary so as not to build excessive back-pressure and affect the charge burning rate, or worse, a plug and explosion. The filter selected was MSA's gasline filter loosely packed with No. 1 grade steel wool and fine screen. Placement of the filter was just downstream of the thermocouple and 7-inch nipple normally used to collect solid sublimate.

An examination of the solids collected was encouraging even at the higher gas evolution rates. The quantity of these solids was of no consequence, amounting to approximately 2 g in the nipple and 2 to 3 g in the gas-line filter.

The use of LiH additive in the chemical charge presented an unexpected problem relating to filtration. The thermal decomposition of LiH gives free lithium which apparently undergoes a replacement reaction with sodium salts. The result is that free sodium is produced and distills out of the reaction residue. When the canister transfer lines and filter are washed, a reaction occurs with the water.

2.3 Task 3 - Thermal Stability Studies

The contract required that thermal stability tests be conducted on the final gas generator formulation to insure that it met military specifications for storage. Tests chosen were an accelerated storage test at 165°F for 30 days and a modified MIL-STD-304 test. This latter consisted of a cyclic storage between temperature limits of dry ice to 165°F.

Six full-scale charges were to be pressed and loaded into canisters, equipped with a pressure gage, rupture disc and suitable closure. The pressure was to be recorded as a function of time, with success or failure dependent upon the ultimate safe working pressures for the canister, and the success of an eventual balloon inflation with the test sample.

Our thermal stability test work encompassed first the basic sodium borohydride-dihydrazinium sulfate formulation studied in Task 1. Following problems with this mixture apparently from reaction in the solid phase, we investigated the stability of other possible candidate buoyancy gas generator formulations, and finally the microencapsulation of the reagents as a means of isolating them from each other.

This section summarizes the studies outlined above. Additional detail can be found in Appendix B.

2.3.1 Studies on the Basic 4:1 Sodium Borohydride-Dihydrazinium Sulfate Formulation

The basic 4:1 SB/HS formulation with LiH additive was selected from Task 1 as having the combination of properties that could closely approach the contract requirements. This formulation had an average molecular weight of 4.7 for the product gases of the nine runs, 1391-121 to -146 (Table 10, Appendix A) and had a delivery rate that could obviously be tailored for optimum heat properties.

The initial tests contained no added lithium hydride, testing reagents "as received" and with several degrees of pretreatment. Table 4 summarizes the data showing the percent available of hydrogen released from the charge after storage at room temperature for 24 hours.

The data from samples 1-3 indicated a purity problem, which we suspected to be due to moisture on the dihydrazinium sulfate (HS). In Sample 4, treatment brought the HS moisture content, as measured by the Karl Fisher method, to 0.1%. Some improvement was observed, but gas release continued giving a 12% release after 472 hours when the test was terminated.

The data indicated that reagent purity was at least part of the problem. However, impurities cannot account for all of the gas

TABLE 4 - GAS RELEASE AT ROOM TEMPERATURE FROM SODIUM BOROHYDRIDE-DIHYDRAZINIUM SULFATE FORMULATIONS

Sample Description	Percent Available H_2 Released, 24 Hr
1. SB as-received HS - once dried, ground after drying	4.0
2. SB - vacuum dried (120°F) HS - vacuum dried (120°F) after grinding	2.2
3. SB - vacuum dried (120°F) HS - extracted with Ethanol and dried as in (2).	1.5
4. SB - vacuum dried, ground, and vacuum dried (120°F) HS - vacuum dried, ground, and vacuum dried (120°F)	1.3
5. SB - liquid ammonia extracted and vacuum dried HS - methanol extracted and vacuum dried	2.3
6. SB - liquid ammonia extracted, vacuum dried HS - new supplier - ground and vacuum dried (120°F)	3.2

released. They may, however, be a catalyst to further reaction in the solid phase.

Samples 5 and 6, therefore, were attempts to remove possible catalytic impurities or avoid them with a choice of dihydrazinium sulfate from a different supplier. Trace amounts of water or hydrazine, for example, could be a favorable solvent for the production of hydrazine bis-borane according to the equation

$$2\ NaBH_4 + (N_2H_4)_2H_2SO_4 \longrightarrow Na_2SO_4 + N_2H_4(BH_3)_2 + N_2H_4 + 2H_2$$

The N_2H_4 produced would complex with sodium borohydride and eventually promote further solid-phase reaction. As is evident from the table, neither attempt was successful.

Mixtures with added lithium hydride were not tested. While conducting the previous tests, sample pellets with added lithium hydride being readied for test firings, in one instance, underwent a premature ignition in the test facility and, in a second, ignited while being assembled for firing in the dry box. It was

then noted that powder samples with added lithium hydride appeared to moisten and heat while being blended prior to being pressed into pellets; obviously the result of a solid-phase reaction.

2.3.2 Studies on Other Possible Candidate Formulations

Monohydrazinium sulfate, the hydrochloride salts of hydrazine, and hydrazinium fluoroborate were all tested as reagents with sodium borohydride for possible hydrogen generator mixtures. Monohydrazinium sulfate (MHS) proved to be exceptionally stable, while the other three were no improvement over dihydrazinium sulfate.

Monohydrazinium sulfate can be made virtually anhydrous. The material can be vacuum-dried at higher temperatures without fear of decomposition, and can be prepared free of excess acid or hydrazine.

A sample of MHS containing 0.1 percent water was formulated with twice the mole quantity of sodium borohydride and pelleted. No gas evolution occurred at room temperature over 312 hours. A second pellet at 122°F gave about 2 percent release of hydrogen in 24 hours and leveled off. This may have been due to a leak, but subsequent checks with the sample indicated exceptional stability.

The monohydrochloride and dihydrochloride salts of hydrazine can be obtained in high purity. The dihydrochloride, when pelleted with sodium borohydride, gave only a 0.46% release of hydrogen after 245 hours at room temperature and about a 4% release at 122°F after 24 hours. Although more stable, this formulation would obviously not meet military specifications. The monohydrochloride, after blending and being pelleted, gave about 2.5 percent hydrogen release after 24 hours at room temperature.

The increased storage stability obtained by substituting monohydrazine sulfate for dihydrazine sulfate to prevent premature release of H_2 off-gas suggested hydrazinium fluoroborate as another substitution. The tightly bound single hydrazine to hydrofluoroborate could lend storage stability and the fluoroborate ion would not be readily reduced by the hydride hydrogen during high temperature H_2 off-gas generation. The latter reduction reaction is responsible for the H_2O and H_2S impurities with monodihydrazinium sulfate formulations.

Hydrazinium fluoroborate is not a commercial reagent. For this test it was prepared from hydrazine hydrate and hydrofluoroboric acid according to a procedure given by Booth and Martin.[2]

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2. Booth, H.S., and Martin, D. R., Boron Trifluoride and Its Derivatives, John Wiley & Sons, Inc., p. 134, 1949.

This compound can be made completely anhydrous by simple drying. Pellets of 100 g and 3.5 g sizes were prepared of the stoichiometry of the equation

$$2NaBH_4 + N_2H_4 \cdot HBF_4 \longrightarrow 2BN + NaBF_4 + NaH + 6H_2$$

for stability and hydrogen generation rate-product purity tests.

The 165°F storage pellet was surprisingly reactive. In something less than 1/2 hour the off-gas release measured over 125 psig, which would be at least 30 percent of the hydrogen available. The room temperature storage sample lost an equivalent of 4.2 percent of the H_2 content in 8 hours. Because of these results, the 100 g pellet for the burn-rate test was set aside.

2.3.3 Microencapsulation Studies

Microencapsulation was investigated as a means of separating the basic reagents to prevent interaction during storage in the present pellet charge. It consists of placing a thin non-reactive coating around either or both components. The success of the technique depends on the completeness of the coating and maintaining the integrity of the coating during the subsequent pellet-forming operation. Heavier coatings naturally give a greater chance of success, but in this case would lower the efficiency of the charge.

Microencapsulation is a technique used commercially for stabilization, time-delay reactions, and improving flow properties of various solid materials. Many types of coatings are available and several techniques are employed to achieve encapsulation. Phase separation, vapor phase deposition and solution polymerization are three which have been employed extensively. Although the principles are not complex, the techniques have been developed to a high degree.

Two were employed here: (1) phase separation; and (2) solution polymerization. Although we were not successful in meeting stability requirements, our results were such to indicate that the technique had considerable promise towards meeting the goal with additional effort.

This section summarizes the detailed studies conducted. Additional information can be found in Appendix B.

2.3.3.1 Encapsulation by phase separation - Phase separation was used to coat both sodium borohydride and dihydrazinium sulfate with the following:

- polyethylene oxide
- polyvinyl alcohol
- ethyl cellulose
- polyvinyl acetate

Organic, rather than aqueous phase separations, were used in all cases since both sodium borohydride and dihydrazinium sulfate are either reactive towards, or soluble in water. The coating procedure developed basically by Dobry[3] generally was as follows:

> The film-forming material was dissolved in an organic liquid which was immiscible with the material to be coated. Rapid agitation dispersed the solid particles uniformly and a second organic liquid, in which the film-forming material is not soluble, added to slowly bring it out of solution. As the film material comes out of solution, it coats or encapsulates the suspended particles. Filtration recovers the coated material, which is then washed and dried by a suitable method.

Sodium borohydride was encapsulated with polyethylene oxide (Polyox WSR-10, Union Carbide Corporation), ethyl cellulose, and polyvinyl acetate (VINAC B-25, Air Products and Chemicals, Inc.). Attempts to obtain suitable coatings with polyvinyl alcohol (COVOL 9702, Corn Products, Inc.) were not successful.

Dihydrazinium sulfate was coated with polyethylene oxide (Polyox WSR-10), polyvinyl alcohol (COVOL 9702 and 9722), and polyvinyl acetate (VINAC B-25). Unsuccessful attempts were made to obtain coatings with ethyl cellulose.

Mixtures of these coated materials gave pellets with varying degrees of stability, all of which were more stable than the uncoated blends, but none of which showed suitable stability at 165°F, the required limit. The results are summarized in Table 5.

The best results were obtained with Sample No. 1494-31, which employed a 6% polyethylene oxide (Polyox WSR-10) on sodium borohydride mixed with a 10% polyvinyl acetate (VINAC B-25) coated dihydrazinium sulfate. A hydrogen loss of 7% in 30 hours at 165°F was recorded. The VINAC was coated on the dihydrazinium sulfate in benzene. The VINAC-coated product was salt-like, but agglomerated. A similar test (1494-41) in which ethyl acetate was used as the solvent, gave a similar product, but one which was not quite as stable (5.5% loss of H_2 in 8 hours at 165°F). A test of 5% VINAC-coated sodium borohydride with the VINAC-coated dihydrazinium sulfate (Sample No. 1494-56) was stable for 26 days at 75°F with no pressure buildup, but gave 15% of the available hydrogen after 28 hours at 165°F. This sample employed the dihydrazinium sulfate coated in ethyl acetate, and more likely should have employed the sample prepared in benzene, which had earlier proved more stable.

3. Dobry, A., and Boyer-Kawenoki, F., Phase Separation in Polymer Solutions, J. Polymer Science, p. 90, January 1947.

TABLE 5 - THERMAL STABILITY COMPARISONS OF COATED MIXTURES

Test No.	SB Coating	HS Coatings	Results at 75°F	Results at 165°F
1494-14	Polyox (6%)	PVA - (6%) COVOL 9702	1.5% (45 hr)	8.0% (8 hr)
1494-17	Polyox (6%)	PVA (12%) COVOL 9722	5.5% (64 hr)	Not tested
1494-20	Ethyl cellulose (10%)	Polyox (10%)	43% (24 hr)	Not tested
1494-25	Polyox (6%)	Polyox (10%)	5.0 (100 hr)	10.5% (6 hr)
1494-31	Polyox (6%)	VINAC B-25 (10%)	Stable	7.0% (30 hr)
1494-41	Polyox (6%)	VINAC B-25 (10%)	Stable	5.5% (8 hr)
1494-56	VINAC B-25 (5%)	VINAC B-25 (5%)	Stable	15.0% (28 hr)

2.3.3.2 Encapsulation by solution polymerization - Two unsuccessful attempts were made to coat dihydrazinium sulfate with polyethylene by an in-situ polymerization process. The process is described by Herman[4], who encapsulated cellulose fibers using an ethylene treatment of a Zeigler catalyst-impregnated fiber. The polyethylene normally produced by this process is the high density, higher-melting form which should show to an advantage at 165°F storage.

In the first attempt, 75 g of dihydrazinium sulfate was slurried in 750 cc of toluene, and 1.1 cc (10 mmols) of titanium tetrachloride catalyst, plus 4.8 cc (10 mmols) of aluminum triethyl added. Ethylene was then passed into the slurry at 141 g/min and the temperature raised to 150°F. Apparently the Zeigler catalyst did not form properly, because ethylene was continually lost. After 1.3 hours, reaction was terminated and the remaining catalyst destoyed by addition of methanol. Product recovery was by

4. Herman, D. F., Kruse, V., and Bravcato, J. J., "Polyethylene Encapsulated Cellulose," J. Polymer Sci., Part C., No 1., p. 75-95)1965).

filtration and vacuum drying. Qualitatively, the product dissolved completely in water and thus was assumed to have no polyethylene coating.

A second attempt was modified so that a nearly simultaneous addition of titanium tetrachloride and aluminum triethyl catalyst was made. These reagents produced the desired dark brown color of Ziegler catalyst. However, passing in ethylene at 155°F resulted in only the partial take-up of the ethylene, as evidenced by the off-gas rate. The product, recovered and dried by the same procedure as above and tested in water for degree of encapsulation, appeared to be partially coated, but the major portion appeared to be water-soluble. With the failure of these two attempts, this phase of the encapsulation was discontinued.

3. CONCLUSIONS

3.1 Storage stability appears to be the only factor limiting the use of the sodium borohydride-dihydrazinium sulfate system as a site marker buoyancy gas generator. The buoyancy of the generated gas, generation rate and temperature, all appear to be within acceptable limits whether in the blend of the two main ingredients, or with added lithium hydride.

3.2 The charge size, based on the yield of gas from the sodium borohydride-dihydrazinium sulfate system, and the remaining components (i.e., filter, ignitor, canister, etc.) are all within the expected weight limits, making it virtually certain that the total system would meet the 2 1/2 pound limitation.

3.3 Filtration was adequately accomplished with Johns Manville Microquartz filter media. Additional media over that employed in our test would be needed to meet insulation requirements.

3.4 No unexpected factors were found that would change our initial opinion on the expected low costs of a gas generator based on the sodium borohydride-dihydrazinium sulfate system.

3.5 Microencapsulation of the charge components is a very real possibility for achieving the necessary storage stability. Our limited study resulted in significant improvement, but was necessarily limited because of insufficient funds.

3.6 A stable system based on the sodium borohydride-monohydrazinium charge also appears to be a means for achieving an economical and useful gas generator unit. The system demonstrated better storage stability than the dihydrazinium sulfate-based system, but needs work in lowering the molecular weight of the produced gas. Lithium hydride showed evidence of being the proper additive.

3.7 The production of 50 cartridges based on the sodium borohydride-dihydrazinium sulfate system, as presently developed, would not be advisable. The storage stability would present an unknown hazard both to production and the test team, and may eventually be a problem of disposal.

4. REFERENCES

1. Wood, Benjamin F., IMPROVED ELEVATED SITE MARKER, Technical Report No. 74-07, December 1973. U. S. Army Land Warfare Laboratory, Aberdeen Proving Ground.

2. Booth, H. S., and Martin, D. R., BORON TRIFLUORIDE AND ITS DERIVATIVES, John Wiley & Sons, Inc., p. 134 (1949).

3. Dobry, A., and Boyer-Kawenoki, F., PHASE SEPARATIONS IN POLYLER SOLUTION, J. Polymer Science, p. 90, January 1947.

4. Herman, D. F., V. Kruse and J. J. Bravcato, "Polyethylene Encapsulated Cellulose," J. Polymer Science, Part C., No. 11, pp. 75-79 (1965).

5. GLOSSARY OF TERMS

Symbol or Term	Description
g	Grams
l/g	Liters per gram
cm^3	cubic centimeters
m^3	cubic meters
in.	inches
CFM	cubic feet per minute
SCFM	standard cubic feet per minute
NPT	national pipe thread
HS	dihydrazinium sulfate $(N_2H_4)_2\ H_2SO_4$
MHS	monohydrazinium sulfate $N_2H_4 \cdot H_2SO_4$
HBB	hydrazine bisborane $N_2H_4(BH_3)_2$
SB	sodium borohydride $NaBH_4$
HMB	hydrazine monoborane $N_2H_4BH_3$
HFB	hydrazine fluoroborate $N_2H_4 \cdot HBF_4$
mmols	millimoles

6. APPENDIX A - CHEMICAL CHARGE STUDY DETAILS

This section details the sodium borohydride (SB) - dihydrazinium sulfate (HS) system formulation studies. The test facility, formulation procedure and gas generation study technique has been adequately described earlier in Section 2.1.

6.1 4:1 SB to HS Studies

Table 6 summarizes the runs to determine burn rate and gas products of the free standing charge configuration. The first Run 1391-36 was erratic, apparently due to the pressure buildup from plugging occurring at the Snap-Tight connector. This condition was interpreted from the five temperature and gas evolution surges experienced during the run. The second Run 1391-42 utilized a pipe nipple connector which eliminated the plugging, allowing smooth delivery of gas.

The charges were approximately 3 inches in length. Based on previous in-house-research end-grain burning rate data, run times of about 4 minutes would be expected. Thus, the burn time of 2 minutes and less for free standing charges were significant improvements toward achieving the program goal of 1 minute.

A problem in obtaining unbroken charges required estimation of density results which made burn rata data suspect. The charges when removed from the die mold breaks into two and sometime three pieces. Runs 1391-57 to 73 were attempts to correct this problem through the addition of fibers in the formulation.

The addition of steel fibers, 1 inch in length in 1391-57, was attempt to obtain a pressed charge that would maintain its integrity after having been removed from the mold. The steel fibers had a tendency to ball up in the blending operation, and the resultant pressed charge broke, as usual, at the lower 1/8 of the pellet. Run 1391-60 was formulated with 1/2 inch steel fibers but a 5 percent addition was not effective in holding the pressed charge together. Again the lower 1/8 section broke away.

The addition of glass fibers was also unsuccessful in preventing pellet fracturing. Run No. 1391-63 contained 5 percent 1/2" long chopped glass fibers which mixed readily throughout the formulation in a ball mill operation. The pressed pellet, however, was very weak and could be broken

TABLE NO. 6

SODIUM BOROHYDRIDE AND DIHYDRAZINIUM SULFATE - 4:1 RATIO - ADDITIVE STUDIES

CHARGE DATA							RUN DATA						
RUN NO.	SB g.	HS g.	ADDITIVES	SB/HS	DENSITY g./cc	TIME MIN.	MAX. TEMP. °F.	TOTAL GAS FT^3/STP	g.CHG/ FT^3	H_2 MOL %	N_2 MOL %	H_2O MOL %	AVG. MOL. WT.
1391-36	100	103		4:1	1.2 (1)	2	530	5.7	35.6	80.6	14.4	5.0	7.1
1391-42	100	103		4:1	1.2 (1)	1.7	580	6.1	33.3	87.7	7.3	5.0	5.2
1391-50	100	103		4:1	1.2 (1)	2.7	470	5.8	35.2	85.1	9.9	5.0	5.9
1391-57	100	103	[Steel Fibers]	4:1	1.1 (1)	2.0	522	5.6	36.3	87.2	7.8	5.0	5.3
1391-60	100	103	[Steel Fibers]	4:1	1.1 (1)	2.5	480	6.0	33.8	86.0	9.0	5.0	5.7
1391-63	100	103	[Glass Fibers]	4:1	- (2)	1.2	635	6.0	33.8	87.4	7.6	5.0	5.3
1391-67	100	103	[Pwdrd. Glass]	4:1	1.1 (1)	6.0	265	5.0	40.6	86.2	8.8	5.0	5.7
1391-73	100	103	[Glass]	4:1	1.1 (1)	3.5	- (3)	5.4	37.6	84.[illegible]	10.9	5.0	6.2
1391-77	100	103	[Heat Tabs]	4:1	1.1 (1)	1.2	500+	6.5	31.3	87.5	7.5	5.0	5.3
1391-80	100	103	[Heat Tabs]	4:1	1.2 (1)	1.8	660+	6.3	32.2	86.0	9.0	5.0	5.7

(1) Approximate value, broken candle.
(2) Candle in several pieces.
(3) Temp. Recorder Malfunction.

easily at any point. This charge, when set up as usual for gas evolution measurement, apparently presented a very high surface for reaction, because the gas evolution rate and effluent temperature was the highest obtained up to that time. A repeat run (No. 1391-73) was made to determine if the high rate of gas evolution could be attributed to the open structure of the candle charge. Ignition apparently was instantaneous but a slow steady gas evolution resulted. Unfortunately, no temperature record was obtained because of instrument failure.

A 5 percent addition of finely powdered glass fibers of the type used in MSA oxygen candles was used in Run No. 1391-57. Pressing in the usual manner gave a two piece charge, with 1/8 of the bottom broken away. The ignition of this charge was apparently rapid, but a long term gradual temperature rise over 6 minutes coupled with a steady slow gas evolution occurred.

In an effort to obtain a more rapid, reliable ignition sequence, additional heat was added to the ignitor materials. It had been observed from gas temperature and evolution data that some charges burned slowly for periods of 20 to 30 seconds after ignition before accelerating to a more normal rate. This delay accounted for some of the time variability in what otherwise were identical runs.

In addition to the usual ignitor of the Holex squib and heat paper, in order to increase the available heat, three heat tabs were added. The effect on the 4:1 charge appeared to be beneficial, (runs 1391-77 and 80), but because of the broken charges, could not be accurately assessed. The effect on the 5:1 formulation charges discussed later, however, was very pronounced.

The maximum temperature achieved during the run is an inverse function of the run time, as would be expected. Assuming that the reaction(s) involved will not be altered drastically with temperature, approximately the same reaction heat must be accounted for in all runs. Thus, a quicker reaction would dictate a higher maximum temperature.

In general, the gas yield and composition of all the charges, regardless of the method of ignition or additive appears to be reasonably constant. Based on this consistency, a correction for presumed water vapor content was made to bring the results more in line with that later found to be present. Water vapor concentration of 5 percent was used as an averaging value in recalculation of hydrogen and nitrogen values in Table 6. Although hydrogen sulfide could be detected, the Mass Spec. analytical results did not confirm its presence above 0.5 percent.

6.2 5:1 SB to HS Studies

Studies were also conducted on 5:1 SB:HS formulations in hopes of affecting the gas composition and lowering the reaction temperature. The composition and effluent temperature of the gas generated is a function of the reagent ratio SB:HS in the solid charge. Small scale studies carried out previous to this program on the SB-HS system were run at SB:HS ratios of 1:1 to 10:1 in which the hydrogen content ranged from 52 to 91%, respectively. Above the 4:1 SB:HS ratio, which is stoichiometric, the excess SB decomposes endothermically and should lower the effluent gas temperature and possibly raise the hydrogen content of the effluent gas.

Table 7 summarizes the 5:1 SB:HS runs to determine effective change in burn rate, gas products and temperature lowering. On the first formulation(1391-47), the pellet broke into four pieces when released. Only three sections were charged into the canister. Inadvertently, a 39g piece was left in the die mold. The ignition and gas evolution of this charge was not particularly different from the 4:1 ratio charges, but the effluent gas temperature was about 100°F lower. The 2.2 minute reaction time would extrapolate to 2.6 min for a full charge, not significantly slower than the 4:1 reaction time. The gas composition of 88.4 mol% also compares closely to the 4:1 ratio as does the yield data 33.8 g chg/ft^3.

A repeat run(1391-52) was made in which the total formulation of 5:1 SB-HS was recovered in two pieces. Upon ignition the gas evolved at the rate of approximately 0.2 cu. ft., per 15 sec. interval over a total run time of 7 min. The temperature of the effluent gas reflected the slow gas evolution as it gradually rose from room temperature to 235°F in 3 min. This same slow burn was obtained in Run 1391-55. A three piece charge was ignited requiring 2 minutes to reach a 155°F effluent temperature, and a maximum of 335°F. The run time was reduced from 7 min. to 5 min. Notice again the maximum temperature achieved during the run is an inverse function of the run time. The problem of long reaction time was attributed to low initial ignitor heat.

6.3 Ignitor Modifications

Heat tabs were added to the ignition sequence to initiate a more positive rapid ignition, and gave obvious improvement. Two duplicate runs were made (Nos. 1391-82 and 85) with run times of 2.5 and 1.2 minutes observed. The shorter duration of Run 85 probably was due to the presence of loose chips recovered from a partially broken pellet during die mold release.

TABLE NO. 7

SODIUM BOROHYDRIDE AND DIHYDRAZINIUM SULFATE - 5:1 RATIO STUDIES

CHARGE DATA							RUN DATA						
RUN NO.	SB g.	HS g.	ADDITIVES	SB/HS	DENSITY g./cc	TIME MIN.	MAX. TEMP. °F.	TOTAL GAS FT^3/STP	g.CHG/ FT^3	H_2 MOL %	N_2 MOL %	H_2O MOL %	AVG. MOL. WT.
1391-47	104	68	-	5:1	1.2	2.2	440	5.6	33.8	86.4	8.6	5.0	5.6
1391-52	125	103	-	5:1	1.1	7.0	235	5.2	43.9	86.3	8.7	5.0	5.7
1391-55	125	103	-	5:1	1.1	5.0	335	6.2	37.8	86.3	8.7	5.0	5.7
1391-62	125	103	heat tab ign.	5:1	-	2.5	535	6.9	33.2	87.8	7.2	5.0	5.2
1391-65	125	103	heat tab ign.	5:1	-	1.2	644	6.6	34.6	89.8	5.2	5.0	4.6

In general, the gas yield in both 4:1 and 5:1 SB-HS is the highest when maximum temperature and short run times occur. The gas composition is slightly higher in hydrogen, with slightly lower molecular weight for 5:1 SB-HS formulations, regardless of temperature or method of ignition.

Our studies at this point had been made on charges which fractured into 2 and sometimes 3 pieces upon removal from the die. In addition, ignition delays of 20 to 30 seconds had been experienced. Possibly because of this, burn times of otherwise identical formulations and prepared charges have been inconsistent, and thus attempts to compare the effect of variables such as added SB were inconclusive.

The problem of ignition delays was attacked with the use of a portion of the original formulation as a (5 g) loose powder squib as a secondary igniter in place of the heat tabs. This concept was previously used by MSAR to obtain consistent ignitions of hydrazine bisborane (HBB)*. The squib was used in the seven runs summarized in Table 8, and ignitions of the squib occurred without delay. The runs consist of 2 with pellets pressed at the usual high pressures and 5 pellets of lower density from lower pressure compression. In the two high density (Runs 1391-92 and 96), a 20 second delay occurred after the squib burned before normal pellet burns occurred. But with the less dense pellets (Runs 1391-100, 104, 108, 111, and 113), total ignition of the pellet surface apparently occurred rapidly.

The reduced pellet forming pressure was primarily initiated to obtain whole pellet charges, with apparently successful results. The charges for Runs 1391-92 and 96 (run 96 was transition from 2" I.D. to 2 1/4" I.D. Diemold) were pressed at 8,060 psig as usual, and resulted in broken pellets. In Run 1391-100 the pressure was reduced to 2080 psig, resulting in an unbroken pellet. These results were confirmed in Runs (1391-104, 108, 111 and 113) obtaining unbroken pellets, with densities of 1.1 to 1.2 g/cc.

Decreased forming pressures have apparently given double benefit in achieving unbroken pellets and nearly instantaneous ignition. Pressures of 2860 psig versus 8,060 psig employed in the preparation of previous charges, resulted in very little decrease in density along with the above benefits. The decreased density also significantly increased the burning rate.

*The Development of a Flotation System
Contract No. N00024-69-C-5397,
Naval Ship Systems Command

The reduced density-increased burning rate results were confirmed in 5:1 SB-HS studies,(Runs 1391-108, 111 and 113) and summarized in Table 8. Generally,these gas products reflected the earlier results with higher forming pressure. A slightly higher hydrogen content and additional total gas was produced.

The water content of the effluents in Table 8 was found in sufficient quantities to be of concern. Several analytical procedures indicated concentrations in excess of 5 percent. In the first attempt (Run 1391-92) a Panametrics Co. Inc., Model 1000 Dewpoint instrument equipped with an aluminum oxide and gold in-line sensor was employed. This system is reportedly capable of supplying dynamic moisture concentration data. Unfortunately, the instrument almost instantly read off-scale upon ignition of the charge. Its highest calibration value is 12,000 ppm or 1.2 percent water content. On the recommendation of a Panametrics representative one of their probes was calibrated to a 90°F dewpoint (4.8% water concentration) using a Minneapolis-Honeywell Dewpoint Sensor in a controlled humidity atmosphere. This probe, used in Run No. 1391-96, also went off scale within 15 seconds after ignition.

The Panametrics data is questionable. Primary amines and other gases seriously interfere with the sensor. Therefore, to check the unit, a dry nitrogen sweep was maintained on it for hours, but it could not be restored to the initial readings. Only after washing with benzene and drying overnight at 175°F did the sensor probe respond correctly.

In Runs 1391-100 and 104 a Minneapolis-Honeywell (MH) Dewpoint Sensor was installed to obtain dynamic in-line data without success. The gas was evolved over 1 1/2 to 2 minutes but it took the MH unit 5-6 minutes to stabilize.

Gas chromatography (G.C.) gave our first apparently reliable indication of the water content of the effluent. Samples of the gas taken for the mass spec analyses for hydrogen and nitrogen were first warmed slightly to avoid errors due to condensation of moisture on the walls of the sampling tubes,and analyzed. It is realized that water might possibly have condensed out of the gas in our experimental set-up prior to our sampling section, but we felt that this possibility was small. The values ranged between 3.4 and [illegible] percent.

TABLE NO. 8

SODIUM BOROHYDRIDE AND DIHYDRAZINIUM SULFATE GAS GENERATION RESULTS SHOWING WATER CONTENT

CHARGE DATA					RUN DATA							
RUN NO.	SBg	HSg	SB/HS	DENSITY g/cc	TIME MIN.	MAX. TEMP. °F	TOTAL GAS ft^3/STP	g CHG/ft^3	H_2 MOL/%	N_2 MOL/%	H_2O MOL/%	AVG. MOL WT.
1391-92	100	103	4:1	2 Pieces	1.8	650	6.0	33.8	84.4	9.0	6.6	5.4
1391-96	100	103	4:1	2 Pieces	2.0	720	6.1	33.3	81.9	12.7	5.4	6.2
1391-100	100	103	4:1	1.2	1.3	860	6.1	33.3	84.2	10.0	5.8	5.5
1391-104	100	103	4:1	1.2	1.3	810	7.1	28.6	88.2	8.4	3.4	4.7
1391-108	125	103	5:1	1.1	1.0	900+	6.4+(1)	-(1)	84.7	7.2	8.1	5.9
1391-111	128	103	5:1	1.1	1.0	875	6.8	33.6	87.8	5.9	6.3	5.2
1391-113	125	103	5:1	1.1	1.0	840	6.9	33.0	~88	Lost	7.5	5.1

(1) Loss due to equipment failure.

The hydrogen and nitrogen values recorded in Table 8 are corrected values based on the GC analyses for moisture. The mole percent water was first substracted from the total and the ratio of H_2 and N_2 in the remainder obtained from mass spec analyses. A further refinement of the gas chromatography method for establishing the moisture content of the effluent resulted in what appears to be accurate, reproducible data. It was found necessary to condition the G.C. column after each determination due to absorption of water by the column. Failure to do so tended to give high moisture content values. The old procedure was still in use for Runs 1391-92, 96, 100, 104, 108, 111 and 113. Therefore the average molecular weight of these samples is thus lower somewhat from previously reported values.

6.4 Chemical Charge Studies with NH_4Cl and LiH Additives

Formulation studies were made to determine the effect if the use of additives such as NH_4Cl and LiH to cool and/or improve the hydrogen content of the effluent. A major problem with the SB-HS system is the considerable heat released during the burning of the charge. A good deal of this heat, which must be dissipated before the hot gases reach the balloon, is due to the cleavage of the N-N bond of hydrazine in the dihydrazinium sulfate (HS). Since presumably not all of the heat is required to sustain reaction, some of it could be eliminated or used to sustain an endothermic reaction that otherwise would not go. In this manner, the total heat could be reduced.

The replacement of some of the HS in the formulation with ammonium salts such as NH_4F, NH_4Cl, or $(NH_4)_2SO_4$ not only may serve to cool the reaction, but could add materially to its efficiency. Table 9 shows a comparison of the theoretical hydrogen production from these systems with that of our present system.

TABLE 9

HYDROGEN GENERATION SYSTEM YIELDS

SYSTEM	HYDROGEN PRODUCED (LITERS/GRAM)
$4NaBH_4 + (N_2H_4)_2H_2SO_4$	0.70 - 8.75
$NaBH_4 + NH_4F$	1.20
$NaBH_4 + NH_4Cl$	0.98
$2NaBH_4 + (NH_4)_2SO_4$	0.86

The substitution of NH_4Cl additive for HS was used in Runs 1391-115 and 118 (Table 10) to cool the effluent. Approximately 20 percent of the HS was removed and NH_4Cl (13.6g) substituted in an effort to provide the necessary nitrogen for BN formation, and cut down on the energetic N-N bond content. These two runs were three minutes long with about 50 sec. ignition delay after the 5g loose powder squib ignited. The maximum effluent temperature reached was low, 455°F, as expected for such long burn times. The gas effluent contained the most H_2S observed so far; 0.5 and 0.7 mol% for 1391-115 and 118, respectively. Based on the long burn time, NH_4Cl did not appear to provide any improvement over the basic 4:1 SB-HS formulations.

Lithium hydride was added to 4:1 SB-HS formulation to effect a reduction of the water and nitrogen content in the effluent by the means of the equations:

$$\text{(a)}\ LiH + H_2O \longrightarrow LiOH + H_2$$

$$\text{(b)}\ 6LiH + N_2 \longrightarrow 2Li_3N + 3H_2$$

Lithium hydride was added in sufficient quantity to remove all of the water and half of the nitrogen based on a 5 mol percent water and 10 mol percent nitrogen content in the effluent. Table 10 shows clearly that the water content is less when LiH is included. In Run 1391-121 and all of those following, the moisture is below 4.3 mol percent with all but one below 4.0. Run 1391-133, which gave the high value, is not considered a typical run in that a high forming pressure (8060 psig) was used, and it self-ignited in the canister.

Nitrogen reduction was not evident. The H_2/N_2 ratio of Table 10 shows no apparent trend towards higher values. It is possible that free lithium is only transient in the charge melt and undergoes a replacement reaction with sodium salts. When the canister, transfer lines and filter are washed, a violent reaction occurs with the water that is more like sodium than lithium.

A higher percentage of LiH failed to give any additional advantage in lowered water content, or materially affect the H_2/N_2 ratio. Runs 1391-131 and 146, summarize the data from two such runs in which the LiH content was increased 50% to 7.2 weight percent.

A bonus effect was obtained with the addition of LiH in the removal of hydrogen sulfide (H_2S) from the product gases. The quantity of H_2S in the product was sufficiently low, 0.5 mole percent or lower, so as to be of questionable accuracy for reporting.

TABLE NO. 10

SODIUM BOROHYDRIDE AND DIHYDRAZINIUM SULFATE WITH LITHIUM HYDRIDE ADDITIVE GAS GENERATION RESULTS

CHARGE DATA							RUN DATA								
RUN NO.	SB (g.)	HS (g.)	SB/HS	ADDITIVE (WT. %)	DENSITY (g/cc)	TIME (MIN.)	MAX. TEMP. (°F)	TOTAL GAS (Ft^3/STP)	g CHG/ft^3	H_2 (MOL%)	N_2 (MOL%)	H_2O (MOL%)	H_2S (MOL%)	H_2N_2	AVG. MOL WT.
1391-115	100	82.5	4:1(2)	(NH_4Cl) 7.0	1.1	3.0	455	5.4	36.4	86.0	7.9	5.7	0.5	10.9	5.7
1391-118	100	82.5	4:1(2)	7.0	1.1	3.0	430	5.0	39.2	84.8	8.9	5.7	0.7	9.5	6.0
1391-121	100	103	4:1	(LiH) 4.9	1.1	1.0	540(1)	6.7	31.9	90.5	7.1	2.4	0.0	12.7	4.5
1391-125	100	103	4:1	4.9	1.1	1.0	900+	6.0	35.6	87.8	8.8	3.4	0.0	10.0	5.2
1391-127	100	103	4:1	4.9	1.1	.5	900+	6.0	35.6	91.0	7.0	2.0	0.0	13.0	4.3
1391-129	100	103	4:1	4.9	1.1	.5	900+	6.0	35.6	91.0	7.2	1.8	0.0	12.6	4.3
1391-131	100	103	4:1	7.2	1.1	.5	900+	6.2	35.3	89.0	7.1	3.9	0.0	12.5	4.8
1391-133	100	103	4:1	4.9	1.2	-	-	-	-	86.9	8.8	4.3	0.0	9.9	5.4
1391-136	100	103	4:1	4.9	1.1	.25(3)	900+(3)	3.5(3)	-	89.6	8.8	1.6(4)	0.0	10.2	4.7
1391-143	100	103	4:1	4.9	1.1	.75	900+	6.4	32.6	89.3	7.3	3.4(4)	0.0	12.2	4.8
1391-146	100	103	4:1	7.2	1.0	.5	900+	5.2	41.0	91.5	6.8	1.7(4)	0.0	13.4	4.2
1391-155	100	103	4:1	None	1.1	.67	900+	6.2	32.8	82.5	6.5	11.0(4)	0.0	12.7	6.6

(1) Not reliable due to equipment failure.
(2) Based on total NH Groups from $(N_2H_4)_2 H_2SO_4$ and NH_4CL.
(3) Not reliable due to excessive high delivery, new lot $(N_2H_4)_2 H_2SO_4$.
(4) One determination via septum tube.

A faster burn rate was experienced midway through our study with LiH. Also the effluent temperatures have been higher, as would be expected of generally faster reactions. The effluent temperatures have been higher since changing to the lower-density runs and question that LiH was not responsible for the increase.

However rather disturbing runs were made with LiH possibly affecting the stability of the mix that can seriously reflect on its potential as a solid hydrogen source. We had two pre ignitions on charges; one occurred with the charge in the test set up and ready for ignition, and the other in the inert gas chamber while installing the pressed charge in the test chamber.

Run 1391-133, which pre-ignited in the test facility, was compressed at 8,060 psig to attempt to slow the burn rate by raising the pellet density. While installing the charged canister on the gas measuring system, heating of the canister and a gas evolution of about 1 cfm were observed. The facility was sealed, the charge fired, and a rapid burn occurred.

Run 136 was a duplicate of 133 to see if a reason for the self-ignition could be found. The mixing operation on the ball mill showed a more rapid tendency for the free-flowing powder formulation to ball up and become wet in appearance as well as to heat up as though a reaction was taking place. The mixing was stopped and the mix set aside to see if the heating continued.

After several hours, it was obvious that the mixture was cooling. The formulation was allowed to set for several days and pressed at reduced pressure to a density of 1.1g/cc. Upon removal from the die the charge fractured into 2 pieces and was still rather wet looking on the surface.

When this charge was ignited by the usual method, an extremely rapid gas release occurred. It was impossible to read the wet test meter and the temperature went off scale in less than 10 seconds and returned in 15 seconds suggesting reaction completion. The low 3.5 cu. ft. reading is interpreted as only a partial accounting. Gas, over and above 10 cfm, will blow by measuring buckets in the wet test meter, which undoubtedly occurred in this case.

In the next Run (1391-143) removal of water from both SB and HS were of major concern to try to correct the run-away reaction rates. The SB and HS had been drying for several days while previous studies were made. The HS was taken to the dry box and ground mechanically to a fine powder, while the SBwas ground in a mortar. Analysis of HS after grinding showed 0.4 wt% H_2O, approximately the same as earlier dried HS. A basic 4:1 SB to HS formulation was mixed on the roller mill as a free flowing powder for approximately 1/2 hour with no particular change in flowability. However, in the second 1/2 hour of mixing the formulation became sticky and began to ball up and show signs of heating. Mixing was suspended and the sample returned to the dry box overnight. The mix was pressed the following day, obtaining one piece pellet with a density of 1.1 g/cc and no indication of heat evolution. On testing, a rapid ignition was experienced with a 45 second run, producing 6.4 cu. ft. of gas.

At this point, it was assumed that the formulation procedures, with dry reagents were safe enough to proceed with additive testing. We recognized, however, that we still had a basic stability problem to study. Run 146 was a duplicate of run 131 to evaluate the effect of an additional 50 percent LiH to the basic 4:1 SB to HS formulation. Although the run was rapid, it appeared normal with respect to the previous LiH runs.

An attempt to repeat run 146, however, ran into trouble. A formulation of 103g of HS was mechanically ground exactly the same in all respects as 1391-146. The LiH was a preground commercial product, and the SB (100g) was oven-dried and ground to uniform powder in a mortar and pestle comparable to all previous runs. The usual mixing procedures were followed on the ball-mill roller system. We were encouraged to observe that the formulation was free-flowing after 3/4 hour. This was attributed to finally obtaining dry reagents. On pressing, an excellent pellet with a density of 1.05 g/cc was obtained. However, while measuring the length of this pellet in the dry box it was noticed that it was excessively warm even through the rubber and cotton inspector gloves. The charge was quickly inserted into the canister, but no sooner had the charge contacted the squib when a whisp of smoke was observed. The operator quickly left the dry box and the chamber was soon filled with smoke. Fortunately, the lack of air in dry box prevented the released hydrogen from igniting.

In checking the formulation reagents for the cause of self-ignition other than higher pellet density, it was learned that a new lot of HS was being used starting with Run 1391-133. It was also learned that in this run, and in previous runs especially with LiH added, balling of the formulation occurred during the blending operation, as if it had become moist. Obviously the purity, or perhaps more specifically, the dryness of the reagents has a considerable effect on the stability of the mix even at room temperature when LiH additive is involved.

An investigation of the reagents failed to reveal any reason for this self-ignition. The HS analysed 0.2 wt% H_2O with an appropriate 4.5 pH in water, not significantly different from previous materials. The only observational difference is the free flowing nature that this formulation had even up to pressing. It may be that not enough time was allowed for the LiH or SB to react with contained water before the pressing operation. Pressing with this unreacted water increased reaction rate and generated enough heat to start reaction prematurely.

At this point a single gas generation run was made without LiH to determine if the higher purity reagents in the basic 4:1 SB-HS formulation would have any effect and shed any light on the pre-ignitions and higher burning rates encountered in the LiH studies. Run 1391-155(Table 10)was formulated without LiH additive using 103g of HS, mortar and pestel reground, purified by alcohol extraction and vacuum drying at 122°F,and 100g SB, vacuum dried at 122°F, and finely ground. On ball mill mixing no balling of this mix occurred over a period of one hour, and only a slight indication of heat evolution indicated. A low density pellet was pressed and set up in the usual canister with the 5g ignition squib set up. Ignition occurred without delay and a very rapid gas evolution resulted. The burn time was about 40 seconds compared to 30 seconds with the "as received" reagents. This is faster than the 1 min. runs earlier considered generally as the standard. Only the water content analysis in this run differed markedly from the LiH study runs, which especially in this case shows the effect of LiH additive.

6.5 Investigation of Other Hydrazine Salts

Concurrent studying under Task No. 3,Thermal Stability Testing, continued to have problems with the stability of the basic 4:1 SB-SH formulation despite all attempts to improve reagent purity. The SB was extracted

with liquid ammonia, increasing the purity from 97 to 99 percent based on active hydrogen. Dihydrazine sulfate was extracted with methanol and rigorously vacuum dried to remove moisture. When mixed and pelleted, a gradual release of hydrogen was monitored at room temperature, the amount of which far exceeded that expected from residual 0.1 mol% water in the SB-HS.

At this point a review in thinking as to the cause of preignition or premature gas release suggested that some of the hydrazine in HS is being released and acting as a reaction solvent. As stated in the Thermal Stability Studies Section, Runs 1391-171 and 176, a liquid was observed on the surface of the formulated pellets when the apparatus was degassed to atmospheric pressure. It determined that normally present trace water produces the necessary solvent for SB and HS to react to form the hydrazine adducts and hydrogen gas according to the equation:

$$4NaBH_4 + (N_2H_4)_2H_2SO_4 \longrightarrow Na_2SO_4 + N_2H_4(BH_3)_2 + 2NaBH_4 \cdot N_2H_4 + 2H_2$$

The $^{2}NaBH_4 \cdot N_2H_4$ complex is a known liquid and may be a most desirable solvent for the above reaction.

To avoid this problem, monohydrazine sulfate (MHS) was evaluated with SB. This compound can be made completely anhydrous and should not release N_2H_4 if a slow reaction occurs. The assumed reaction was

$$2NaBH_4 + N_2H_4 \cdot H_2SO_4 \longrightarrow 2BN + Na_2SO_4 + 7H_2$$

A half-scale run (No. 1391-191) was conducted to determine the burn rate and gaseous products. A formulation consisting of 68g $NaBH_4$ (97 percent active H_2) and 116.5g MHS (0.1 percent water) yielded a 1.25g/cc pellet. Ignition was successful and instantaneous using the same combination used with HS-SB. The gas was delivered over a two minute period with a large drop in flow after 80 seconds. The run data and gas analysis in Table 11 shows the gas mixture would be a very poor substitute for helium with an estimated molecular weight of 8.5 to 9.

In order to determine if a lower molecular weight gas could be produced from MHS and SB the concentration of SB was varied to determine the effect on burn rate and gaseous products. Obviously sulfate is being reduced, therefore runs were varied by charging SB in concentrations of 10 percent excess, stoichiometric, and 10 percent deficient to ffect the displacement of hydrogen sulfide, water and nitrogen, and increase hydrogen yield.

TABLE 11 - SODIUM BOROHYDRIDE AND MONOHYDRAZINIUM SULFATE GAS GENERATION DATA

RUN NO.	SB-MHS RATIO	TIME MIN.	MAX. TEMP. °F	WT. CHARGE (g) Ft^3 GAS	TOTAL GAS Ft^3/STP	H_2 (MOL%)	N_2 (MOL%)	H_2O (MOL%)	H_2S (MOL%)	(H_2N_2)	AVG. MOL. WT.
1391-191	2.0	2.0	845°F	41.4	4.4	73.5	11.1	8.2	7.2	6.6	9.1
1494-43	2.0	2.0	1000°F+	41.4	4.4	70.7	13.7	12.4	3.1	5.2	9.8
1494-46	2.2	1.7	1000°F+	37.6	5.1	74.4	10.9	11.1	3.5	6.9	8.8
1494-49	1.8	1.2	900°F	41.6	4.3	70.2	12.4	11.7	5.7	5.7	9.9

Three additional runs (1494-43, 46 and 49), were made with 2.2, 2.0 and 1.8 mol ratios of SB to MHS. Burn rate and effluent data, illustrated in Table 11, show that the SB concentrations had little effect on the course of the general reaction. The incorporation of LiH additive may significantly reduce the H_2S and H_2O; however the product gas mixture as now constituted, will not meet ultimate mil spec requirements.

Before LiH can be tested in the above formulation, stability tests must be carried out at room temperature and up to 155°F.

7. APPENDIX B - THERMAL STABILITY STUDY DETAILS

This section gives details on the thermal stability studies summarized earlier under section 2.3.

7.1 Studies Based on the Sodium Borohydride-Dihydrazinium Sulfate System

Thermal stability tests were to be conducted on the final gas generator formulation to insure that it meets military requirements. Six full scale charges were to be pressed and loaded into canisters equipped with a pressure gage, rupture disc and suitable closure. The temperature requirements were from dry ice temperature to 165°F, using a modified MIL-STD-304 procedure.

The basic 4:1 SB-HS, LiH additive, formulation was found in the Chemical Charge Studies Task 1 to have burn rate properties that could closely approach the one minute delivery time for 10 cfm gas. With an average molecular weight of 4.7 for the product gases of the nine Runs 1391-121 to 146, (Table 10) compares very favorable with 4.0 for pure helium.

The above formulation was thus selected for thermal stability evaluation. In the mixing process of formulation of SB-HS in all runs and especially with LiH added, balling of the formulation occurred during the blending-roller mill operation, as if it had become moist.

In the first tests only the basic 4:1 SB-HS formulation was evaluated on a small scale to determine just how much reaction might be taking place while blending the mixture at room temperature. Since both SB and HS are hygroscopic, some loss of hydrogen due to hydrolysis from the contained water, was expected during first contact, obviously in the mixing operation.

Three different mixtures, consisting of 7 grams of SB and HS (4:1 mix), were ground and placed one on top of the other in 50 cc flasks equipped with appropriate high vacuum stop cocks and fittings.

Mix No. 1 was composed of SB as received, 97% active hydrogen, and once-dried HS mechanically ground in drybox after drying.

Mix No. 2 was composed of SB vacuum dried at 122°F for 24 hours, and HS vacuum dried at 122°F after having been mechanically ground to a powder.

Mix No. 3 was composed of vacuum dried SB as above and twice dried HS as above which was extracted with ethanol to remove possible free sulfuric acid.

After removing the nitrogen blanket from the reagents, stirring was begun and the gases collected. Table 12 is a summary of the results.

TABLE 12 - HYDROGEN INVOLVED FROM TEST FORMULATION 1391-136 AT ROOM TEMPERATURE

MIX	FIRST HOUR mmols	24 HOURS mmols	48 HOURS mmols	H_2 RELEASED 24 HRS. (%)*
1	14.4	8.5	5.4	4.0
2	10.2	2.1		2.2
3	4.7	3.9		

*Based on 6.5 ft^3 gas produced per 203g charge ≈ 12.7 liters per 14g charge.

Obviously the purity, or perhaps more specifically, the dryness of the reagents has a considerable effect on the stability of the mix at room temperature. It is also apparent, however, that even with our dryest reagents; as much as 1.5% of the available gas, predominantly hydrogen, was released on standing at room temperature.

Careful drying of the reagents was rechecked to eliminate, if possible, water as source of instability. Both the SB and HS were vacuum dried at 50°C, ground and then redried. The measured moisture on the HS was down to 0.1%.

All handling operations were conducted in a dry nitrogen-filled glove box. Nearly equal amounts (25.8g HS and 25.0g SB) of HS and SB were charged into a 250cc Fisher-Porter apparatus equipped with a pressure gage and sampling valves. Blending was attempted in a rolling mill, but the weight of gages and hardware made this impractical. A magnetic stirring bar was later included to supplement mixing. The mixture was maintained at room ambient.

In the first test, pressure built to 11 psig, about 10 mmols, with some heat evolved. Samples obtained for mass spec analysis showed 0.15 mol% of ammonia and 99 mol% hydrogen. The following Table 13, summarizes the total off-gas evolution. Curve 1391-159 of Figure 5 shows a plot of the data.

TABLE 13 - HYDROGEN EVOLVED FROM TEST FORMULATION 1391-159 AT ROOM TEMPERATURE

ΔTIME HOURS	TOTAL TIME HOURS	ΔOFF GAS mmols	TOTAL OFF GAS mmols
16	16	13.4	13.4
24	40	12.4	25.8
8	48	7.1	32.9
68	116	35.7	68.6
20	136	13.7	87.3
32	168	23.6	105.9
40	208	19.8	125.7
96	304	47.5	173.2
24	328	7.1	180.3
24	352	18.6	198.9
24	376	11.7	210.6
96	472	28.3	238.9

After 472 hours the experiment was terminated. The total gas evolution was approximately 12% of that available, far exceeding that expected from the water content on the HS. The solids were caked and incapable of further stirring.

The reagent purity of both HS and SB, beyond that of just 0.1 to 0.2 percent residual water content, was next investigated to promote stability.

The SB was purified by extraction and recrystallization from liquid ammonia, which raised its purity from 97 to 99 percent. The HS was extracted with methanol (CP grade) and redried at 122°F in-vacuo, hopefully to remove soluble acid impurities. The water content after drying was measured at 0.2 wt%.

Approximately 7 grams each of SB and HS were charged one on top of the other in 50 cc flask in the dry box. Following removal to a vacuum line, the reactor was evacuated at -196°C and allowed to warm. Gas evolution began soon after reaching room temperature and stirring began to slowly deteriorate. The off-gas contained about 1 percent ammonia. The noncondensable analyse 99.7 mol percent H_2.

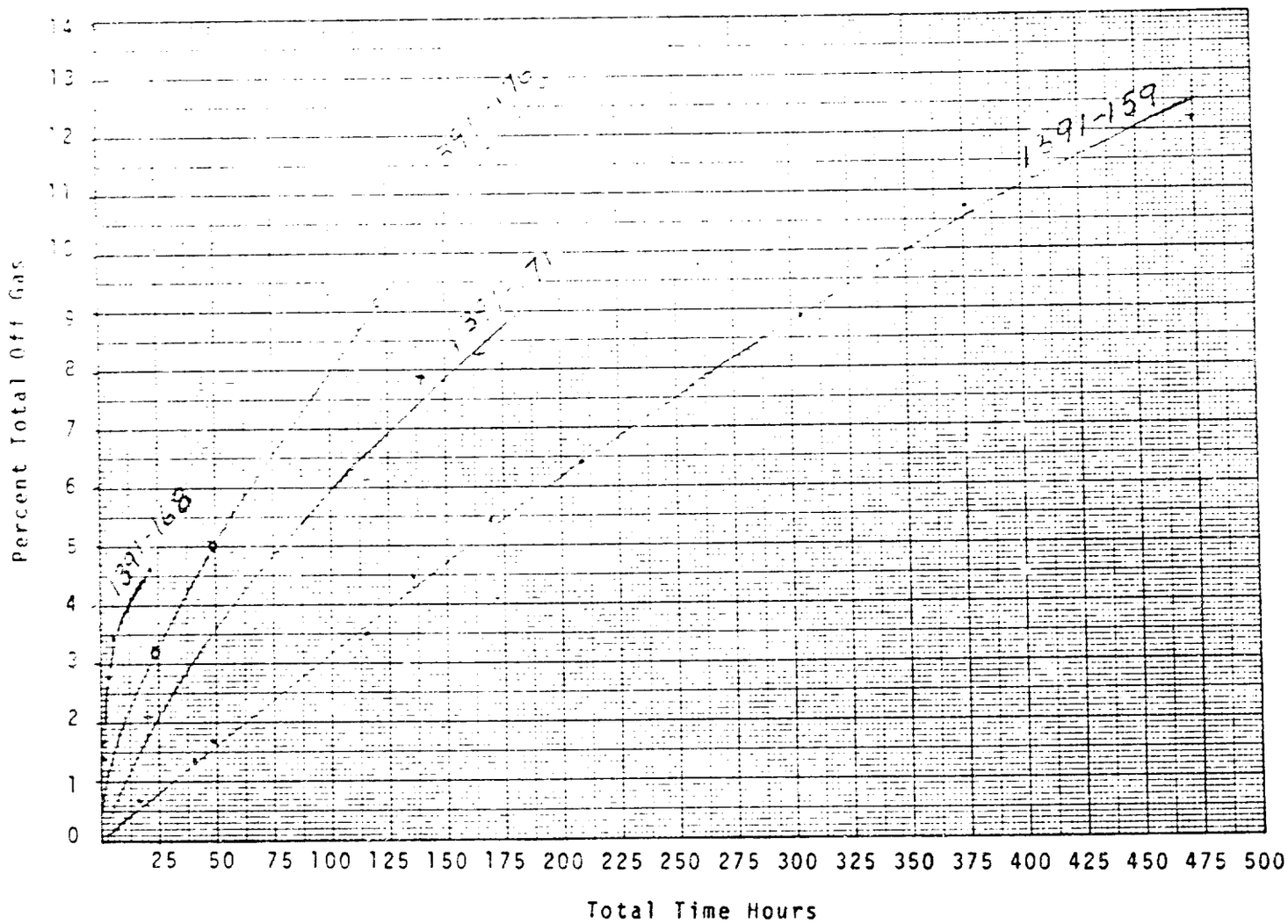


Figure 5 - Comparison of SB and HS, 4:1 Charge at Room Temperature Thermal Stability

This mixture continued to off-gas with time as follows:

TABLE 14 - HYDROGEN EVOLVED FROM TEST FORMULATION 1391-168 AT ROOM TEMPERATURE

ΔTIME HOURS	TOTAL TIME HOURS	ΔOFF GAS mmols	TOTAL OFF GAS mmols
1.0	1.0	7.3	7.3
2.0	3.0	7.6	14.9
2.5	5.5	3.7	18.6
21.0	26.5	6.5	25.1

A plot of the gas released as percent released versus time is shown as curve 1391-168 in Figure 5, and shows the blend to be obviously much less stable than the previous mixture.

A small pellet of the same blend was stored concurrently at room temperature in a Fisher-Porter apparatus. The atmosphere was removed from the apparatus and back-filled with H_2. Table 15 shows the time versus off-gas relationship. A plot of this data is designated as curve 1391-171 in Figure 5.

TABLE 15 - HYDROGEN EVOLUTION FROM TEST FORMULATION 1391-171 AT ROOM TEMPERATURE

ΔTIME HOURS	TOTAL TIME HOURS	TOTAL OFF GAS PSIG	TOTAL OFF GAS mmols
20	20	12	2.8
96	116	35	8.2
24	140	44.5	10.5
24	164	46.5	11.0
96	260	55.0	13.0

Again the data show that the basic 4:1 SB-HS formulation reacts prematurely at room temperature to release gas.

Hydrazine sulfate from a new supplier was tested to determine if the premature release of hydrogen from SB-HS formulations may be caused by trace impurities in the HS. A quantity of HS was obtained from Fairmount Chemical Company, a major supplier of hydrazine chemicals. Dehydration was carried out at 120 to 122°F invacuo, as recommended by

Audrieth(1) quite successfully. The recovered HS contained less than 0.1 percent water and an N-N value of 12.4 mmols/g compared to 12.3 mmols/g theory. These N-N values compares with 97 percent N-N values for Eastman Chemical Company material.

Pellets of this material blended with 99+% SB (4:1 SB to HS) were tested at room temperature and 122°F in Fisher-Porter reactor tubes. The blending, pelletizing, and loading operations were all conducted in a dry nitrogen atmosphere. The apparatuses were pre-tested with hydrogen at 50 psi.

Curve 1391-176 Figure 5 shows that the relative rates of gas release at room temperature from the formulation prepared with Fairmount HS is no better than the Eastman material. Curve 1391-189 (Figure 6) shows similar data at 122°F. The test was short lived, only 10 hours, during which time 6.6% of the total hydrogen available was released.

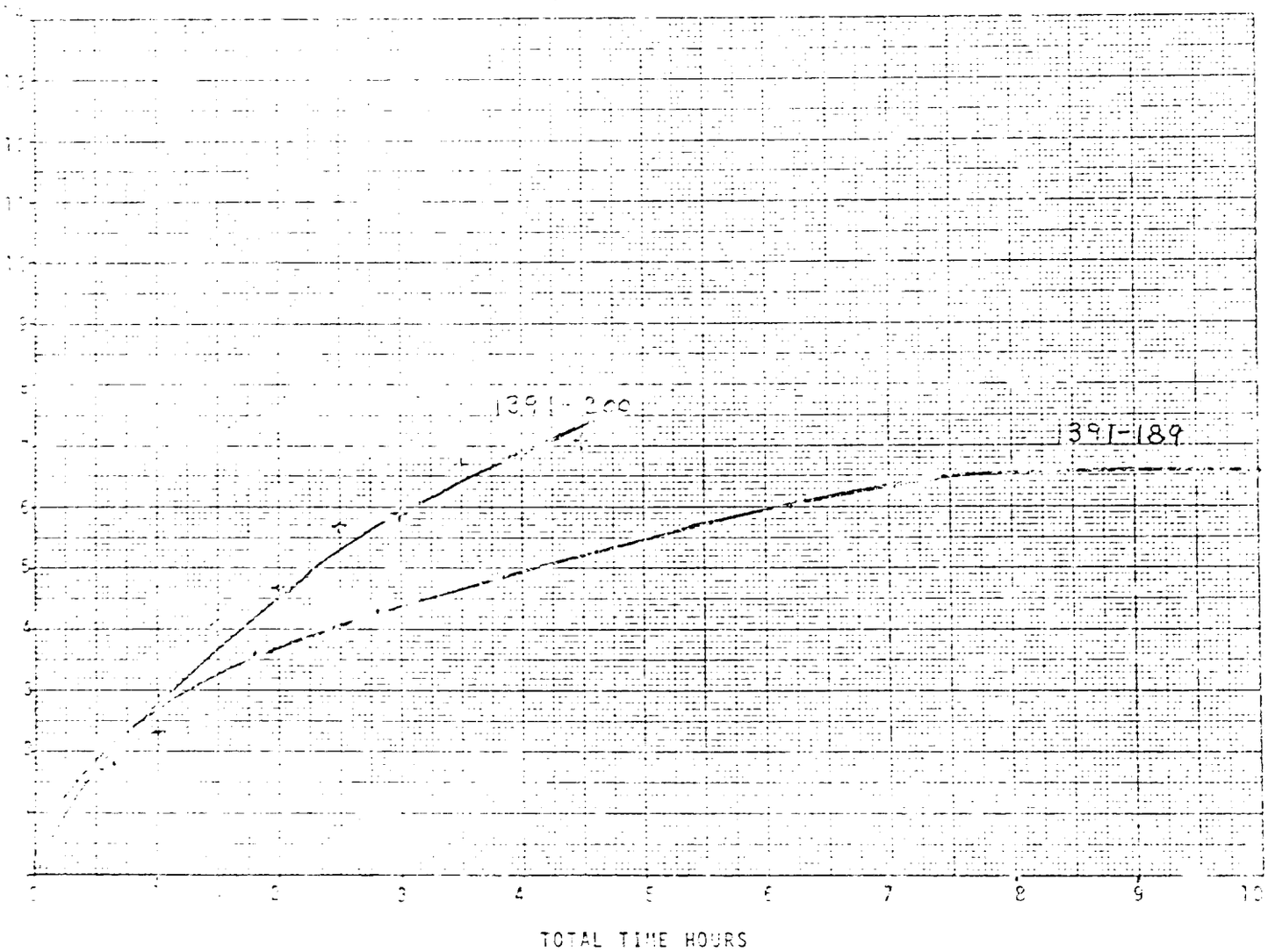
At this point a review in thinking as to cause of premature gas release suggested that some of the hydrazine in dihydrazinium sulfate is being released and acting as a reaction solvent. In Runs 1391-176 and 171, a liquid was observed on the surface of the formulated pellets when the apparatus was degassed to atmospheric pressure. Probably what happened is that trace amounts of water produce the necessary solvent for HS and SB to react to form $N_2H_4(BH_3)_2$, hydrazine bisborane (HBB), according to the equation:

$$4NaBH_4 + (N_2H_4)_2H_2SO_4 \longrightarrow Na_2SO_4 + N_2H_4(BH_3)_2 + 2NaBH_4 \cdot N_2H_4 + 2H_2$$

The N_2H_4 has not been observed in the gas phase because it forms a complex with SB, and eventually a most desirable solvent for the above reaction. Assuming the above theory, dihydrazine sulfate and SB will always gas when mixed together because a small amount of interreaction will result from even trace amounts of water, and once started, the reaction produces its own solvent for the formation of hydrazine bisborane (HBB).

(1) Audrieth L.F. and B. Ackerson OGG "The Chemistry of Hydrazine" J. Wiley & Sons Inc. New York, Chapman & Hill Ltd. London 172, (1951).

Figure 6 - Comparison of Sb and HS, 4:1 Charge at Room Temperature, Using Fairmount-supplied HS



7.2 Thermal Stability of Sodium Borohydride with other Hydrazine Salts

To avoid the hydrazine release problem described in the previous section, monohydrazine sulfate (MHS) was evaluated with SB. This compound can be made completely anhydrous because it is relatively nonhygroscopic[1] and should not release N_2H_4 if a reaction occurs with SB. If trace amounts of water is present when MHS and SB are mixed, simple hydrolysis of SB should first occur due to the acidic nature of MHS according to the following equation:

$$2NaBH_4 + N_2H_4H_2SO_4 \xrightarrow[\text{Trace}]{XH_2O} 2\text{-}X\ NaBH_4 + N_2H_4 \cdot H_2SO_4 + XNaOH + XH_3BO_3 + XH_2$$

Notice that hydrazine exchange or release does not occur and NaOH is a known stabilizer for SB. Should trace quantities of water cause SB to partially react with MHS the following classic reaction would occur in which $N_2H_4BH_3$ (hydrazine monoborane HMB) is produced with hydrogen release.

$$2NaBH_4 + N_2H_4H_2SO_4 \xrightarrow[\text{Trace}]{H_2O} N_2H_4BH_3 + NaHSO_4 + NaBH_4 + H_2$$

Again, hydrazine release does not occur to become a reaction solvent for decomposition and premature gas release. As earlier discussed in the chemical charge studies, the hydrogen generation assumed reaction is:

$$2NaBH_4 + N_2H_4H_2SO_4 \longrightarrow 2BN + Na_2SO_4 + 7H_2$$

A 3.5g pellet of the above stoichiometry was formulated and pressed in dry box from 2.2g MHS and 1.3g SB. Analysis of the MHS showed 0.1 percent water. The SB was 99 percent pure based on active hydrogen. The condition of the SB-MHS during and after the mixing operation was very different from that of SB-HS. A free-flowing crystalline powder remained throughout, and no heat was evolved, nor the ammonia odor observed.

(1) Audrieth L.F. ibid.

A room temperature storage test, after leak testing at 50 psig H_2 pressure, for 13 days (312 hours) showed no gas evolution, as indicated by the lack of pressure build-up. A second pellet stored at 122°F gave off-gassing plotted as curve 1391-181, Figure 7. The decreasing pressure was found to be due to a slight leak in our apparatus. Retightening and additional 122°F and a subsequent 165°F storage showed that a 30 day storage might be possible, if pressures to 10 psig could be acceptable in canister hardware. A somewhat similar test result was obtained, with MHS and SB Run 1494-1 and will be discussed in a latter section on Microencapsulation.

Although the 2:1 SB-MHS formulation showed significant improvement over 4:1 SB-HS at both room temperature and 165°F stability, the gas produced would not meet mil. Spec. The gas generation results from this formulation,(see Run 1391-191 Chemical Charge Studies),were an estimated molecular weight of 8.5 to 9, approximately twice that of helium.

The hydrochloride salts of hydrazine were also studied as alternatives to the sulfates. The dihydrochloride was first chosen because it can be easily obtained in high purity. A 3.5g pellet was formed with SB, 99 percent pure, and the hydrochloride 0.2 percent water content, according to the following stoichiometry:

$$2NaBH_4 + N_2H_4 \cdot 2HCl \longrightarrow 2NaCl + 2BN + 7H_2$$

The room temperature stability test showed this formulation to be reasonably stable compared to HS formulations. The data are summarized in Table 16 following and Figure 8.

TABLE 16 - DATA SUMMARY FOR 1391-177

DURATION HOURS	PRESSURE (psig)	TOTAL OFF GAS (percent)
0.0	2.5	0.00
5.0	3.0	0.09
20.5	2.5	0.00
29.0	3.0	0.09
53.0	3.5	0.18
125.0	4.0	0.27
173.0	4.0	0.27
197.0	5.0	0.46
221.0	5.0	0.46
245.0	5.0	0.46

Figure 1 - Comparison of SB and MPS, 2:1 Charge, 122°F
Thermal Stability

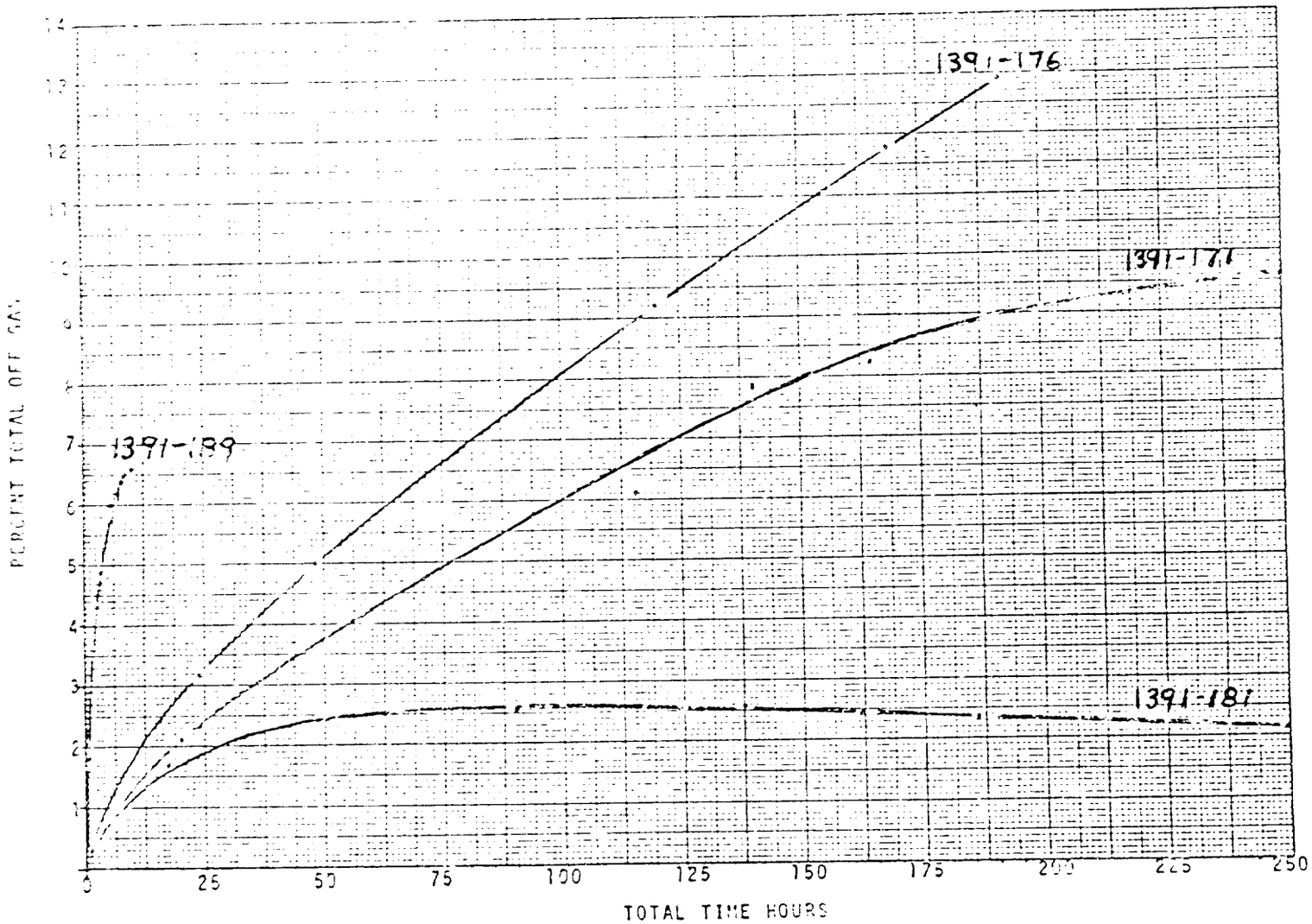
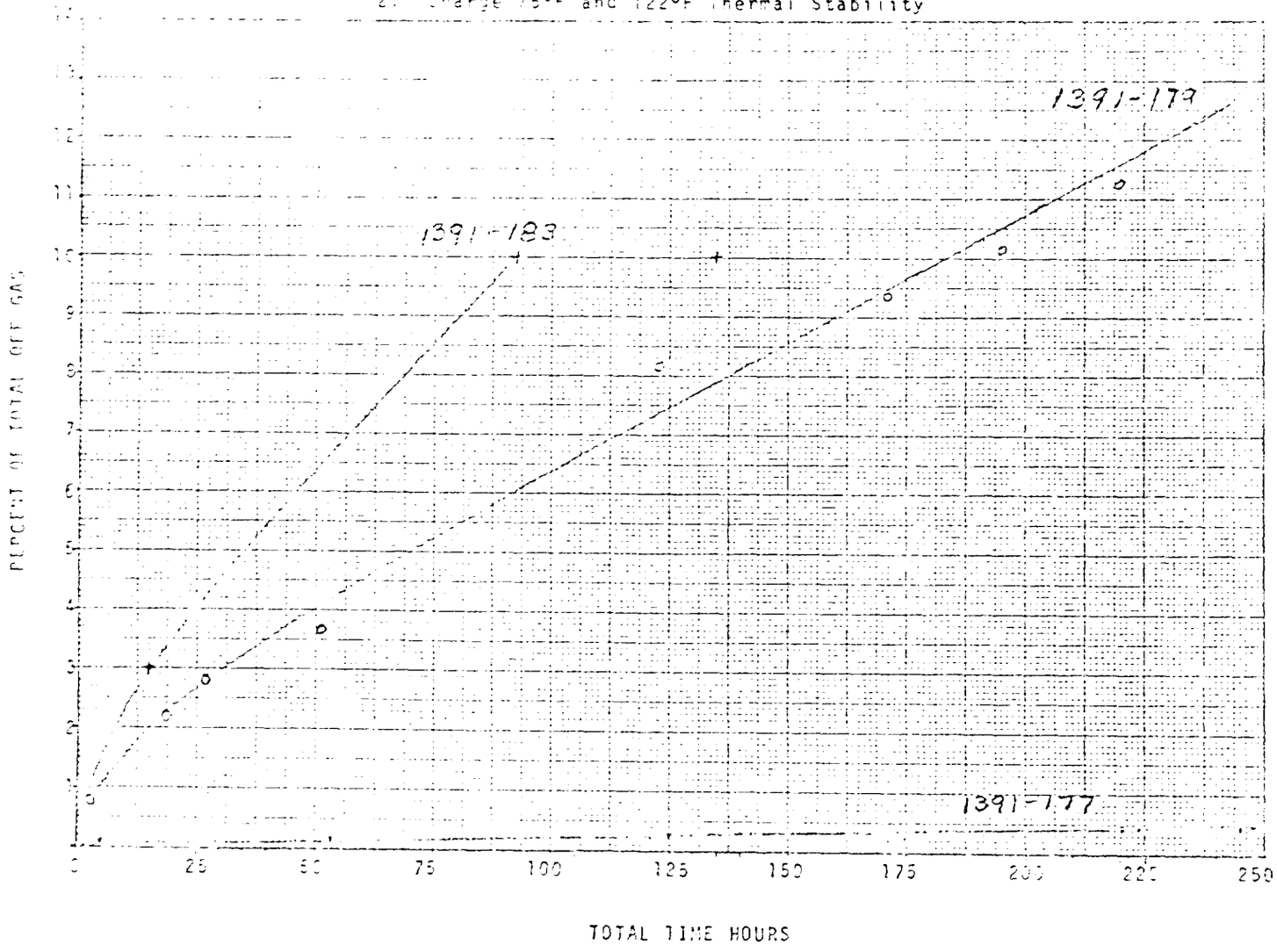


Figure [illegible] - Comparison of Sb: $N_2H_4 \cdot 2HCl$ and Sb: $N_2H_4 \cdot HCl$, 2:1 Charge 75°F and 122°F Thermal Stability



A duplicate pellet was formulated and tested for thermal stability at 122°F. The test procedure followed an overnight leak test under 50 psig H_2 pressure. The results are listed below. A plot of the data is shown in Figure 8.

TABLE 17 - DATA SUMMARY FOR 1391-183

DURATION HOURS	PRESSURE (psig)	TOTAL OFF GAS (percent)
0.0	0.0	0.0
1.0	0.5	0.1
15.0	12.0	3.0
87.0	37.0	10.0
135.0	37.0	10.0

The thermal stability at 122°F was terminated under the presumption that a leak developed approximately 87 hours into the test. In any event, enough gas was released from the formulation at 122°F to suggest that the 165°F Mil. Spec. stability would not be possible.

Similar tests were conducted with hydrazine monohydrochloride with SB according to the following stoichiometry:

$$2NaBH_4 + N_2H_4HCl \longrightarrow 2BN + NaCl + Na + 6\text{-}1/2\ H_2$$

Hydrazine monohydrochloride is hygroscopic. However, we happened to have an appreciable quantity of this material which had been dried several years ago by an azeotropic distillation technique. This material was dried at 122°F invacuo and analyzed for water content. The analysis for water by the usual Karl Fisher technique was, of necessity, modified using glacial acetic acid as solvent.

Although the water content was far above the norm, a pellet was prepared and loaded into a Fisher-Porter apparatus. The room temperature gas evolution rate was high for this sample 1391-179 as shown by the followng Table 18. A plot of the data is shown in Figure 8.

TABLE 18 - DATA SUMMARY FOR 1391-179

DURATION (Hours)	PRESSURE (psig)	TOTAL OFF GAS (Percent)
0.0	2.0	0.0
2.5	5.5	0.8
18.0	12.0	2.2
26.5	14.5	2.8
51.0	19.0	3.7
123.0	38.0	8.1
171.0	45.0	9.4
195.0	49.0	10.2
219.0	54.0	11.3
291.0	38.0	21.1

Obviously the monohydrochloride is incompatible with SB, at least with the possible 0.5 percent water content. This sample when degassed to atmospheric pressure showed the liquid coming to the surface of the pellet. This liquid is presumably a sodium borohydride-hydrazine complex, the result of hydrazine release that also forms with HS-SB formulations, discussed earlier in this section(page 54).

In reviewing the SB-hydrazine salt formulations to this point we must conclude that, regardless of the starting purities, a solid-solid reaction occurs between the borohydride and HS, with the classical reaction to produce either hydrazine bisborane or hydrazine monoborane. In either case, H_2 is produced which would cause problems in storage.

7.3 Microencapsulation

Microencapsulation was investigated as a means of separating the basic reagents to prevent interreaction in the pellet. A thin layer, placed between the HS and SB, may not allow reaction at 165°F, but allow reaction upon ignition in the high-heat reaction zone.

Microencapsulation is accomplished by several methods. One, using organic phase separation, doesn't require a particularly specialized equipment. A. Dobry [1] et al provides a basic explanation of this approach, which was employed in our work during this period.

[1] A. Dobry and F. Boyer-Kawenoki, "Phase Separation in Polymer Solution, "J. Polymer Science (January, 1947), p.90.

Microencapsulation or coating of the reagents sodium borohydride (SB) and dihydrazine sulfate (HS) with a wall membrane to restrict their reactivity below 165°F was tried with several polymeric materials. The process used was phase separation or coacervation, one of the oldest and best known methods. Organic phase separation, rather than aqueous, was used in all cases because HS and SB are hygroscopic and soluble in water. In the sequence of operations: a macromolecular wall material such as polyethylene oxide or polyvinyl alcohol, is dissolved or suspended as a sol in an organic liquid. The core material HS, or SB, to be encapsulated must be immiscible with that organic to permit emulsification. Rapid agitation or stirring is required to disperse the particles uniformly in the solution. Next, by adding a second organic solvent in which the wall material is not soluble, the wall material comes out of solution (ie coacervates) and surrounds the suspended solid reagent HS or SB.

A summary of all the encapsulation results and the thermal stability tests with the various coating materials is presented in Table 20. The successful encapsulation is considered one which separates and protects HS and SB so that when blended, pelletized, and stored at 165°F they are unreactive to one another. This is determined by their not releasing off gas when sealed in a closed container.

7.3.1 Polyethylene Oxide Encapsulation Studies

Polyethylene oxide polymer was the first wall membrane material to be evaluated. The following process described is typical of the organic phase separation encapsulation. The material to be coated, SB or HS, (in this case SB) was slurried in dry hexane. The film-forming polyethylene oxide, a Union Carbide Polyox, the lowest molecular weight (WSR-10), [illegible] was dissolved in a minimum of acetonitrile, [illegible] drop-wise to the substrate SB-hexane slurry while [illegible] stirring throughout. Recovery of the [illegible] was by filtration. The SB polyox product [illegible] was [illegible] treated with a hexane wash on the glass [illegible] to remove hexane, followed by a dry-nitrogen [illegible] was accomplished in a 122°F vacuum oven.

The [illegible] encapsulation with polyox was accomplished [illegible] physical properties changes to indicate difficulties. [illegible] product was recovered which was not significantly [illegible] from the starting material. Based on the active [illegible] of the starting and final products shown below, a [illegible] coating was rejected.

Active hydrogen of starting SB = 105.9 mmols/g

Active hydrogen of encapsulated SB = 97.3 mmols/g

Encapsulation of HS with Polyox following the same above procedure to produce a 5 percent protective coating did not produce the phase separations understood to be a prerequisit for an efficient coating of the substrate. The dry salt-like starting HS took on a wet appearance as the acetonitrile-Polyox solution was added. In addition, two immiscible liquids were obtained on product recovery. Possibly the acetonitrile had dissolved some of the HS and also retained some of the Polyox. A separation of this filtrate to identify these components was not considered of value. Analysis of the recovered HS (1391-197 shown below), which showed a 5 percent change in N-N bond content, could be interpreted as 5 percent Polyox coating.

Analysis of starting HS = 12.4 mmols/g

Analysis of coated HS = 11.7 mmols/g

Pellets of the coated SB and HS of a 4:1 stoichiometry were prepared for stability testing at room temperature and 165°F. The total pellet weight prepared in each case was 3.5g, essentially the same as that used in the uncoated SB-HB comparison tests. The Fisher-Porter apparatuses were tested overnight with 50 psig H_2 pressure.

The test at room temperature was very encouraging; over a period of 27 days no pressure developed. A leak test was conducted after 7 days with H_2 (50 psig), but no pressure was lost over a 24 hour period. This compares to the uncoated with formulation 1391-171, which built 60 psig pressure in eleven days under similar conditions.

The test 1391-200 at 165°F was not as encouraging. Table 19 indicates percent H_2 loss over 4 hours to be about 6.5 percent. There is no comparable run for uncoated HS and SB formulations at 165°F however Figure 6 shows it to have about the same stability as the uncoated formulation 1391-189 at 122°F.

TABLE 19 - DATA SUMMARY FOR 1391-200

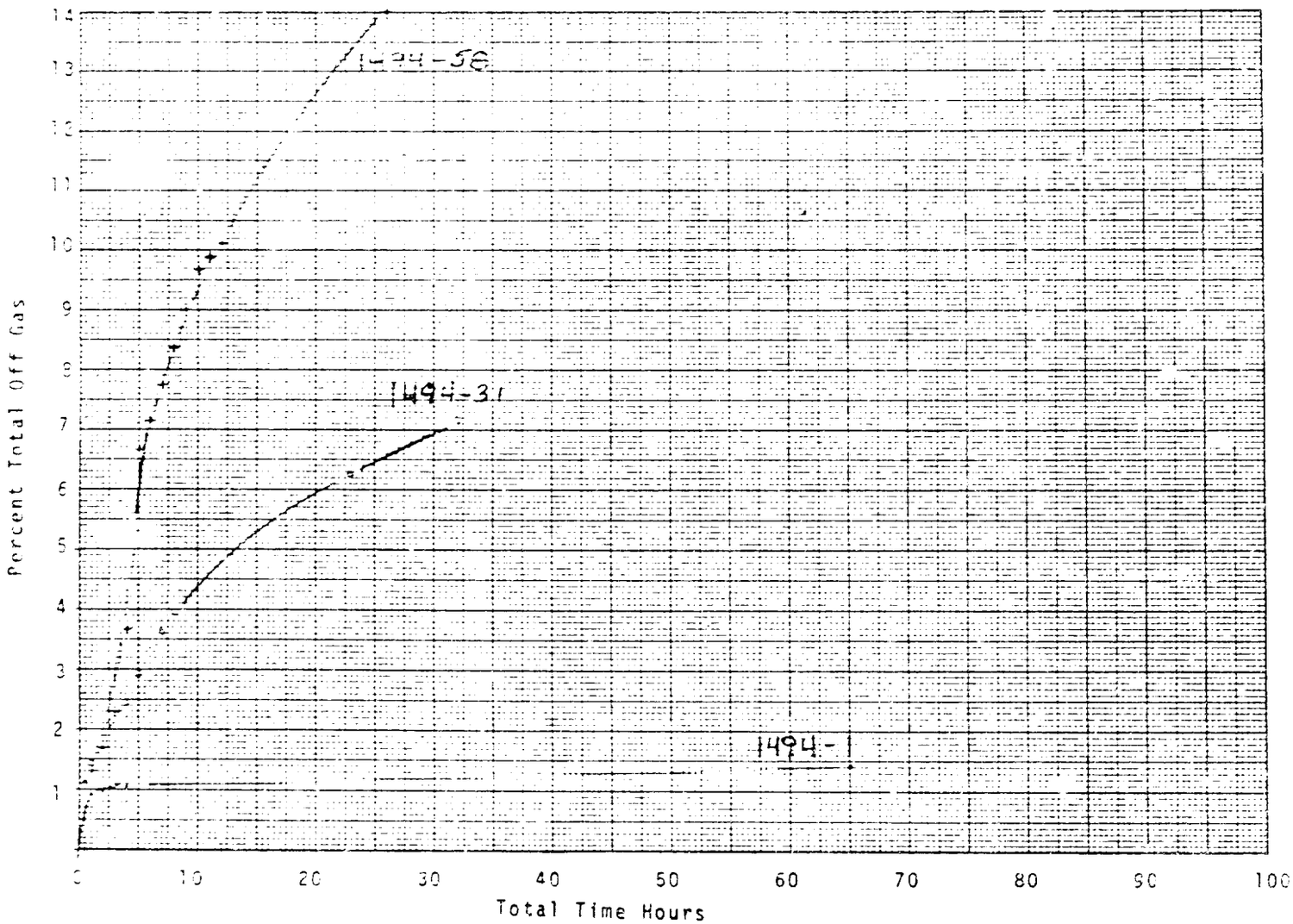
DURATION (hours)	PRESSURE (psig)	TOTAL OFF GAS (percent)
0.5	0.0	0.0
1.0	8.0	1.7
1.5	13.0	2.8
2.0	19.0	4.1
2.5	22.0	4.7
3.0	24.0	5.7
3.5	25.0	5.9
4.0	28.0	6.1
4.5	29.0	6.9
5.0	30.0	7.1

A similar formulation(1494-1) with SB-Polyox coated and as received MHS, was tested at 165°F to determine the comparitive storage stability with uncoated SB, Run(1391-181). Figure 9 shows there may be some improvement in stability with Polyox encapsulated SB incorporation. Further confirmation of MHS stability with the various encapsulated SB products, or coating MHS itself, was not considered favorable because of the high molecular weight gas product composition reported in the Chemical Charge Task section.

Reconsideration of the earlier Polyox WSR-10 encapsulation of HS, 1391-200 and SB 1391-194, that had exhibited stability at 75°F, but became unstable at 122°F suggested the rerun number 1494-25. The substitution of methanol for hexane in the coacervation process was successful in producing a free flowing product. However even with a possible 10% coating, this HS when formulated with the earlier 1391-194 SB resulted in a 5% H_2 loss in 100 hrs at 75°F. This compares with no loss in 550 hours with the earlier polyox encapsulated HS, 1391-200. Also the 10.6% H_2 loss at 165°F in 6 hours further shows that either the process or the encapsulation wall material is inadequate.

Run 1494-27 was a modified rerun of 1391-194. In this run the Polyox is dissolved in CH_3CH then SB is slurried in. Next hexane is added dropwise to coacervate the Polyox. This process was not successful as the earlier 1391-194. The two immisible liquid layer problem reoccurred and the product stuck together in one lump.

Figure 9 - Comparison of Polyox Encapsulated SB and HS, 4:1 Charge at 165°F and Uncoated at 122°F



7.3.2 Polyvinyl Alcohol Encapsulation Studies

Polyvinyl alcohol in various grades are commercially used for film forming and coatings. Several screening runs were made to test PVA as a wall membrane material. Generally the same process used with the Polyox is repeated.

Run 1494-13, in Table 20, is self explanatory. The polyvinyl alcohol (PVA) dissolves readily in DMSO, but when SB is added an off gasing occurs. Obviously a reduction was taking place showing SB, PVA and DMSO are not compatible.

Run 1494-14 PVA encapsulation process of HS did not duplicate the prescribed prerequisit[3], as two immiscible liquids were produced during the coacervation step. However, a reduction in N-N content analysis from 12.3 mmols/g to 9.8 mmols/g could be interpreted as a 21 percent coating on the HS. The room temperature 75°F, test for 45 hours, as plotted in Figure 10, as 1494-15 showed a 1.5% hydrogen loss. Whereas as the 165°F storage test, see Figure 11, produced an 8% loss in 8.5 hrs.

A repeat encapsulation of HS with PVA using DMSO-methanol as the solvent-non solvent, (Run 1494-17), appeared to produce a 12% coating and a free flowing powder product. However when this HS-PVA encapsulation product was formulated with SB-Polyox encapsulation product, 1391-194, a 5.5% hydrogen loss was measured in 64 hours at 75°F. This result was a duplicate test, one of which was slated for 165°F testing if the 75°F stability warranted.

7.3.3 Ethyl Cellulose Encapsulation Studies

Ethyl cellulose film forming polymer was tested as coating wall membrane for SB in Run 1494-20. The ethyl cellulose caused the SB particles to adhere to one another. A moderate grinding and pulverizing was necessary to make free flowing enough for formulation. Although the ethyl cellulose was obviously present the product when formulated with HS-Polyox (1494-20) produced 4.3% of the total hydrogen in 24 hours at 75°F.

The preceding ethyl cellulose encapsulation process was repeated with HS in Run 1494-23. Solution of ethyl cellulose in ethyl acetate and subsequent slurrying of HS was

(3) A. Dobry et. al, ibid.

TABLE 20 - ENCAPSULATION-THERMAL STABILITY RESULTS

RUN NO.	SUBSTRATE REAGENT	WALL MATERIAL	SOLVENT	NONSOLVENT	ENCAPSULATION RESULTS	THERMAL STABILITY RESULTS
1391-194	SB	Polyox WSR-10	CH_3CN	Hexane	Free flowing powder recovered with 6% coating based on change in active H_2	Formulated with 1391-290, stable at 75°F. No change in 27 days, unstable at 165°F, 7.1% H_2 loss in 5 hours
1391-290	HS	Polyox WSR-10	CH_3CN	Hexane	HS caused CH_3CN to separate from hexane, possible 5% coating based on N-N analysis	Same as above
1494-13	SB	Polyvinyl Alcohol Covol 9702	DMSO	Hexane	SB reacted with DMSO, no encapsulation	Could not formulate for stability tests
1494-14	HS	PVA Covol 9702	DMSO	Hexane	HS-DMSO-Hexane immiscibility disrupted coating process, loss of PVA	Formulated with SB-Polyox 1391-194, not stable at 75°F, 1.5% H_2 loss in 45 hrs, loss at 165°F 8% in 8.5 hrs.
1494-17	HS	PVA Covol 9722	DMSO	Methanol	Free flowing powder recovered 12% coating based on N-N analysis	Formulated with 1391-194, not stable at 75°F, 5.5% loss in 54 hrs; not tested at 165°F
1494-19	SB	Ethyl Cellulose	Ethyl Acetate	Hexane	Salt like mass recovered requires moderate grinding to break up;possible 10% coating	Formulated with 1494-25, not stable at 75°F, 4.3% H_2 loss in 24 hrs; loss at 165°F not tested
1494-23	HS	Ethyl Cellulose	Ethyl Acetate	Hexane	Hexane caused ethyl cellulose to precipitate rather than encapsulate HS	Could not formulate for stability tests
1494-29	HS	Ethyl Cellulose	Ethyl Acetate	None	Vacuum evaporation encapsulation HS; all stuck together	Could not formulate for stability tests
1494-35	HS	Polyox WSR-10	CH_3CN	Methanol	Free flowing powder recovered possible 10% coating	formulated with SB-Polyox 1391-194, not stable at 75°F, 5% loss in 100 hrs, 10.5% loss in 6 hrs at 165°F
1494-37	SB	Polyox WSR 10	CH_3CN	Hexane	Two immiscible layers formed due to SB salting out, discarded	Could not formulate for stability tests
1494-41	HS	Polyvinyl Acetate Vinac B 25	C_6H_6	Hexane	Salt like mass all stuck together, possible 10% coating	Formulated with SB Polyox 1391-194, stable at 75°F; [illegible]% loss at 165°F in 30 hrs
1494-44	HS	Polyethylene	-	Toluene	Ethylene polymerization on HS via Ziegler catalyst. The latter over reacted with HS	Could not formulate for stability tests
1494-49	HS	Polyethylene		Toluene	Same as above, polyethylene forms but precipitates, not encapsulate	Could not formulate for stability tests
1494-48	HS	Polyvinyl Acetate Vinac B 25	Ethyl Acetate	Hexane	Salt particles adhere to each other, possible 10% coating	Formulated with SB-Polyox 1391-194, stable at 75°F, [illegible]% H_2 loss at 165°F in 8 hrs
1494-55	HS	Vinac B 25	Ethyl Acetate	Hexane	Waring blender application, 10% coating all stuck together	Could not formulate for stability tests
1494-53	HS	Vinac B 25	Ethyl Acetate	Hexane	Waring blender application, 5% coating possible, particles adhere to one another	formulated with SB Vinac B 25 1494-56
1494-56	SB	Vinac B 25	Ethyl Acetate	Hexane	Waring blender application, 5% coating possible	formulated with HS Vinac B 25 1494-53, stable for 20 days at 75°F, 15% H_2 loss at 165°F in 28 hrs

Figure 10 - Comparison of PVA and Polyox Encapsulated SB and HS, 4:1 Charge at 75°F

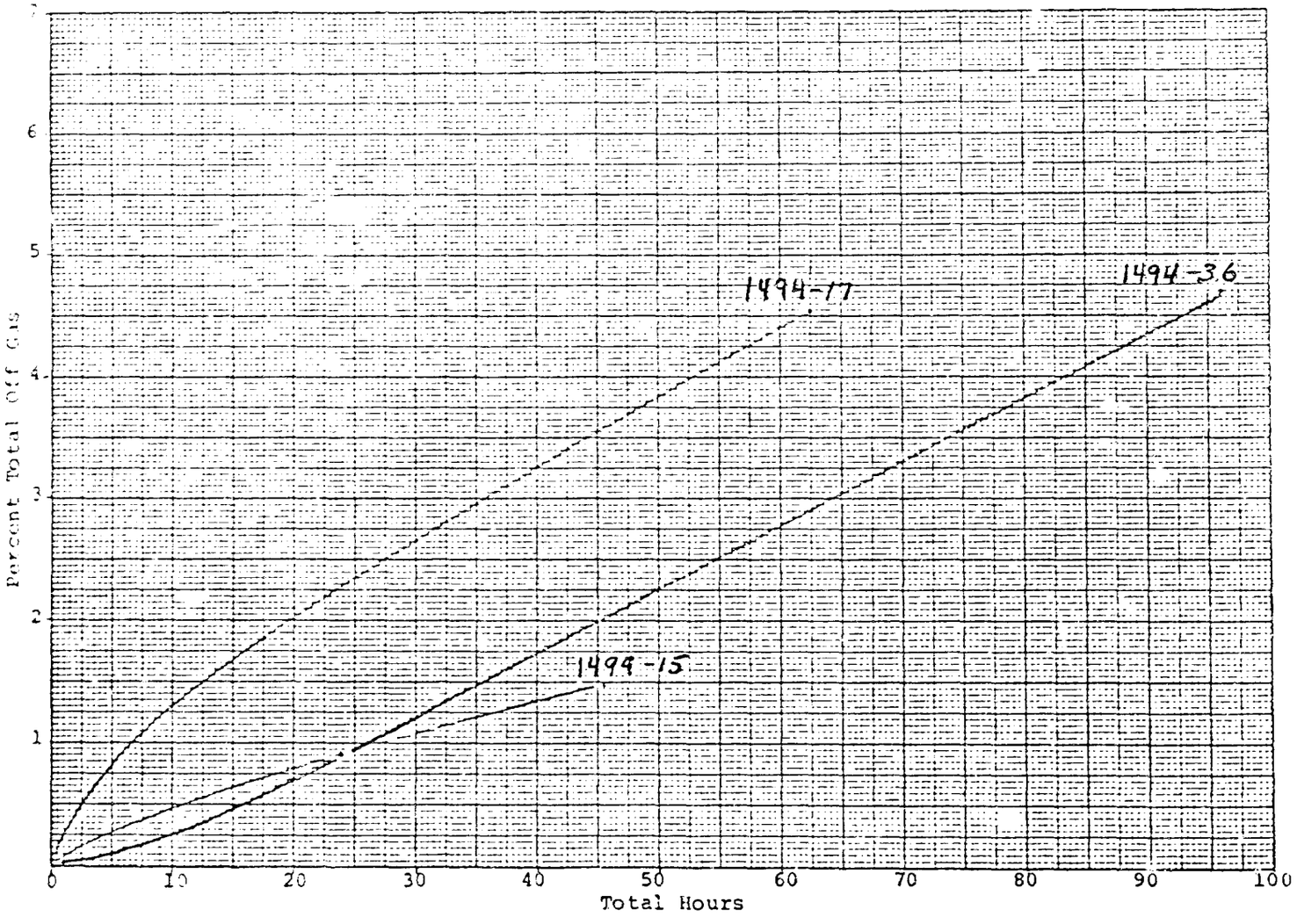
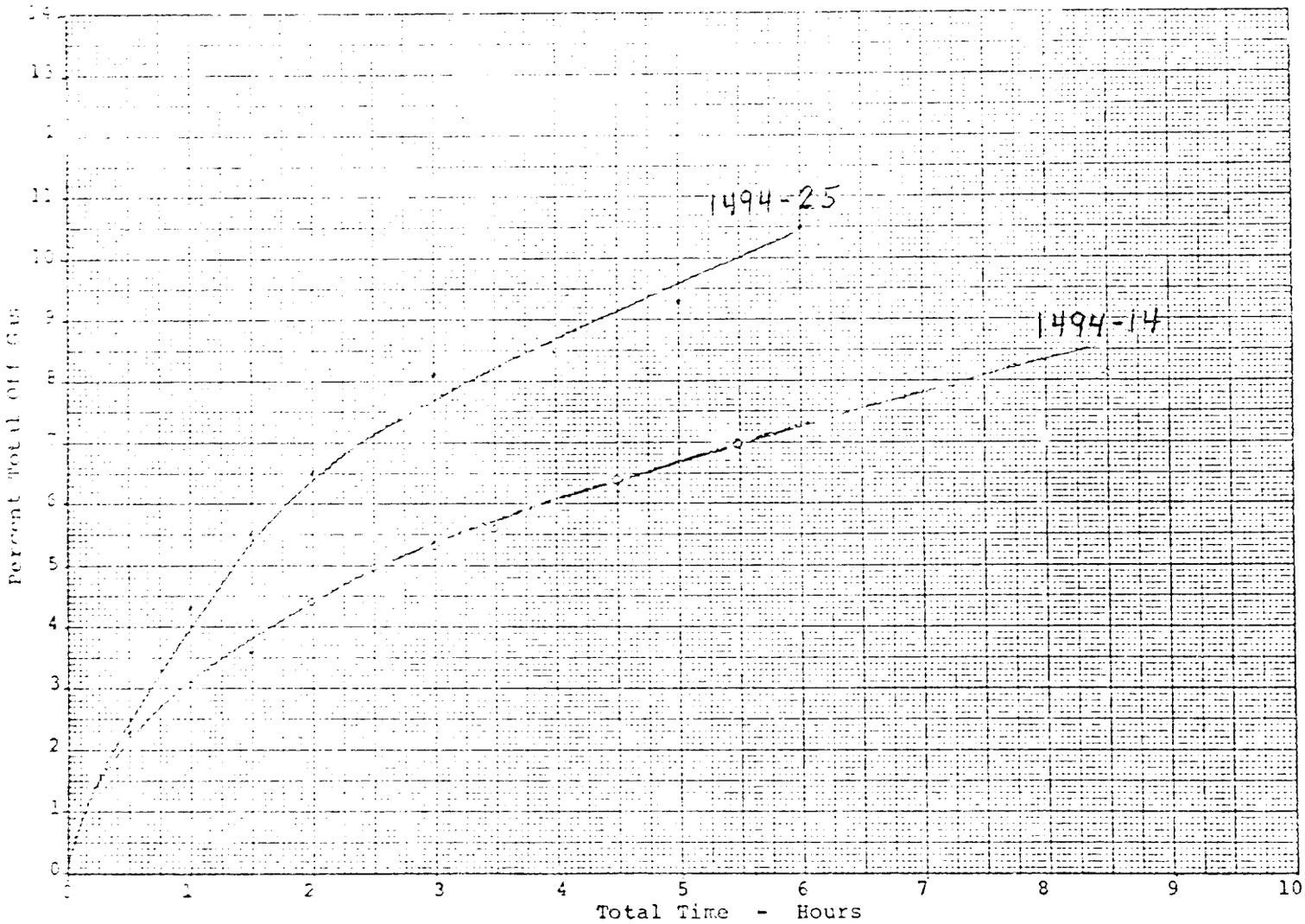


Figure 11 - Comparison of PVA and Polyox Encapsulated SB and HS, 4:1 Charge at 165°F



normally very effective. When hexane was added dropwise to the slurry to coacervate the cellulose,a precipitate formed. Tests showed the precipitate to be ethyl cellulose and the HS to be uncoated. Therefore no formulation or thermal stability tests was made on this product.

Encapsulation of HS was attempted with ethyl cellulose via a Rinco rotating evaporator in Run 1494-29. First the ethyl cellulose was dissolved in ethyl acetate to which the insoluble HS was added. Next the coating process was attempted by a flash evaporation of the solvent in a rotating round-bottom flask on the Rinco evaporator. As the last solvent evaporated, the HS balled up rather than remain free flowing. It was necessary to cut the product out of the flask with a spatula. The final product could not be readily pulverized in order to formulate and therefore was not subject to a thermal stability evaluation.

7.3.4 Polyethylene Encapsulation Study

An encapsulation process is described by D. F. Herman et al[4] in which cellulose fibers were enveloped with wall membrane polyethylene by the use of Zieger catalyst and ethylene. This process was selected to encapsulate HS or SB with a protective covering of polyethylene to promote storage stability to 165°F. The polyethylene normally produced by this process is the high density, higher melting form.

Polymer growth on the cellulose, according to Herman et. al., follows a cellulose interaction with $TiCl_4$ catalyst. The system must be relatively water free but the catalyst is supposed to react with OH groups on the cellulose. Therefore,in our case it was planned that since HS and SB would probably contain trace quantities of hydrated water at best, these sites would provide the catalyst active sites. Following the deposition of active catalyst sites on HS or SB surface, ethylene is next added. Typically,complete take up and polymerization of ethylene monomer occurs to produce a polymer shell.

In the first attempt, run no. 1494-34, 75g of HS was slurried in 750 cc of toluene. The first step in the catalyst generation, was addition of 1.1 cc or (10 mmols) $TiCl_4$, which produced a yellow-orange colored solution and discolored the HS. The excellent slurry characteristics was

(4) Herman DF, V. Kruse and J.J. Bravcato, "Polyethylene Encapsulated Cellulose," J. Polymer Sci. Part C No. 11, p. 75-95 (1965).

also destroyed. By replacing the external stirrer with a stronger one and breaking up the coagulated HS, a slurry was regenerated. The second step of the catalyst generation was the addition of 4.8 cc (10 mmols) $AlCl_3$ which produced a gray solvent, with the HS retaining its tan color. Unfortunately this does not compare with the dark brown color characterized in the D.F. Herman etal paper[4]. Ethylene was then passed into the slurry, at 122 cc/mm, (0.141g/min) and the temperature was raised to 60 to 20°C. Apparently the proper Zeigler catalyst did not form because ethylene was continually lost via off gas. After 1.3 hours, reaction was terminated and catalyst destroyed by addition of methanol. Product recovery was by filtration and vacuum drying. Qualitatively the product dissolves completely in water and thus was assumed to contain no polyethylene.

A second attempt run(1494-39)was modified so that nearly simultaneous addition of $TlCl_4$ and $AlCl_3$ catalyst reagents produced the desired dark brown Zeigler catalyst color. This also allowed the HS to slurry continuously. Passing in ethylene at 60 to 70°C resulted in only the partial take up, as evidenced by off gas rate. The product was recovered and dried by the same process as above and tested in water for degree of encapsulation. This product appeared to be a mixture of soluble HS and insoluble polyethylene flock. The major portion appeared water soluble. This indicates that the Zeigler catalyst did not attach to the HS but rather remained suspended in solution, a situation normally, producing polyethylene precipitate.

The lack of success in polyethylene encapsulation of HS, because of adverse catalyst reactivity; and probably greater reactivity of catalyst reagents with SB dictated discontinuing the polyethylene studies.

7.3.5 Polyvinyl Acetate Encapsulation Studies

A sample of polyvinyl acetate, grade VINAC B-25, was obtained from Air Products and Chemicals, Inc. It was recommended as an excellent film forming homopolymer, which has a softening point of 311°F. It is also readily soluble in almost all common solvents except aliphatic hydrocarbons. These desirable features, coupled with the lack of OH of PVA, and hygroscopic nature of polyethylene oxides, were the basis for testing VINAC as a possible wall coating material.

A microencapsulation of HS with VINAC using benzene and hexane coacervation produced a salt like mass(1494-31)with individual particles stuck together. The particles were broken apart and blended with Polyox coated SB and pelletized. At room temperature no off gas was measured over 144 hours. But at 165°F,approximately seven percent of the total contained H_2 was released in 32 hours. The rate of evolution is illustrated in Figure 9 as 1494-31.

Encapsulation of HS with VINAC B-25, polyvinyl acetate, was continued in Run 1494-41, from ethyl acetate solvent using a partial evaporation technique and a hexane coacervation process. The polyvinyl acetate was first dissolved in ethyl acetate, then HS added to make up an equivalent 10 percent coating. This slurry was next continually rolled and subjected to a partial vacuum. When the solvent was reduced to near dryness, so as to allow the HS to tumble freely without sticking together, hexane was added. Hexane caused the slurry to become immobile almost instantaneously. The product was recovered by decantation and vacuum oven drying, resulting in a stuck together salt mass. No formulations were attempted with this product because any blending operation would necessitate cutting and regrinding,thus destroying encapsulation wall membranes.

Further attempts to encapsulate with polyvinyl acetate were carried out in a Waring blender. This instrument,capable of high speed mixing,was employed in several similarly related encapsulation procedures described in various U.S. Patents. The blender is set up in a nitrogen filled dry box for the encapsulation operation. In run 1494-51 a 10 percent coating of VINAC on HS starts by solution of resin in ethyl acetate to which HS is added. Resin coacervation or coating is provided by addition of hexane dropwise to the above HS slurrying at high speed in the blender. Recovery is by decanting the organic solvents and several rewashes and reslurrys with hexane. The dried product was a nonflowable, stuck-together mass of HS, approximately the same as 1494-41. Possibly the reason for the HS to be stuck together was that a 10 percent wall membrane was in excess and causes the HS particles to cement together.

To investigate this theory a 5 percent encapsulation run(1494-53)was repeated as described above. The product was still tacky and stuck together but not as much as the previous run. It was possible to break up the dry mass with a spatula. This product was storage tested in run 1494-58 to be discussed later.

A comparison run 1494-56 was made in the Waring blender in which a 5 percent VINAC-encapsulated SB was prepared. Again hexane was added to a slurry of SB in VINAC-ethyl acetate solution. The product recovered after decant and several reslurry hexane washes was not a free flowing salt. However, it could be readily broken up in to a powder more easily than 1494-53 HS encapsulation. This product was formulated in the following Runs 1494-58 storage test.

The thermal stability and shelf life storage stability test run 1494-58, of pellets of VINAC encapsulated SB and HS, (4:1 ratio), was tested at room temperature and 165°F in Fisher-Porter reactor tubes. No gas was released at room temperature in 5 days (120 hours) from this formulation. Figure 9 shows the relative rate of gas release at 165°F of 15 percent in 28 hours. Although the higher temperature storage instability suggests poor protection by the VINAC polymer encapsulation, the room temperature storage results are superior to all uncoated reagent formulation storage tests.