

NASA: BARIUM - Chemical Formulas/Suppliers

source: gisgaia / SOshanna

This is the "Description of Preferred Embodiments" link in the NASA Barium Patent listed above. Astounding that this information was generated in 1969 and now, 30 years later, there is evidence of Barium saturation in our atmosphere.

www.delphion.com/details?...etd=1#detd [NOTE: The text has been enlarged for easier reading]

The Barium/Fuel mixtures are listed below along with the suppliers. There is much technical info along with helpful hints(?) contained in this description, for example "This system caused clogging of the feed valves due to precipitation of the Ba(NO3)."

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Description of Preferred Embodiments:

Referring now to the drawings and more particularly to FIG. 1, there is shown a segment of a suitable carrier vehicle 10, such for example a rocket motor. Vehicle 10 is employed to carry fuel tank 11, insulated oxidizer tank 13 and combustion chamber 15, along with the necessary instrumentation, from earth into the upper atmosphere or into interplanetary space. Fuel tank 11 is in fluid connection with combustion chamber 15 and oxidizer tank 13 is in fluid connection with combustion chamber 15 by way of respective conduits 17 and 19. A pair of valves 21 and 23 are disposed within the respective conduits 17 and 19. Valves 21 and 23 are adapted to be selectively and simultaneously opened by a suitable battery-powered timing mechanism, radio signal, or the like, to release the pressurized fuel and oxidizer from tanks 11 and 13. The fuel and oxidizer then flow through conduits 17 and 19 and impinge upon each other through a centrally positioned manifold and suitable jets (not shown) in combustion chamber 15 where spontaneous ignition occurs. The reaction products are then expelled through the open ends of combustion chamber 15 as plasma which includes the desired barium neutral atoms and barium ions as individual species.

The fuel utilized in fuel tank 11 is either hydrazine (N₂ H₄) or liquid ammonia (NH₃) while the oxidizer employed is selected from the group consisting of liquid fluorine (F₂), chlorine trifluoride (ClF₃) and oxygen difluoride (OF₂). When using hydrazine as the fuel, barium may be dissolved therein as barium chloride, BaCl₂, or barium nitrate, Ba(NO₃)₂, or a combination of the two. When using liquid ammonia as the fuel, barium metal may be dissolved therein. The combination found to produce the highest intensity of Ba^o and Ba⁺ resonance radiation in ground based tests involved a fuel of 16 percent Ba(NO₃)₂, 17 percent BaCl₂ and 67 percent N₂ H₄; and as the oxidizer, the cryogenic liquid fluorine F₂ and in which an oxidizer to fuel weight ratio was 1.32.

Other combinations of ingredients tested are set forth in Table I below:

TABLE I

System Optimum O/F Percent Ionization Calculated
16.7% BaCl ₂ -
83.3% N ₂ H ₄ /ClF ₃
2.36 68.0
26% BaCl ₂ -
74% N ₂ H ₄ /ClF ₃
2.08 70.0
50% Ba(NO ₃) ₂ -
50% NH ₃ /ClF ₃
1.52 -
42.9% Ba(NO ₃) ₂ -
57.1% N ₂ H ₄ /ClF ₃
1.19 50.0
16.7% BaCl ₂ -
83.3% N ₂ H ₄ /F ₂
1.95 68.8
26% BaCl ₂ -
74% N ₂ H ₄ /F ₂
1.71 70.6
21% BaCl ₂ -
9% Ba(NO ₃) ₂ -
70% N ₂ H ₄ /F ₂
1.57 68.5
17% BaCl ₂ -
16% Ba(NO ₃) ₂ -
67% N ₂ H ₄ /F ₂
1.31 68.1
13% BaCl ₂ -
21.5% Ba(NO ₃) ₂ -
65.5% N ₂ H ₄ /F ₂
1.34 63.7
9% BaCl ₂ -
30% Ba(NO ₃) ₂ -
61% N ₂ H ₄ /F ₂
1.04 63.7
42.9% Ba(NO ₃) ₂ -
57.1% N ₂ H ₄ /F ₂
0.976 43.0
42.9% Ba(NO ₃) ₂ -
57.1% N ₂ H ₄ /OF ₂
0.694 46.9
26% BaCl ₂ -
74% N ₂ H ₄ /OF ₂

1.22 52.8

The conditions under which each of the combinations listed in Table I were tested were ambient and the percentage ionization was calculated by equations set forth in NASA Contract Report CR-1415 published in August 1969.

The chemical supplier and manufacturers stated purity for the various chemicals employed are set forth in Table II below:

Chemical
Supplier Purity

N2 H4
Olin Mathieson Chemical
Technical Grade
Company, Lake Charles,
97-98% N2 H4
Louisiana (2-3% H2 O)

NH3
Air Products and Chemicals
Technical Grade
Allentown, Pa.

BaCl2
J. T. Baker & Co. Reagent Grade
Phillipsburg, N.J.

Ba(NO3)2
J. T. Baker & Co. Reagent Grade
Phillipsburg, N.J.

F2 Air Products & Chemicals
98%
Allentown, Pa.
ClF3
Allied Chemical Co.
99.5%
Baton Rouge, La.
OF2
Allied Chemical Co.
98%
Baton Rouge, La.

A solubility study of various mixtures containing Ba(NO3)2, BaCl2 and N2 H4 was made at room temperature and is shown in the triangular plot of FIG. 2. Seven solutions that were used in the tests enumerated in Table I are indicated by reference letters in FIG. 2 as follows:

- a. 16.7% BaCl2 - 83.3% N2 H4
- b. 26% BaCl2 - 74% N2 H4
- c. 21% BaCl2 - 9% Ba(NO3)2 - 70% N2 H4
- d. 17% BaCl2 - 16% Ba(NO3)2 - 67% N2 H4
- e. 13% BaCl2 -21.5% Ba(NO3)2 -65.5% N2 H4
- f. 9% BaCl2 - 30% Ba(NO3)2 - 61% N2 H4
- g. 42.9% Ba(NO3)2 - 57.1% N2 H4

A mixture below the Saturation Line, that is toward the Ba(NO3)2 or BaCl2 corners contained a solid and a solution phase whereas the salts were in complete solution above the saturation line.

All fuel mixtures or systems described were easily handled except the 50 percent Ba(NO3)2 -50 percent NH3 system. This system caused clogging of the feed valves due to precipitation of the Ba(NO3)2. In addition the light values obtained using this system was relatively low.

In testing of each of the fuel mixtures set forth in Table I the Ba° light was greater than the Ba+ light for a given oxidizer/fuel ratio in each of the mixtures. The maximum light occurred in all systems at a point located between the stoichiometric O/F and 3 percent less than the stoichiometric O/F. The stoichiometric O/F is defined as being equivalent to the oxidizer to fuel weight ratio in a balanced equation assuming the salt is converted to free Ba, F to HF, Cl to HCl and O to H2 O. For example, one system tested had an O/F ratio of 142 grams oxidizer per 100 grams fuel or 1.42/1.00. If the barium is assumed to be converted to BaF2 then the stoichiometric O/F is 1.47. Since the greatest light output in all cases occurred with O/F less than stoichiometric it is apparent that little of the Ba was combined as BaF2 or BaCl2. This was confirmed by spectrographic analysis.

In Table II the various systems are listed in decreasing light output or relative light intensity as measured by phototubes in millivolts, thereby indicating the relative barium yield.

TABLE III

SYSTEM MAXIMUM RELATIVE
(percent weight for fuel)
INTENSITY, millivolts
Ba° 5535 A
Ba+ 4554 A

17% BaCl2 -16% Ba(NO3)2 -67% N2 H4 /F2
27600
11800
13% BaCl2 -21.5% Ba(NO3)2 -65.5% N2 H4 /F2
23600

8340
 21% BaCl₂ -9% Ba(NO₃)₂ -70% N₂ H₄ /F₂
 20600
 9100
 9% BaCl₂ -30% Ba(NO₃)₂ -61% N₂ H₄ /F₂
 16600
 5970
 26% BaCl₂ -74% N₂ H₄ /F₂
 16600
 6520
 26% BaCl₂ -74% N₂ H₄ /OF₂
 11800
 2100
 16.7% BaCl₂ -83.3% N₂ H₄ /F₂
 9100 3350
 42.9% Ba(NO₃)₂ -57.1% N₂ H₄ /F₂
 9000 1800
 42.9% Ba(NO₃)₂ -57.1% N₂ H₄ /OF₂
 7300 1330
 42.9% Ba(NO₃)₂ -57.1% N₂ H₄ /ClF₃
 663 94
 50% Ba(NO₃)₂ -50% NH₃ /ClF₃
 221 44

From the above information, it is readily seen that the 17 percent BaCl₂ -16 percent Ba(NO₃)₂ -67 percent N₂ H₄ /F₂ system gave the greatest amount of light intensity of the 4554 Å Ba⁺ and 5535 Å Ba^o spectral lines. Ambient tests showed that the optimum oxidizer to fuel ratio of this system was 1.32 to 1.00. This system containing 8.52 weight percent barium was estimated to be 68.1 percent ionized. Also since this system had the largest relative light intensity it would be expected to give the greatest amount of Ba^o and Ba⁺ and would appear to be the optimum system for a barium payload. In all systems tested it was found that the relative light reached a maximum at the O/F corresponding to the stoichiometric equation yielding barium as one of the reaction products and that the relative light output was sensitive to the O/F. Moving to either side of the optimum O/F caused a sharp decrease in relative light. In vacuum tests the ignition of each system tested was smooth and like the ambient tests, took place in the combustion chamber. The rapid expansion in vacuum caused a decreased atom and ion density in the luminous flame which caused the light intensity to be about 1/37 to 1/50 the intensity measured in ambient tests. The percentage ionization was approximately the same for vacuum and ambient tests.

The operation of the invention is now believed apparent. Initially, fuel tank 11 is charged with the fuel containing the desired quantity of dissolved barium salt and pressurized with helium. The fuel tank pressure may be in the range of 6.89 to 20.06 $\times 10^5$ Newton/meter².

Oxidizer tank 13 is also charged with the appropriate oxidizer and pressurized. Cryogenic oxidizers such as OF₂ and F₂ are condensed from gases in the closed oxidizer tank which must be maintained enclosed in a liquid nitrogen bath. The oxidizer feed valve 23 and conduit 19 must also be maintained at liquid nitrogen temperature with a liquid nitrogen jacket when employing a cryogenic oxidizer.

The noncryogenic oxidizer, ClF₃, may be pressurized into the closed oxidizer tank 13 from a supply bottle with super dry nitrogen. Combustion chamber 15 is formed of stainless steel, aluminum, or the like F₂ compatible metals and is internally partitioned by the manifold, not shown. The conduits 17 and 19 terminate in a manifold having injector orifices (not shown) mounted 90° to each other within each end of chamber 15 and sized for pressure drops of 5.24 to 10.2 $\times 10^5$ Newton/meter² across the orifice. Fuel and oxidizer flows are in the range of 2.05 to 6.82 Kg/sec each. The entire system is carried into the upper atmosphere or interplanetary space by rocket vehicle 10 where, in response to a suitable signal, timing mechanism or the like, valves 21 and 23 may be selectively opened and closed and the pressurized liquid fuel and oxidizer will flow through conduits 17 and 19 into combination unit 15. When the hypergolic liquids impinge upon each other, they spontaneously ignite to expel reaction product gases or plasma including the highly luminous barium neutral atoms and barium ions as individual species. All of the barium reaching the combustion chamber is vaporized and released through the opposite ends thereof so that a high yield efficiency is obtained. The resulting high flame temperature, approximately 4,000°K., and some as yet not determined chemical activation, produces a relatively large amount of barium ions in the flame which is a highly desirable condition. It has been estimated from spectroscopic measurements that the degree of ionization may be as high as 75 percent in the released plasma in comparison to being on the order of 1 percent for the previously used Ba-CuO solid system which depends almost entirely on solar photoionization, a time-dependent phenomena which further reduces the usable barium yield of this known system.

Thus, it is readily apparent that the present invention provides an inherently more efficient process of producing barium clouds wherein the degree of ionization in the released plasma is much greater. The selectively opening and closing of valves 21 and 23 gives the possibility of a payload with multiple releases permitted due to the start and stop capabilities of the liquid system. Also, the liquid system of the present invention gives the possibility of controlling rates so that a trailtype release can be obtained as well as a point-source type. In addition, the liquid system of the present invention effects the formation of barium atoms and ions at the time of combustion and expansion at high temperatures and results in little opportunity for the barium to condense during release. There are obviously many variations and modifications to the present invention that will be readily apparent to those skilled in the art without departing from the spirit or scope of the disclosure or from the scope of the claims.

 Blessings to all - rhonda
 May this effort benefit all sentient beings in creation...
 OM AH HUM VAJRA GURU PADMA SIDDHI HUM - HRIH