Characterization of Alternate Source Densified Basic Magnesium Carbonate for Smoke Generation

Zhaohua Luan,[a] Gary Chen,[a] Lyle Miller,[b] Michael Whittaker[b] and Raymond Cutler[b]

[a] US Army Research, Development and Engineering Center, Picatinny Arsenal, New Jersey 07806, USA.

[b] Ceramatec, Inc., 2425 South 900 West, Salt Lake City, Utah 84119, USA.

ABSTRACT

Densified Basic magnesium carbonate (DBMC) is an important chemical used widely in military for smoke generation, such as in M18/M83 smoke grenades, M8 smoke pot, battlefield effect simulator, and other miscellaneous pyrotechnic sub-components. However, its domestic production had long ceased, and the US Army currently relies on a sole foreign source, Dead Sea Bromide of Israeli, for the supply of the material. The aim of this work is to identify, evaluate and establish alternative source suppliers of DBMC. Among six supply sources identified for assessment, the DBMC samples from Lehmann and Voss of Germany and Melox Chemicals of India more closely resemble the material currently used in the Army in terms of their physiochemical and thermal properties as outlined in military spec MIL-DIL-11361E. The heavy metals and other trace constituents were also assessed with satisfactory results. These two DBMC source supplies are, therefore, down selected for further evaluation in complete smoke devices for performance data.

Introduction

Densified basic magnesium carbonate (DBMC) in pyrotechnic applications usually refers to compounds containing magnesium carbonate, $MgCO_3$, magnesium hydroxide, and water.[1] There are two well-known DBMC phases with distinct particle morphologies,[2-3] one is commonly called light phase with a 4:1:4 chemistry, hydromagnesite ($4MgCO_3 : 1Mg(OH)_2 : 4H_2O$), and another one referred as heavy phase 4:1:5 with higher water content, dypingite ($4MgCO_3 :1Mg(OH)_2: 5H_2O$). Weight loss for these two phases upon heating is slightly different, 58.5 % and 56.9 % for heavy and light respectively. In a typical pyrotechnic smoke formulation, DBMC functions as a coolant through a multi-stage decomposition.[1,4] It releases water and then carbon dioxide during combustion, which aids in the production of desirable smoke without flaming.

The US Army currently uses DBMC for smoke generation in a variety of weapon systems, such as M18/M83 smoke grenades, M8 smoke pot, battlefield effect simulator and other miscellaneous pyrotechnic sub-components, with an annual usage of over 25 metric tons.[1] However, the domestic DBMC production by Rohm&Haas has long ceased, and the Dead Sea Bromide of Israel is currently the Army's sole DBMC supplier. In this work, six DBMC supply sources were identified, and the DBMC samples from each of those sources have been examined in terms of their physiochemical properties, such as composition, particle size, density, against military spec MIL-DIL-11361E. A down-selection was made to further evaluate their performance in complete smoke devices.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **27 MAR 2012**	2. REPORT TYPE **Technical**	3. DATES COVERED **12-10-2010 to 27-03-2012**

4. TITLE AND SUBTITLE **Characterization of Alternate Source Densified Basic Magnesium Carbonate for Smoke Generation None**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Zhaohua Luan; Gary Chen; Lyle Miller; Michael Whittaker; Raymond Cutler**	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Zhaohua Luan,Building 1090/1609,Picatinny Arsenal,NJ,07806-5000**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Densified Basic magnesium carbonate (DBMC) is an important chemical used widely in military for smoke generation, such as in M18/M83 smoke grenades, M8 smoke pot, battlefield effect simulator, and other miscellaneous pyrotechnic sub-components. However, its domestic production had long ceased, and the US Army currently relies on a sole foreign source, Dead Sea Bromide of Israeli, for the supply of the material. The aim of this work is to identify, evaluate and establish alternative source suppliers of DBMC. Among six supply sources identified for assessment, the DBMC samples from Lehmann and Voss of Germany and Melox Chemicals of India more closely resemble the material currently used in the Army in terms of their physiochemical and thermal properties as outlined in military spec MIL-DIL-11361E. The heavy metals and other trace constituents were also assessed with satisfactory results. These two DBMC source supplies are, therefore, down selected for further evaluation in complete smoke devices for performance data.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**5**	

Experimental

Materials. No US supply sources were identified in a market research. Among six potential DBMC supply sources under consideration, two samples were provided by Lehmann & Voss of Germany from two different lots, designated as sample L&V-1 and L&V-2, and one received from Solvay of Italy as sample Solvay. Another three were from India, designated as sample Melox, Osian and Shree, respectively. The sample Shree is clearly out of the specification in terms of density and was not further evaluated. The Army provided its DBMC material, sourced from Dead Sea Bromide of Israel, as Army Control.

Characterization. Bulk density was determined using a Scott Volumeter in accord with ASTM B329. Tap density was measured using an ASTM B527 compliant testing apparatus Agilent 50-3000. Surface area was measured using a Micromeretics Tristar analyzer with a multipoint BET method. Moisture content was measured as specified in the military spec MIL-DTL-11361E using a VirTis 25ES chamber with controlled temperature and pressure. Micrographs were recorded using a JEOL JSM-500/LV scanning electron microscope. X-ray diffraction (XRD) patterns were obtained using a Phillips PW 3040 powder diffractometer with Cu Kα radiation and a graphite monochromator operating at 45 kV and 35 mA with 0.02º step size and 1 s step time.

For particle size measurement, a Beckman LS 230 light scattering instrument was employed with a setup specified in the military spec MIL-DIL-11361E. About 0.1 grams of powder was dispersed in 25 ml of deionized water with 1 ml of 0.25 wt % ammonium polyacrylate aqueous solution (Colloid 102 by Rhone Poulenc) as dispersant and followed with an ultrasonic horn for 5 mins prior to measurement. Additional runs were done in 2-propanol, rather than deionized water, using 0.25 wt. % phosphate ester (RE-610 by Rhodia) as dispersant.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) was performed using either a TA Instruments Q5000 or a Netzsch STA 409 analyzer with simultaneous differential thermal analysis. Differential scanning calorimetric analysis were done as specified in MIL-DTL-11361E except that high purity He was substituted for Ar.

For the trace and heavy metal analysis, the various procedures specified in the military spec MIL-DTL-11361E were closely followed in most cases, except for iron and calcium contents, where inductively coupled plasma spectroscopy (ICP) and atomic absorption spectroscopy (AA) were employed, respectively. Arsenic, lead, and the five other heavy metals were all determined by ICP methods, while soluble substances in water or hydrochloric acid, as well as magnesium as magnesium oxide, were determined by the gravimetric tests specified in the military spec MIL-DIL-11361E.

Results and Discussion

Physical and Thermal Analysis. Table 1 shows test results of bulk and tap density, surface area and particle sizes, measured both in water and 2-propanol, of all DBMC samples as well as the corresponding specifications from military spec MIL-DIL-11361E, denoted as Mil Spec. As can be seen from the data, the physical properties of the DBMC materials under consideration vary greatly. The sample L&V-2 from Germany and the sample Melox from India most closely resembling the Army Control in terms of density and particle size. The Sample Osian of India and Solvay of Italy show very fine particle size and low density in comparison to the Army Control, and are clearly out of the military specification.

As expected, all DBMC samples give similar XRD patterns,[5] which can be better indexed to a light hydromagnesite phase rather than a heavy dypingite phase. SEM imaging of samples[5] indicates none of these DBMC samples possess exactly identical morphology to the Army Control which is spherical in nature, though the sample L&V-2 and Melox are the closest matches. However, the impact of such a difference in morphology on smoke generation remains to be seen in performance test.

Table 1. Physical Characteristics of Densified Basic Magnesium Carbonate Samples.

Sample	Density (g/cc)		Surface Area	Particle Size (μm)	
	Bulk	Tap	(m^2/g)	Water	2-propanol
MIL Spec	(n/a)	0.2-0.6	(n/a)	7-20	(n/a)
Army Control	0.35	0.57	11.4	11.9	14.1
L&V-1	0.38	0.69	16.2	18.9	20.7
L&V-2	0.37	0.64	10.1	14.7	14.2
Melox	0.20	0.46	20.9	7.3	9.6
Osian	0.11	0.29	23.7	0.8	25.1
Solvay	0.08	0.19	33.2	0.4	8.6

As far as thermal properties, shown in Table 2, TGA reveals that all DBMC samples have almost the same MgO content consistent with Army control and Mil Spec data, but vary slightly in endothermic characteristics. Both TGA and DSC data[5] show at least two significant thermal events, attributed to decomposition and evolution of CO_2 and moisture, but none of these endothermic events, even that of the Army Control, falls in the exact range as specified in MIL-DIL-11361E. The measured moisture content also varies, but is considered an easily manageable production parameter. The differences in endothermic characteristics are likely to have no significant impact on smoke generation as they all rapidly evolve gases within 25°C of each other, but this yet to be further examined in performance test.

Table 2. Thermal Properties of Densified Basic Magnesium Carbonate Samples.

Sample	Moisture Content (%)	MgO Content (%)	Endotherm (°C)	
			1st	2nd
MIL Spec	1.0 max	40.0-43.5	235-250	435-450
Army Control	0.76	42.9	260	454
L&V-1	0.73	43.6	272	466
L&V-2	1.15	45.0	285	469
Melox	2.12	43.3	276	441
Osian	- 0.13	42.3	264	440
Solvay	0.67	43.5	285	454

Trace and heavy metal analysis. Some DBMC samples under consideration were further subjected to a chemical composition analysis for their trace and heavy metal contents. Table 3 shows material solubility and total MgO content, measured via gravimetric test, in comparison with that of Army control sample and Mil Spec.

Table 3. Material Solubility and Total MgO Content of Selected DBMC Materials

Sample	Solubility (wt%)		Assay as MgO (wt%)
	HCl solution	Water	
Mil Spec	0.02 max	0.50 max	40 -43.5
Army control	0.009	0.16	40.6, 41.1
L&V-2	0.002	0.07	43.1, 42.8
Melox	0.019	0.22	42.7, 41.6
Osian	0.048	0.68	40.4, 40.8

As can be seen from the data on Table 3, the material L&V-2 and Melox pass the solubility test, while Osian fails both solubility test in HCl aqueous solution and the water. As for MgO content, the data from all samples tested are generally in the range specified in Mil Spec.

Table 4 shows trace and heavy metal analysis results. None of DBMC samples tested contained significant amount of heavy metals such as arsenic, lead, mercury, barium, bismuth, cadmium chromium, and well within Mil Spec.

However, the specification from military spec MIL-DTL-11361E is not consistent in term of iron content. Table 1 in paragraph 3.2 of the military spec gives an upper limit of 0.02 %, while the paragraph 4.4.6.2 gives an upper limit of 0.002 %. The analysis procedure calls for preparing a solution of 10 ppm in iron, and using that solution in the manner described will give an upper limit of 0.002 %. The sample L&V-2 was higher than the limit of 0.002 %, but well below the limit of 0.02 %. The iron contents for other samples are within the Mil Spec. Considering these commercially available DBMC materials are food grade products, any impact of such a low level content of iron on the environment is negligible and will have no impact on smoke generation.

Table 4. Trace and Heavy Metal Content of Selected BMC Sample Materials.

Sample	Trace or Heavy Metal								
	Calcium	Iron	Arsenic	Lead	Mercury	Barium	Bismuth	Cadmium	Chromium
Mil Spec	0.45 max	0.002	2 max	10 max	20 max	20 max	20 max	20 max	20 max
Army Control	0.06	0.0015	0	1.5	0	0.35	0.25	0.58	2.5
L&V-2	0.20	0.0036	0	0.9	0	0.35	0.14	0.47	2.0
Melox	0.45, 0.44	0.0013	0	1.7	0	0.31	0	0.45	0.14
Osian	0.11	0.0015	0	1.4	0	1.1	5.3	0.50	0.20

Summary and Conclusions

Commercially available DBMC materials have been examined against military specification MIL-DTL-11361E in terms of their physiochemical and thermal properties. While no material is an exact duplicate of the Army control in terms of physiochemical characteristics, at least two of the DBMC materials investigated, L&V-2 and Melox, closely resemble what was specified in the military specification and are expected to work as well as the DBMC material sourced from the Dead Sea Bromide. The material L&V-2 from Germany show properties very close to the Army control. Melox material is currently used by Indian Army for smoke generators and generally meets most specifications though it possesses very different particle morphology than what the Army currently uses.

It is therefore recommended that the DBMC materials from L&V and Melox should be considered as potentially source of material supply, and further assessed for performance data in complete weapon systems, such as M18 smoke grenades.

As a footnote, the military Spec MIL-DTL-11361E appears written based on the material currently in use, and is too restrictive or otherwise narrowly defined. It should be revised with more updated information once smoke generation testing is complete.

Acknowledgements

Authors thanks Kerry Henry-PM-JS, John Blackmer-PM-JS, Derek Dereiter-PM-CCS and Jessica A Perciballi-ARDEC for project management support.

References

(1) Christopher, F; Gary, C.; *Proceedings of the International Pyrotechnics Seminar* **2008**, 35, 83-93.
(2) Khan, N.; Dollimore, D.; Alexander, K.; Wilburn, F. W.; *Thermochimica Acta* **2001,** 367-368, 321-333
(3) Botha, A.; Strydom, C.A. *Hydrometallurgy* 2001, 62 (3), 175.
(4) Rusin, D. L.; Denisyuk, A. P.; *PCT Int. Appl.* **2005**, WO 2005023370 A2 20050317.
(5) Miller, L.; Whittaker, M.; Cutler, R; Evaluation of Basic Magnesium Carbonate, Ceramatec Report RD-R-062-NBD (April 2011).