



**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals****Sub-Committee of Experts on the Transport of Dangerous Goods****Fifty-fourth session**

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Item 2 (c) of the provisional agenda

**Recommendations made by the Sub-Committee on its fifty-first,
fifty-second and fifty-third sessions and pending issues:****Listing, classification and packing****Transport of barium carbonate as non-dangerous good****Submitted by the expert from Spain*****Introduction**

1. Barium carbonate is a barium compound, and therefore by defect classified as UN 1564, BARIUM COMPOUND, N.O.S, in Division class 6.1.
2. Nevertheless, according to the information available, barium carbonate may not be toxic as can be shown by the information and tests provided.
3. To facilitate international trade and to avoid different interpretation of the applicable prescriptions for the transport of dangerous goods, it would be interesting to clearly exempt barium carbonates from the scope of the Model Regulations, as has already been done for Barium sulphate by special provision (SP) 177: *“177 Barium sulphate is not subject to these Regulations.”*
4. During the fifty-third session of the Sub-Committee, Spain submitted informal document INF.32, which included this proposal, justified by some test results for Barium Carbonate. Spain was asked to submit a formal document, taking into account the comments provided by the Sub-Committee experts (refer to ST/SG/AC.10/C.3/106 paragraphs 60-62), including additional test results for the barium carbonate from other sources of information.

* In accordance with the programme of work of the Sub-Committee for 2017–2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, paragraph 98 and ST/SG/AC.10/44, para. 14).

Background

5. Barium carbonate is one of the most widely used products in the ceramic sector, as well as in the production of tiles and bricks. Other applications are the manufacture of special types of glass, as a component of frits for glazing enamels, porcelains, and structural clay and to create barium ferrite powder that is used in certain magnets.
6. There is one European manufacturer of barium carbonate, whereas the other producers are principally Chinese and Indian. Barium carbonate is a manufactured product made from barite ore, through the following process:
 - (a) Barite ore (barium sulphate) is reduced to barium sulfide;
 - (b) Barium sulfide is dissolved in water and leached to remove impurities;
 - (c) The barium sulfide solution is reacted with carbon dioxide gas to produce, as a precipitate, barium carbonate;
 - (d) The barium carbonate precipitate is filtered to remove excess water and then dried.
7. As it is obtained as result of an industrial process, only small variations in between the different barium carbonates from different origins should exist.
8. Barium carbonate is commercialized under four forms, free-flowing barium carbonate, precipitated barium carbonate, liquid barium carbonate and granular barium carbonate, depending on the granulometry of the product and if it is mixed with water to be commercialized as a liquid.

Test results

9. The following documentation is annexed to this document:
 - (a) UN Model Regulations Data Sheet (see annex)
 - (b) Safety data sheet of barium carbonate (see informal document INF.7)
10. The data presented in the Model Regulations data sheet has been obtained based on a specific study with tests.
11. Additionally, the information presented to the European Chemicals Agency (ECHA) for classification of barium carbonate is available at:
<https://www.echa.europa.eu/web/guest/registration-dossier/-/registered-dossier/15337/9>
The direct link to the information on toxicity of this dossier is:
<https://www.echa.europa.eu/web/guest/registration-dossier/-/registered-dossier/15337/7/3/2>
12. The test results presented there for oral toxicity indicate that barium carbonate is toxic with an LD50 of 1690 mg/kg, which is a much bigger dose than the upper limit for oral toxicity for packing group III (300 mg/kg), and therefore is not considered to be toxic, according to the classification criteria in the Model Regulation.

Tests on humans

13. After the last session of the Sub-Committee, Spain has also been looking for further information specifically related to tests on humans and appreciates the help received from China and Japan in this field.

14. The OECD website gives different information for barium carbonate (CAS number 513-77-9), for example under the following links:

- <https://www.echemportal.org/echemportal/substancesearch/substancesearchlink.action>:
- <https://www.echemportal.org/echemportal/substancesearch/page.action?pageID=134>
- <http://www.safe.nite.go.jp/english/ghs/06-imcg-1320e.html>

15. In some of these documents it is mentioned that the LDLo¹ value to humans in oral exposure is 57 mg/kg, or that based on the minimum oral lethal dose of 57mg/kg in humans (Document CICAD² 33), the substance was classified as Category 3.

16. All these data are based on the same report RTECS³ (1985) presented in the English webpage of National Institute of Technology and Evaluation of Japan (NITE). The barium carbonate is classified as Category 3 for the oral acute toxicity based on the minimum oral lethal dose of 57 mg/kg in humans (CICAD 33, 2001), while recognizing that there are findings that LD50 = 418mg/kg (SIDS (2006) and EHC 107 (1990)), 800 mg/kg and 118-800 mg/kg (CICAD 33 (2001)) in the oral administration tests with rats.

17. All data which NITE have taken into consideration for classifying barium carbonate are available on the webpage of the relevant organizations:

- SIDS <https://hpvchemicals.oecd.org/UI/handler.axd?id=7618b672-b87f-4cb7-b7ed-1e3a268d16e0>
- EHC 107; <http://www.inchem.org/documents/ehc/ehc/ehc107.htm>
- CICAD <http://www.inchem.org/documents/cicads/cicads/cicad33.htm>

18. The Spanish Association of Importers of Raw Materials for Ceramic Use has asked a consulting company expert in the classification field (EBRC Consultants, Hannover, Germany) to further investigate the human data tests, and its response has been the following:

- (a) “In CICAD 33, 2001 the following is cited: According to RTECS (1985), the lowest lethal acute oral doses for barium chloride and barium carbonate are 11.4 and 57 mg/kg body weight, respectively; for barium carbonate, a dose as low as 29 mg/kg body weight causes flaccid paralysis, paraesthesia, and muscle weakness.” RTECS cited values TDLo⁴ between 2.86 mg/kg and 800 mg/kg and LDLo between 17 mg/kg

¹ LDLo: Lethal Dose Low--the lowest dose (other than LD50) of a substance introduced by any route, other than inhalation, over any given period of time in one or more divided portions and reported to have caused death in humans or animals.

² Concise International Chemical Assessment Document 33: This report contains the collective views of an international group of experts and does not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, the International Labour Organization, or the World Health Organization.

³ RTECS (1985) Registry of Toxic Effects of Chemical Substances 1985. US National Institute for Occupational Safety and Health.

⁴ TDLo: Toxic Dose Low-The lowest dose of a substance introduced by any route, other than inhalation, over any given period of time and reported to produce any toxic effect in humans or to produce tumorigenic, reproductive, or multiple dose effects in animals.

and 800 mg/kg, respectively but the important value of 57 mg/kg is not currently stated in RTECS (versions of RTECS have been published in 2004, where this value appears, but not in the versions from 2009 and 2012). We must assume that the database administrator had valid reasons for omitting this in their revision(s) since 2004. This would fit with our findings that the basis for this information is not traceable.

(b) Furthermore, most of these are “case reports” that should be rated with RL4⁵”, referring this to data for which a reliability rating is not assignable.

(c) Analysing literature which refers to the value (57 mg/kg) of interest, it was found that “Hayes, W.J., Jr., E.R. Laws, Jr., (eds.). Handbook of Pesticide Toxicology. Volume 2. Classes of Pesticides. New York, NY: Academic Press, Inc., 1991., p. 499” cited the following:

“When barium carbonate was mistakenly used as an X-ray contrast medium, six patients survived 133 g each (about 1900 mg/kg) but another died after only 53 g. The author cited earlier reports indicating that as little as 4 g (about 57 mg/kg) has proved fatal. However, such incidents must be rare, for in one large outbreak with no deaths among 85 cans⁶, it was estimated, on the basis of analysis of the contaminated food, that the most severe cases received about 15 g of barium carbonate (about 214 mg/kg). This rate is less than the LD50 for the rat but sufficient to kill some rats. It seems likely that vomiting is important in protecting people who ingest barium carbonate.”

However, Hayes, (1991) is also merely secondary literature that refers to an article of Dean, G., 1950. However, the value of 57 mg/kg, is not specifically mentioned there. Instead, Dean, (1950) described 7 case reports of barium carbonate administration where only 1 of them was fatal (Dose 66.5 g that refers to ~ 1g/kg). In conclusion, we could not find any reliable primary literature mentioning the value referred to in CIDAD 33, 2001 (57 mg/kg).

Given the lack of contextual information and relevant details of one isolated incident without describing the other circumstances of poisoning (was barium carbonate the only substance administered, were there other causes of death involved, injuries, general health condition etc.) and in view of an overall data base that by weight-of-evidence points to a much higher value for the acute oral toxicity, we do not believe that the paragraph (see above) cited in Hayes, (1991) alone is sufficient to support classification of barium carbonate as acute toxic Category 3.”

Analysis

19. According to the available test data, based on recent systematic tests (not based on humans), barium carbonate is not toxic. For tests on humans, it is not possible to trace back to a primary literature result the only source of data which would imply a classification as toxic. All other test data on humans, which are more recent and better documented, support the classification as non-toxic.

⁵ REACH guidance:

https://echa.europa.eu/documents/10162/13643/information_requirements_r4_en.pdf) requires us to validate each piece of information in a registration (or CLP) dossier, according to a reliability rating scheme acc. to Klimisch et al (1997). The designation RL4 refers to data for which a reliability rating is not assignable.

⁶ 85 cans of contaminated food were consumed by humans, with no deaths.

20. Not all the substances to which the Model Regulations do not apply are explicitly mentioned therein, as a general principle applies by which, if the criteria of none of the classes are fulfilled, the regulations are not applicable. Nevertheless, for barium compounds, as SP 177 applicable to UN 1564, already clearly exempts barium sulphates from the Regulations, this may induce to think that all other barium compounds are covered by the Model Regulations. Therefore, Spain suggests to also clearly exempt barium carbonate from the Regulations.

Proposal

21. Taking into account the information already included in informal document INF.32 (fifty-third session) and following the discussion in the previous paragraphs of additional information provided, barium carbonate is non-toxic according to the Model Regulation, and consequently should not be covered by transport of dangerous goods regulations.

22. Therefore, the expert from Spain suggests the following modification to SP 177 (new text **underlined and bold**, deleted text ~~stricken through and bold~~):

“177 Barium sulphate **and barium carbonate are**~~is~~ not subject to these Regulations.”.

Annex

DATA SHEET TO BE SUBMITTED TO THE UNITED NATIONS FOR NEW OR AMENDED CLASSIFICATION OF SUBSTANCES

Submitted by..... Date.....

Supply all relevant information including sources of basis classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions. - if necessary state “not know” or “not applicable” - if data is not available in the form requested, provide what is available with details. Delete inappropriate words.

Section 1. SUBSTANCE IDENTITY

- 1.1 Chemical name: Barium Carbonate
- 1.2 Chemical formula: BaCO₃
- 1.3 Other name/synonyms:
- 1.4.1 UN number.....1.4.2. CAS number 513-77-9
- 1.5 Proposed classification for the Recommendations
- 1.5.1 proper shipping name (3.1.2)
- 1.5.2 class/division..... subsidiary risk(s).....packing group.....
- 1.5.3 proposed special provisions, if any.....
- 1.5.4 proposed packing instruction(s).....

Section 2. PHYSICAL PROPERTIES

- 2.1 Melting point or range -----°C decomposition at 1.380 °C
- 2.2 Boiling point or range -----°C
- 2.3 Relative density at:
 - 2.3.1 15°C:
 - 2.3.2 20°C: 4.31
 - 2.3.3 50°C:
- 2.4 Vapour pressure at:
 - 2.4.1 50°C: n.a. kPa
 - 2.4.2 65 °C:.....kPa
- 2.5 Viscosity at 20 °C: n.a. kPa
- 2.6 Solubility in water at 20 °C: >= 0.0014 g/100 ml
- 2.7 Physical state at 20 °C: solid
- 2.8 Appearance at normal transport temperatures, including colour and odour: Barium Carbonate is a white crystalline inorganic odourless solid at room temperature and under atmospheric pressure.
- 2.9 Other relevant properties.....

Section 3. FLAMMABILITY

- 3.1 Flammable vapour
 - 3.1.1 Flash point (2.3.3): n.a. °C oc/cc
 - 3.1.2 Is combustion sustained? (2.3.1.3): yes/no
- 3.2 Autoignition temperature: n.a. °C
- 3.3 Flammability range (LEL/UEL): n.a. %

3.4 Is the substance a flammable solid? (2.4.2): yes/no

3.4.1 ~~If yes, give details:~~ Barium Carbonate is stable at ambient temperature. This substance also does not contain any chemical groups that might lead to spontaneous ignition a short time after coming in contact with air at room temperature (circa 20°C). Furthermore, long-term industrial experience in handling shows that the substance does not ignite in contact with air.

Section 4. CHEMICAL PROPERTIES

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity? yes/no

If yes, state:

4.1.1 Inhibitor/stabilizer used.....

4.1.2 Alternative method.....

4.1.3 Time effective at 55°C.....

4.1.4 Conditions rendering it ineffective

4.2 Is this substance inexplosive according to paragraph 2.1.1.1? (2.1) yes/no

4.2.1 ~~If yes, give details:~~ This substance is void of any chemical structures commonly associated with explosive properties such as metal peroxides, peroxy-acid-anions, azides and halogen oxides.

4.3 Is the substance a desensitized? (2.4.2.4): yes/no

4.3.1 If yes, give details.....

4.4 Is the substance a self-reactive substance? (2.4.1): yes/no

If yes, state:

4.4.1 exit box of flow chart.....

What is the self-accelerating decomposition temperature (SADT) for a 50 kg package?.....°C

Is the temperature control required? (2.4.2.3.4): yes /no

4.4.2 proposed control temperature for 50 kg package.....°C

4.4.3 proposed emergency temperature for a 50 kg package.....°C

4.5 Is the substance pyrophoric? (2.4.3): yes/no

4.5.1 ~~If yes, give details:~~ Since Barium Carbonate represents the highest oxidized form of barium, it is intrinsically not combustible and can safely be assumed not to be ignitable.

4.6 Is the substance liable to self-heating? (2.4.3): yes/no

4.6.1 If yes, give details.....

4.7 is the substance an organic peroxide (2.5.1): yes/no

If yes, state:

4.7.1 exit box of flow chart.....

What is the self-accelerating decomposition temperature (SADT) for a 50 kg package?.....°C

Is the temperature control required? (2.5.3.4.1): yes /no

4.7.2 proposed control temperature for 50 kg package.....°C

4.7.3 proposed emergency temperature for a 50 kg package.....°C

4.8 Does the substance in contact with the water emit flammable gases? (2.4.4): yes/no

4.8.1 ~~If yes, give details:~~ Barium Carbonate does not contain groups that might lead to a reaction with water or damp air, leading to the development of dangerous amounts of gas or gases which may be highly flammable. Furthermore, long-term industrial experience in practical handling of the substance shows that it does not

react with water and, recent experimental testing for water solubility has also not reported any formation of gases.

4.9 Does the substance have oxidizing properties (2.5.): yes/no

4.9.1 If yes, give details: Barium Carbonate does not contain a surplus of oxygen or any structure groups known to be correlated with a tendency to react exothermally with combustible material.

4.10 Corrosivity (2.8) to:

4.10.1 mild steel.....mm/year at not data/not expected °C

4.10.2 aluminium..... mm/year at not data/not expected °C

4.10.3 other packaging materials (specify)

.....mm/year at.....°C

.....mm/year at.....°C

4.11 Other relevant chemical properties

Section 5. HARMFUL BIOLOGICAL EFFECTS

5.1 LD₅₀ oral (2.6.2.1.1): 1690 mg/kg. Animal species: Rat (Sprague-Dawley) male/female

5.2 LD₅₀ dermal (2.6.2.1.2): no data mg/kg. Animal species:.....

5.3 LC₅₀ inhalation (2.6.2.1.3): n.a. mg/litre. Exposure time ----- hours
Or.....ml/m³. Animal species -----

5.4 Saturated vapour concentration at 20°C (2.6.2.2.4.3): n.a. (solid) ml/m³

5.5 Skin exposure (2.8) results: Exposure limitshours/minutes
Animal species.....

5.6 Other data: Testing by inhalation route with Barium Carbonate is not necessary since it was not possible to generate a stable testing atmosphere with an acceptable test concentration atmosphere (ideally 5.1 mg/L). Despite extensive effort, it was only possible to achieve a test item concentration of 0.2 mg/L. The test substance was pestle up to an MMAD below 4. Based on the technical properties of Barium Carbonate, the performance of an acute inhalation toxicity test is neither technically feasible nor scientifically relevant for this type of compound. Due to the MMAD/GSD and the particle size which much higher than the pestle substance used for the pre-study, the low mobility and the negligible volatility of Barium Carbonate, the test material can safely be assumed to have a very low potential for human inhalation hazard during handling or application.

5.7 Human experience:.....

Section 6. SUPPLEMENTARY INFORMATION

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents) Use extinguishing measures that are appropriate to local circumstances and the surrounding environment. Special exposure hazards in a fire. Not combustible. Special protective equipment for fire-fighters. In the event of fire, wear self-contained breathing apparatus.

6.1.2 Spillage.....

Personal precautions: Sweep up to prevent slipping hazard. Avoid dust formation.

Methods for cleaning up: Sweep up and shovel into suitable containers for disposal. Avoid dust formation. Keep in properly labelled containers. Keep in suitable, closed containers for disposal.

- 6.2 Is it proposed to transport the substance in:
 - 6.2.1 Bulk containers (6.8): yes/no
 - 6.2.2 Intermediates Bulk Containers (6.5)?: yes/no
 - 6.3.3 Portable tanks (6.7)?: yes/no
- If yes give details in Sections 7, 8 and 9.

Section 7. BULK CONTAINERS (only complete if yes in 6.2.1)

7.1 Proposed type(s).....

Section 8. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.2)

8.1 Proposed type(s).....

Section 9. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.3)

9.1 Description of proposed tank (including IMO tank type if know).....

9.2 Minimum test pressure.....

9.3 Minimum shell thickness.....

9.4 Details of bottom openings, if any.....

9.5 Pressure relief arrangements.....

9.6 Degree of filling.....

9.7 Unsuitable construction materials.....
