

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

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Global harmonization of transport of dangerous goods regulations with the Model Regulations

Without abiding by classification thresholds, safety recommendations on transport of dangerous goods becomes erratic: the case of potassium and sodium nitrate

Transmitted by Chile

Introduction

1 At the thirty-sixth session of the Sub-Committee of Experts on the Transport of Dangerous Goods in December 2009, International Maritime Organization (IMO) informed the Sub-Committee of the decision taken by DSC 14 to assign a new special provision 964 to UN 1486 (potassium nitrate), UN 1498 (sodium nitrate) and UN 1499 (sodium nitrate and potassium nitrate mixture), when transported in the form of prills or granules, provided these substances do not meet the criteria established in the Manual of Test and Criteria, when tested under O.1 test method.

2 The report of the thirty-sixth session of Sub-Committee of Experts on the Transport of Dangerous Goods ST/SG/AC.10/C.3/72) reflects the discussions that took place and new informal documents (INF.37, INF.43, INF.46) were sent for discussion at the thirty-seventh session of the Sub-Committee of Experts on the Transport of Dangerous Goods.

3 Chile is the largest producer of potassium nitrate and sodium nitrate in the world, and has a vast experience and scientific knowledge on the production, transport, handling, storage and uses of these alkali nitrates and their mixtures, in all their chemical and physical grades.

4 Chile wishes to provide more detailed information on the reasons that justify the special provision 964 assigned by IMO to sodium nitrate, potassium nitrate and their mixtures when in granular or prilled form, by commenting the documents presented to this session by the Netherlands (INF.46) and the European Fertilizer Manufacturers' Association (EFMA, INF.37). Chile wishes also to comment on the Note by the Secretariat (INF.43).

The particle shape/size and chemical composition effects on the outcome of the Test O.1

5 The classification of solid oxidizing substances (pure and mixtures) for transport purposes is carried out by test O.1 of the Manual of Test and Criteria, which requires the substance is tested in the form it is transported. It is true that the intimacy of the mixture with combustible is dependent on the nature of both the oxidizer and the combustible material, as mentioned by the expert from The Netherlands. However, this is the prescribed

way of testing the substance, and it was the way the prilled sodium and potassium nitrates were tested. Yet if the sample is prepared according to the lab test procedure, segregation is minimized. It is more likely to have a better segregation in the real world than in the lab: if liquid fuel is accidentally spilled over prills, the most probable scenario is spilling over a part of the material. In that case the fuel will burn and then, when the fuel is consumed, the fire will stop as calcium, sodium and potassium nitrate do not burn.¹

6. Additionally and most importantly, neither potassium nitrate nor sodium nitrate prills will be well impregnated by the fuel due to their high density and low solubility in the liquid fuel (see also point 14). Therefore, the result found from the O.1 test can be considered conservative. For comparison purposes, the intimacy of the mixture of oxidizer with fuel is extreme in ammonium nitrate *i.e.* both in one and the same molecule: this explains on a simple way the completely different nature of ammonium nitrate compared to the (alkali)-nitrates both in terms of safety as in terms of security (see also points 13-16: section: the analogy with ammonium nitrate and point 19, section: the security aspects).

7. Distinct hazard classification according to UN Recommendations due to different form and/or size is found several times in the list of dangerous goods, indicating that shape and/or size is a common criterium to be taken into account when classifying substances. Therefore, referring to intrinsic properties for classification, as mentioned by both the expert from Netherlands and EFMA, is not a valid argument *per se* to reject a special provision for a specific form of a substance. Otherwise, some special provisions in the UN Recommendations for chemicals based on this criterium should be considered void.

8. An example of a substance mentioned by name in the dangerous goods list, but having a special provision based on shape and therefore exempting it from the corresponding hazard class is UN 1350, sulphur, class 4.1 PG III. It has been assigned special provision 242, which reads as follows:

242 Sulphur is not subject to these Regulations when it has been formed to a specific shape (e.g. prills, granules, pellets, pastilles or flakes).

9. Does this mean that sulphur pearls are not combustible because of this condition? They are combustible, but the physical form causes them to be lowered under the hazard threshold and thus make them safe enough to be transported as non-dangerous.

10. Another example is UN 1454, calcium nitrate, class 5.1 PG III, having the special provision 208, which reads as follows:

208 The commercial grade of calcium nitrate fertilizer, when consisting mainly of a double salt (calcium nitrate and ammonium nitrate) containing not more than 10% ammonium nitrate and at least 12% water of crystallization, is not subject to these Regulations.

11. EFMA indicated in its document this is not a form of calcium nitrate, but a different chemical compound, so exemption is related to the chemical composition, as stated in the special provision. Nevertheless, the commercial form of this form of calcium nitrate, better described as "calcium nitrate ammonium nitrate double salt" (CAS# 15245-12-2), is granular, so the question is: how much of the non-oxidizing assessment comes from the chemical composition and how much because of the particle size/shape? The effect of

¹ Gesellschaft für Materialforschung und Prüfungsanstalt für das Bauwesen Leipzig mbH, Dr. Ing. W. Jank, 10.02.2009. Zündversuche und Ermittlung der Energiefreisetzung in Anlehnung an das SBI-Verfahren (Prüfungen zum Brandverhalten von Bauprodukten – Thermische Beanspruchung durch eine einzelne brennende Gegenstand für Brandprodukte mit Ausnahme von Bodenbeläge) nach DIN EN 13823, Ausgabe Juni 2002, Düngemittel ,KN03

shape/size emerges when grinding the granulated material. When testing the grinded form of commercial grade of calcium nitrate fertilizer under O.1 test method, the substance crosses the threshold and becomes class 5.1 PG II.² This demonstrates that the effect comes from the particle size and not from the chemical composition. The only expected effect derived from chemical composition for calcium nitrate ammonium nitrate double salt, besides the effect of the added ammonium nitrate (see points 13-15), is water content, which is, according to the main manufacturer, between 12 and 15 %. According the Chilean industry, water content (sum of bonded and non-bonded) in crystalline alkali and earth-alkali nitrates generally must exceed 20 - 30% in order to remain above the 5.1 threshold combustion rates when tested under the O.1 method.³

The known experience

12. Being a nitrate, and having the same intrinsic properties of the other (earth)-alkali nitrates, the commercial grade of calcium nitrate fertilizer covered by SP 208 is transported as a non-dangerous goods because its shape makes it safe for transport, and its safety records confirm this.

13. Potassium nitrate and sodium nitrate, when prilled, have been transported as non-dangerous substances since 2003, by using a similar provision to SP 964 provision established in ADR/RID/ADN. This is backed up by its safety record over many decades up to today.

14. Incident records when a substance is transported under conditions of a lower hazard class than its corresponding one are relevant for experience assessment. No incidents because of use of provisions in the ADR/RID/ADN have been recorded in the period mentioned above for potassium and sodium nitrates in prilled forms, which should be added to their safety records over the preceding decades.

15. Most of the uses of nitrates as oxidizing agents are carried out under very high temperatures, normally close to those of decomposition, which, in the case of sodium and potassium nitrate, exceed 500 °C, a condition not seen in transport or storage. Uses in explosives will be further discussed under the security section of this paper.

The analogy with ammonium nitrate

16. Both the expert from The Netherlands and EFMA explain in INF.37 and INF.46 that an exemption from Class 5.1 for prilled potassium and sodium nitrate would be equivalent to exempt prilled ammonium nitrate from the same class.

17. Comparing pure alkali and earth-alkali nitrates with ammonium nitrate is fundamentally flawed in this context: ammonium nitrate belongs to a different physicochemical category since it contains its own combustible material, which result in a lower thermodynamic stability, and a decomposition reaction that has the potential to be explosive under some conditions of stress that are usually seen for chemicals in the real world *e.g.* contamination with organic material. These intrinsic properties are controlled and risks diminished by stabilizing the substance through parameters such as prill density, limitation of the organic content, etc, allowing the substance to be exempted from Class 1.1 and considered for Class 5.1. None of the other pure alkali and earth-alkali

² TNO report TNO-DV 2008 C098rev: Oxidizing properties of some inorganic nitrates, potassium chlorate and potassium perchlorate, January 2009, project number 032.12316/31.

³ SQM internal communication; June 2010.

nitrates show these properties due to the lack of reduced nitrogen (NH_4^+) in their crystalline structure (except to some degree for fertilizer grade calcium nitrate double salt).

18. On the contrary, (earth)-alkali nitrates such as potassium nitrate do not burn and when liquid fuel is spilled upon it and fire breaks out, the fuel will simply burn off.⁴

19. When applying test O.1 to ammonium nitrate, the cellulose:tested substance ratios are unintentionally increased to a level well above those prescribed in the test, resulting in less available oxygen for the combustion of cellulose. A corrected ratio should be used for a better comparison with nitrates lacking ammonium in their structure.

20. Additionally, as suggested by The Netherlands, abundant known experience prevents declassification of ammonium nitrate prills.

21. Conclusion: once safety threshold levels for groups of substances such as oxidizers have been decided upon, they should not be overruled from time to time, neither in one direction nor in the other one, except for a valid reason. If that would be done, it would mean that the threshold levels have been wrongly established. Therefore, since there is no valid reason to include prilled or granulated (earth)-alkali nitrates such as calcium nitrate, potassium and sodium prilled or granulated fertilizers in a hazard class, when, according to the official test method, they are found not to be hazardous. Doing otherwise would undermine the hazard classification system and therefore safety itself.

The Security Aspects

22. The Netherlands mentions that both potassium and sodium nitrate fertilizers are considered precursors for explosives. Chile would like to add that calcium nitrate fertilizer (calcium nitrate ammonium nitrate double salt, CAS # 15245-12-2), for which SP 208 has been assigned, allowing to be transported as non-dangerous, is also considered a precursor for explosives. This has been shown among others in tests by the French government agency INERIS.⁴ Also the current Standing Committee on Explosive Precursors (SCP) of the European Commission has included this calcium nitrate fertilizer together with potassium and sodium nitrate fertilizer, *i.e.*, the most common alkali and earth-alkali nitrate fertilizers, as precursors for explosives in terms of security.⁵

23. Ammonium nitrate (AN) mixtures with nitrogen (N) content as low as 16 %N as AN are also being proposed as precursors for explosives by the EU Commission. This includes calcium ammonium nitrate (CAN, a mixture of AN and limestone) prilled or granulated fertilizer with 27 % N as AN, which however is not considered a hazard in terms of safety. It should be noted that CAN is able to detonate and on itself while the (earth)-alkali nitrates only can deflagrate and then only when a fuel is added.

24. Therefore if security would be an argument not to assign a special provision for prilled potassium and sodium nitrate, then the same argument should be valid also for not exempting prilled or granulated calcium nitrate fertilizer and *à fortiori* calcium ammonium nitrate (CAN) fertilizer since, just as proposed for prilled potassium and sodium nitrate,

⁴ 36th International Pyrotechnics Seminar August 23-27, 2009, Rotterdam The Netherlands. Presentation E-1: Comparison of behaviour of 3 samples of nitrate based powders to classic black powder. C. Rivière*, R. Branka, M.A. Kordek, INERIS.Parc Technologique Alata BP 2, F-60550 Verneuil en Halatte, France.

⁵ THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION, Draft regulation, Marketing and use of explosives precursors, Discussion document for the 10th meeting of the Standing Committee on Precursors, 17 May, 2010

both are not to be considered and currently are not considered a hazard in terms of safety notwithstanding the millions of tons transported and sold worldwide.

The Special Provision 223

25. Chile wishes to acknowledge the note from the Secretariat (INF.43). At the DSC 14 (Ref: UN/SCETDG/36/INF.30), there was not pointed to the similarity between SP 964 and SP 223, the latter being quite general and less specific than SP 964, however with the same requirements for the exemption.

26. Chile supports the harmonization of SP 964 to SP 223 for UN 1486, UN 1498 and UN 1499, considering SP 223 has been assigned to substances belonging to hazard classes 3, 4.1, 4.2, 4.3 class 5.1 (including UN 1477, inorganic nitrates not listed by name), 6.1 and class 8, recognizing then that a significant number of substances listed by name in the UN recommendations are out of the classification when tested.

27. Chile supports also the assignment of SP 223 on a case by case basis, in order to assure proper risk assessment of a substance proposed for this special provision.
