

**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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Item 3 (b) of the provisional agenda

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Ammonium nitrate emulsions
Comments on document ST/SG/AC.10/C.3/2003/31 from Spain

Transmitted by the expert from Norway

The competent authority for Explosives in Norway has received the attached document from Dyno Nobel ASA, which we would like to share with the sub-Committee, see Appendix 1.

Dyno Nobel raises some fundamental issues in their document, and the Expert from Norway shares their concern about these issues. This is particularly so in connection with what is mentioned in paragraph 10 and 11 of the document.

The Expert from Norway is of the opinion that the intention of UN 3375 was to introduce an UN number for **unsensitised** ammonium nitrate emulsions, and that expanding the definition to also include sensitizers is not in the interest of safety. We are afraid of an evolution of the recommendations in a way that the ability to pass Test series 8 will be more important than the actual properties of the substance. This, in our opinion is particularly undesirable when it concerns new substances for which the test regime is still under development.

Appendix 1 to UN/SCETDG/24/INF.28



**RECOMMENDATION TO REJECT THE SPANISH PROPOSAL TO AMEND THE DEFINITION
OF
UN 3375 – AMMONIUM NITRATE EMULSIONS, SUSPENSIONS AND GELS – SPECIAL
PROVISION 309**

**Dyno Nobel ASA
Research and Technology Team**

References:

- A. Recommendation on the Transport of Dangerous Goods - Model Regulations – 12th Edition**
- B. ST/SG/AC.10/C.3/2003/31 25 July 2003**
- C. UN/SCETDG/21/INF.69**

Introduction

1. UN No. 3375 (UN 3375) was adopted as a result of the December 2000 meeting of the Sub-Committee of Experts on the Transportation of Dangerous Goods. The definition of substances included under this UN No. were contained within Special Provision 309 (SP309). The UN No. and its accompanying special provisions were included in the 12th Edition of the Model Regulations of the Recommendations on the Transport of Dangerous Goods.
2. Much discussion has subsequently occurred relating to the testing of substances included in UN No. 3375. Testing designed to support evaluation criteria has been carried out in Scandinavia, Australia, Spain, Canada and South Africa. Dyno Nobel has observed and participated in some of this testing in both Scandinavia and Australia. A test enabling the determination of suitability for transport in bulk has not yet been finalised (modified vented pipe test).
3. Some discussion has recently occurred on the effect of proposals which modify the original intent of UN 3375, which was to designate a specific UN No. for emulsions, suspensions and gels which removed regulatory and community uncertainty over the inclusion of such substances in UN 3139 – oxidising substances NOS.
4. Dyno Nobel's position on the matter of ammonium nitrate emulsions (ANE), suspensions and gels is that not all substances which may be described under this general term are suitable for inclusion in UN 3375. Dyno Nobel stresses the importance of this UN Number in mitigating community and regulatory concerns over the classification of mixtures of substances which are regarded as precursors to explosives. Because it is widely known that the substances included in UN 3375 are precursors to explosives, the reasons for these materials being classified as other than Class 1 must be readily understood by the community and its representatives, such as the regulatory bodies, and this is achieved by the creation of UN 3375 and its supporting test regimes.

Discussion

5. The current new entry for UN 3375, incorporates two descriptive notes, specifically SP 306 and SP 309.

- 5.1. SP 306 notes that:

This entry may only be used for substances that do not exhibit explosive properties.

- 5.2. SP 309 states:

This entry applies to non sensitised emulsions, suspensions and gels consisting primarily of a mixture of ammonium nitrate and a fuel phase, intended to produce a Type E blasting explosive only after further processing prior to use. The mixture typically has the following composition: 60 - 85 % ammonium nitrate; 5 - 30% water; 2 - 8% fuel; 0.5 - 4 % emulsifier or thickening agent; 0 - 10 % soluble flame suppressants and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate. These substances shall not be classified and transported unless authorized by the competent authority.

6. It is important to note that by using the term “*non sensitised emulsions, suspensions and gels consisting primarily of a mixture of ammonium nitrate and a fuel phase,*” this definition specifically excludes those materials which are known to be energetic and are typically described and used as chemical sensitisers to formulations used within the commercial explosives industry.

7. The proposal from the Expert from Spain is detailed in Reference B, as follows;

Amend Special Provision 309 of Chapter 3.3 (amendments are shown in bold) as follows:

“309 This entry applies to non sensitised emulsions, suspensions and gels consisting primarily of a mixture of ammonium nitrate and a fuel phase, intended to produce a Type E blasting explosive only after further processing prior to use.

The mixture for emulsions typically has the following composition: 60-85% ammonium nitrate; 5-30% water; 2-8% fuel; 0.5-4% emulsifier agent; 0-10% soluble flame suppressants; and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.

The mixture for suspensions and gels typically has the following composition: 60-85% ammonium nitrate; 0-5% sodium or potassium perchlorate; 0-17% hexamine nitrate or monomethylamine nitrate; 5-30% water; 2-15% fuel; 0.5-4% thickening agent; 0-10% soluble flame suppressants; and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.

Substances shall satisfactorily pass Test Series 8 of the Manual of Tests and Criteria, Part I, Section 18 and be approved by the competent authority”

8. The Spanish proposal significantly blurs the distinction between Class 5.1 UN 3375 substances and Class 1 explosives by the proposed inclusion of known energetic materials such as perchlorates (sodium and potassium), organic amine nitrates (hexamine and monomethylamine nitrate) and the potential for additional energetic materials. It is preferable that such substances, because of their known sensitising effect on emulsions, suspensions and gels, should be excluded from the definition of UN 3375 in the same way that molecular explosives as sensitising/energy enhancing materials are excluded.

9. The primary basis for the exclusion of ANE from Class 1 substances, as covered by the current definition can be demonstrated to be the requirement for significant physical changes to the form of the matrix, that is, the inclusion of materials which affect the density of the matrix and the distribution of its constituents, without which detonation cannot be sustained. Should materials known to have sensitising effects be included in such matrices in their normal, unaltered form, the separation of ANE from explosives becomes, by definition, substantially less. This has the potential to weaken community confidence in the classification of ANE as a Class 5.1 material (UN 3375).

10. That the “hexamine nitrate or monomethylamine nitrate” compositional ingredients proposed by the Expert from Spain in Reference B, should be classified as sensitising agents within the base material is, in fact, clearly pointed out by UEE in recent patent literature. For example, a UEE patent application lodged in South Africa in 1998 (Application No. 980130; see also corresponding European and US patents, #1,002,777 issued January 22, 2003 and #6,537,399 issued March 25, 2003, respectively) says, “The alkylamine nitrates ... such as methylamine nitrate ... as well as the nitrates from other hydrosoluble amines such as hexamine ... may be used as sensitizing agents.” (Paragraph bridging pages 4 and 5.) Further, Claim 7 of the South African application specifies a “base product” containing “a sensitizing agent selected from the group formed by alkylamine nitrates, ... hexamine nitrates, ...” In addition, it is well known in the industry that the inclusion of sodium perchlorate in water gels or suspensions enhances the sensitizing effect of such water soluble amines. Clearly, the inclusion of such ingredients is in contradiction of the intent of UN 3375.

11. If the position the Expert from Spain is now taking that such ingredients are not “sensitising” to certain suspensions and gels is valid (a position to which Dyno Nobel does **not** accede), then a separate classification for such explosive precursors should be sought. The issue at hand is not whether such suspensions or gels pass the Series 8 tests and, therefore, deserve to be included in the definition as some sort of special subset of ANE, but whether such suspensions or gels meet the ANE definition **and** pass the Series 8 tests. Dyno Nobel believes that UN 3375 was instituted in recognition of the difference between ANE “consisting primarily of a mixture of ammonium nitrate and a fuel phase” and other, more traditional, Class 5 materials, and of the long-term history of the safe shipment of large quantities of ANE throughout the world. Piggybacking classes of materials chemically much different than the originally defined ANE would call into question the very premise upon which UN 3375 is based.

Conclusion

12. Dyno Nobel therefore does not agree with the Spanish proposal to amend the description of “UN 3375 - Ammonium nitrate emulsions, suspensions and gels” to include amendments to the composition of the mixture. Dyno Nobel believes that amending the description of UN 3375 detailed in SP 309 will:
 - 12.1. adversely affect the benefit of separating these mixtures from other oxidising substances, and
 - 12.2. raise questions regarding the similarity of substances included within this UN number to substances normally included in Class 1.

Recommendation

13. Dyno Nobel recommends that:
 - 13.1. the proposal in Reference B (ST/SG/AC.10/C.3/2003/31 dated 25 July 2003) be rejected.
 - 13.2. SP309 not be amended to include materials which enhance the energy or sensitivity of the ANE.
 - 13.3. SP309 as contained in the 12th Edition of the Recommendation on the Transport of Dangerous Goods, Model Regulations stand as written.
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