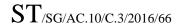
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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

Fiftieth session

Geneva, 28 November-6 December 2016 Item 2 (b) of the provisional agenda Recommendations made by the Sub-Committee on its forty-seventh, forty-eighth and forty-ninth sessions and pending issues: explosives and related matters

Clarification of the classification of ammonium nitrate based fertilizers – proposal for a new Section 39 in the Manual of Tests and Criteria

Transmitted by the expert from Sweden¹

Background

- 1. At the forty-ninth session of the Sub-Committee, the expert from Sweden presented working document ST/SG/AC.10/C.3/2016/29 containing draft amendments to the Manual of Tests and Criteria (the Manual) and the Model Regulations on the Transport of Dangerous Goods (the Model Regulations) for the clarification of the classification criteria for ammonium nitrate (AN) based fertilizers. The document was supplemented by informal documents INF.5, containing a detailed explanation of the proposed amendments, and informal document INF.23 with some additional proposals and points for discussion. The issue was discussed in detail during the meeting of the Working Group on Explosives (EWG), which met in parallel.
- 2. As also explained in the initial paragraphs ST/SG/AC.10/C.3/2016/29, the reason for clarifying the classification of AN-based fertilizers is that they are not sufficiently clear as

¹ In accordance with the programme of work of the Sub-Committee for 2015–2016 approved by the Committee at its seventh session (see ST/SG/AC.10/C.3/92, paragraph 95 and ST/SG/AC.10/42, para. 15).

² ST/SG/AC.10/C.3/2016/29

³ UN/SCETDG/49/INF.5 and UN/SCETDG/49/INF.23, respectively

currently formulated, which leads to misinterpretations (unintended or deliberate). These misinterpretations can lead to potentially unsafe AN-based fertilizers being transported as non-dangerous goods. As many downstream regulations use the transport classification as a basis for other safety measures, e.g. when storing AN-based fertilizers, the risks associated with these products can transfer further along the supply chain. Apart from the risk this poses to transporters, other workers, rescue personnel and the general public, this also leads to unfair competition amongst suppliers, since the transport and handling of supposedly "non-hazardous material" is cheaper and subject to less regulatory restrictions.

3. In order to improve the situation, an *ad hoc* working group under IGUS⁴ took it upon themselves to try to clarify the current provisions for classification of AN-based fertilizers. The group consist of government experts from Sweden, Netherlands, United Kingdom, France and Germany, who act solely on the basis of their knowledge of and experience with AN-based fertilizers. Although not formally part of the group, experts from the European fertilizer industry also have contributed substantially to the work. What is presented in this document is the outcome of the work of these experts over the past two years. Since IGUS has no formal status in the Sub-Committee, this paper is submitted by the expert from Sweden on behalf of the IGUS *ad hoc* working group.

Introduction

- 4. AN-based fertilizers that are considered to be dangerous goods have two dedicated UN numbers: 2067 and 2071. In addition, AN in itself has a dedicated UN number: 1942. Classification as UN 2067 is subject to Special Provisions (SP) 186, 306 and 307, while classification in UN 2071 is subject to SP 186 and 193. SP 306 is also applicable to UN 1942. This paper concerns UN numbers: 2067 and 2071 only, and no changes are proposed for UN1942.
- 5. SP307 and 193 contain the composition limits for AN-fertilizers that can be classified in UN 2067 and UN 2071, respectively. Their written text, which appears to rely on a few implicit understandings and fertilizer-specific terms that are not spelled out, is not very clear, and even to experts may provide quite a challenge. In all, this renders the classification provisions for these UN numbers somewhat unclear, which, as explained above, may lead to potentially unsafe situations. It is overcoming this problem that has been the focus of the work of the ad hoc working group under IGUS and a solution to it is proposed in this document.

Proposal

6. It is proposed to introduce in the Manual a new Section 39 containing all the provisions for classification of AN-based fertilizers. The proposed new Section 39 is presented in Annex 1 to this document. After the introduction and a few definitions, it presents the criteria for classification mainly in the form of a flow chart. A flow chart, correctly constructed, has the advantage of reducing the possibilities for misunderstanding and "falling between the lines" as compared to wording only. As a consequence of the

⁴ IGUS is the International Group of experts on the explosion risks of Unstable Substances, which has been active in the field of hazardous materials, including dangerous goods, for over 50 years. Experts participate in IGUS due to their expertise, and not as representatives of their country or organization. See www.igus-experts.org for further information.

⁵ The numbers and letters in the margins of the flow chart, as well as the grid lines, are to facilitate discussions only and are not intended to be reproduced in the Manual.

proposed new Section, current text in both the Manual and the Model Regulations needs to be amended or removed. These consequential changes are contained in Annex 2 to this document. In Annex 3 to this document the changes to the Dangerous Goods List and the affected Special Provisions 186, 193 and 307 are reproduced for clarity.

- 7. How the proposed flow chart corresponds to the current provisions for AN-fertilizers has been explained in detail in informal document INF.5 to the forty-ninth session of the Sub-Committee. Since no major changes to the flow chart have been made as compared to the one that was presented to that session (ST/SG/AC.10/C.3/2016/29), the interested reader is referred to that document.
- 8. It needs to be emphasized that the proposals contained in this document are not intended to introduce changes to the current classification provisions for AN-based fertilizers. What is proposed herein is a clarification of the provisions in order to avoid, or at least minimize, the possibilities for misinterpretations. However, as the current provisions are not always clear it was necessary to make some clarifications. Furthermore, a somewhat hidden provision for compound fertilizers was found to be obsolete and likely unintended, and is proposed to be deleted. Both the clarifications and the obsolete provision are explained below.

Clarifications made

9. The following clarifications have been made:

(a) Rewording the condition of added material being inert

SP 307 (a), which is applicable to fertilizers with \geq 90% AN, contains the condition that added matter must be "inorganic and inert towards ammonium nitrate". In practice, this condition is difficult to fulfil, since added matter may contain contaminants that are in fact not inert. Therefore this condition has been rephrased to "Does it contain any incompatible materials in amounts that could potentially negatively affect the stability of AN?", see Box D4 of the flow chart. It is supplemented by examples of incompatible materials in 39.3.5, and the requirement in 39.4.8 that any deliberately added materials must be inorganic and inert towards AN.

(b) Placing a limit on the content of ammonium sulphate

SP 307 (a) and (b) contain no wording directed towards ammonium sulphate (AS), and in principle would allow AS to be added in unrestricted amounts. For instance, a fertilizer with 80% AN and 20% AS would seem to fit in SP 307 (b). However, when reading SP307(c) it becomes clear that mixtures of AN and AS have special requirements, which is due to AS being capable of enhancing the explosive power of AN^6 . The above example fertilizer is not allowed to be classified under UN2067 according to SP307(c), since the amount of AN is >70%, but this is not sufficiently clear.

There is thus currently no concentration limit on AS in SP 307 (a) or (b), and the proposal is to introduce one. During the meeting of the Working Group on Explosives at the forty-ninth session of the Sub-Committee, this seemingly new requirement was noted and discussed, and it was concluded

⁶ See the review of several studies in "*Properties of Ammonium Nitrate based fertilizers*", Ph.D. thesis by Harri Kiiski from Helsinki University, Faculty of science, Department of Chemistry, 2009 (Chapter 9, Section 9.3.3)

that introducing such a concentration limit on AS is indeed justified. Because the industry practice is to frequently add up to 5% AS to fertilizers in general, for reasons of product quality, some AS needs to, and from a safety-perspective can, be allowed in all AN-based fertilizers. In the flow chart, therefore, this limit of 5% AS has been set throughout for non-compound fertilizers (see Box D8 and D36 of the flow chart), and it is emphasized by paragraph 39.4.6. If more AS is added the fertilizer is subject to the requirement corresponding to SP307(c) (see Box F44 of the flow chart), unless it is a compound fertilizer.

Compound fertilizers may contain AS as a nutrient and are allowed any amount of AS in the proposed scheme as long as they contain at least 10% inorganic materials excluding AN and AS if the AN-content is >70% (see Box F14 and H14 of the flow chart). This has the effect of restricting the combined amount of AN and AS (the higher the amount of AN the lower the allowed amount of AS, and *vice versa*). Usually, but not necessarily, these inorganic materials provide the primary nutrients phosphorus (P) and/or potassium (K). The requirement of 10% other inorganic materials prevents fertilizers with high contents of AN and AS to escape the conditions of SP 307 (c) by addition of small amounts of materials providing P and/or K, which could qualify them as being compound fertilizers. For compound fertilizers with \leq 70% AN there is no restriction on the AS-content.

(c) Not allowing escape from classification via testing for oxidizing properties

Classification of AN-based fertilizers as oxidizers is done on basis of their composition, as is clear from SP307. The reason for this is that the oxidizing properties of AN are not the most prominent hazard (which is decomposition). In fact AN, like most simple inorganic nitrate salts, is a rather weak oxidizer, and fertilizers with quite high AN contents can escape classification as oxidizers if subjected to testing (tests O.1 or O.3 according to the Manual of Tests and Criteria). Furthermore, it is implicit that this is not intended, since if AN-fertilizers fitting into the descriptions of SP307 were allowed to escape classification as oxidizers via testing there would be no point in specifying the composition in SP307 at all. Therefore it is clarified in 39.4.5 that AN-based fertilizers are not allowed to be exempted from classification as oxidizers based on results from test O.1 or O.3.

(d) Directing fertilizers that do not fit the descriptions

Currently there is no prescription on how to handle AN-based fertilizers that do not fit the descriptions in SP307 or SP193. However, it is clear that fertilizers that do not fit the descriptions because of a too high content of AN, combustible materials and/or incompatible materials (including AS) are considered more dangerous than those fertilizers that do fit the description. In the proposed Section 39, such non-conforming fertilizers are generally referred to a competent authority for possible approval for transport under another UN number (see Box F4, F6, F8, H12, H16, H18, F34, F36 and F42 of the flow chart as well as paragraph 39.4.3). In the case of fertilizers with a very high AN-content (≥90%) in combination with a high content of combustible materials (>0.2%), it is clarified that they can only be classified as explosives (Class 1 for transport)(see Box F6 of the flow chart). It is also specified that non-compound fertilizers with 70% or more AN may not contain AS as a nutrient and hence are not allowed for transport (see 39.4.6 and Box F8 and F36).

(e) Apparent change of applicability for SP307

It is proposed to change the initial sentence of SP307 from "This entry may only be used for uniform mixtures containing ammonium nitrate as the main ingredient [...]" to "This entry may only be used for ammonium nitrate based fertilizers. [...]", as this is in line with the terminology used throughout the proposal. While this could be perceived as a change to the applicability of UN2067, it is in fact bringing SP307 in line with the existing name and description of UN2067 in the Dangerous Goods List (Chapter 3.2 of the Model Regulations), and hence there is no change in practice. The new wording would also not hinder those jurisdictions that currently classify (virtually) pure AN of fertilizer grade as UN1942 (Ammonium nitrate) to continue to do so.

Removal of an obsolete condition

10. Quite late in the work, a provision for compound fertilizers was discovered in Section 38 of the Manual which many experts were unaware of. It is a condition on the content of "excess nitrate" in paragraph 38.2.3.3 of that Section, which is considered to most likely have been forgotten to be removed in connection with the restructuring of the provisions for AN-based fertilizers that took place when the 12th revised edition of the Recommendations on the Transport of Dangerous Goods were written. After discussions with industry representatives and within the Working Group on Explosives, it was decided that this condition, if even applied in practice, has no function since the fertilizers in question are anyhow subjected to the test for self-sustaining decomposition (the "trough test", Test S.1). This provision therefore does not exist in the proposed new Section 39, and is proposed to be deleted from Section 38.

Final words

11. The proposals made through this document have been discussed over the past two years between experts from both government and industry. The work has been presented to the Sub-Committee since its forty-eighth session in December 2015, and discussed within the Working Group on Explosives since then. The expert from Sweden, on behalf of the entire working group under IGUS, wishes to thank all the experts who have been involved for their valuable contributions to the work.

Annex I

New Section 39 to be inserted in the Manual of Tests and Criteria⁷

Section 39

Classification procedure and criteria relating to solid ammonium nitrate based fertilizers

39.1 Purpose

This section presents the United Nations scheme for the classification of solid ammonium nitrate based fertilizers as referred to in the Model Regulations, Chapter 3.3, special provisions 307 and 193.

39.2 Scope

Any new solid fertilizer composition containing ammonium nitrate shall be subjected to the classification procedure as set out in 39.4.

39.3 Definitions

- 39.3.1 An ammonium nitrate based fertilizer is a fertilizer containing ammonium (NH4+) and nitrate (NO3-) ions. See also 39.3.3.
- 39.3.2 A compound fertilizer is a fertilizer that contains at least two of the three primary nutrients nitrogen (N), phosphorus (P) and potassium (K).
- 39.3.3 In determining the ammonium nitrate content, all nitrate ions for which a molecular equivalent of ammonium ions is present in the fertilizer shall be calculated as ammonium nitrate.
- 39.3.4 Combustible substances as referred to in paragraph 39.4 include also non-organic substances that can be oxidized, e.g. elemental sulphur. For organic substances the content of combustibles is calculated as carbon.
- 39.3.5 Materials that are incompatible with ammonium nitrate include e.g. urea, acids, superphosphates with free acid, elemental sulphur, sulphides and most transition metals, including heavy metals (e.g. copper), and chlorides. Note however that this listing is not exhaustive.

39.4 Classification procedure

39.4.1 Solid ammonium nitrate based fertilizers are classified on the basis of their composition and experience and knowledge of their hazardous behaviour. Occasionally, the

⁷ Insertion of this new section has consequences for the Table of Contents of Part III (page 340) and for the General Table of Contents (page iv).

classification is complemented by testing for the ability to undergo self-sustaining decomposition or for explosive properties. These principles are condensed in the flowchart in 39.5.

- 39.4.2 UN No. 2067 may only be used for ammonium nitrate based fertilizers that do not show explosive properties when tested in accordance with Test Series 2 of this Manual.
- 39.4.3 Ammonium nitrate based fertilizers that do not fulfil the requirements for classification as UN No. 2067, can be assigned another suitable UN No. in Class 1 or Class 5, Division 5.1, provided that the suitability for transport is demonstrated and this is approved by the competent authority. This may for instance be when contamination has occurred in e.g. an accident, so that the fertilizer can be transported under a suitable UN No. e.g. in Class 1 as approved by the competent authority.
- 39.4.4 Ammonium nitrate based fertilizers that meet composition limits relevant for inclusion in the class of Explosives as set out in 39.5 shall be classified in that class regardless of the results when tested in accordance with Test Series 2 of this Manual.
- 39.4.5 Ammonium nitrate based fertilizers that meet composition limits relevant for classification as oxidizing solids as set out in 39.5, or are otherwise classified as oxidizing solids, shall not be exempted from that classification on the basis of the results from tests O.1 and/or O.3 in Section 34 of this Manual. See also paragraph 34.3.1 in Section 34 of this Manual.
- 39.4.6 Fertilizers that contain 70 % or more ammonium nitrate shall not contain ammonium sulphate as nutrient, unless they are compound fertilizers with less than 90% ammonium nitrate and with at least 10% inorganic materials excluding ammonium nitrate and ammonium sulphate.
- 39.4.7 Compound fertilizers that meet the composition limits relevant for potential inclusion for transport in Class 9 shall be tested for their capability to undergo self-sustaining decomposition according to the method given in paragraph 38.2.4 of this Manual (test S.1, trough test) and classified according to criteria given there and in 39.5.
- 39.4.8 For ammonium nitrate based fertilizers containing 90% or more ammonium nitrate, any deliberately added matter shall be inorganic and inert towards ammonium nitrate. See also 39.3.5.

39.5 Classification criteria

39.5.1 Ammonium nitrate based fertilizers shall be classified in accordance with the flowchart below.

NOTE to Figure 39.1: AN means ammonium nitrate. AS means ammonium sulphate

Figure 39.1 (a)

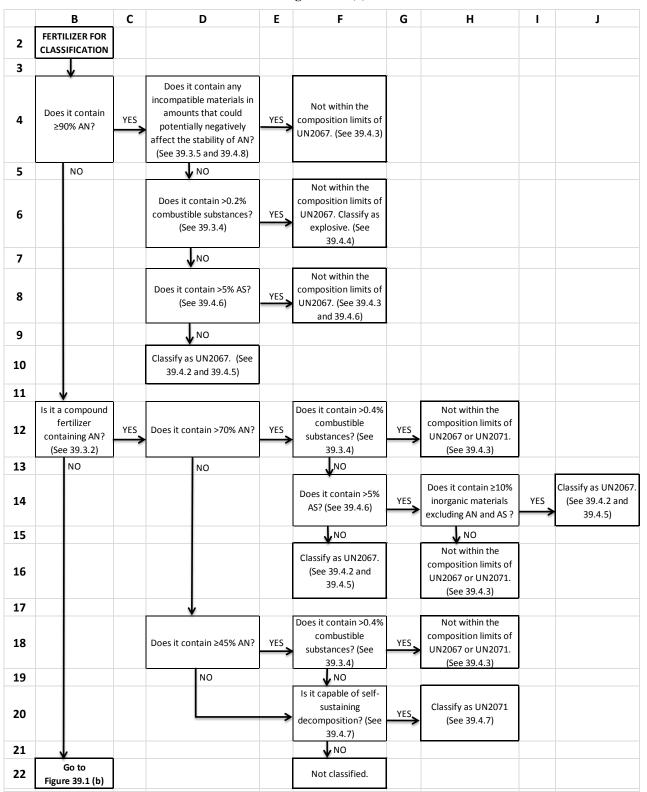
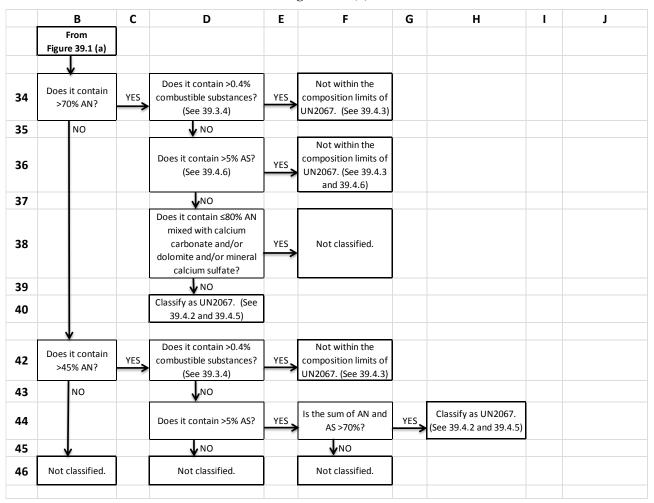


Figure 39.1 (b)



Annex II

Amendments to the Model Regulations and the Manual of Tests and Criteria

A. Changes to the Model Regulations

In Chapter 2.5

- Renumber current 2.5.2.1.2 into 2.5.2.1.3.
- Insert new 2.5.2.1.2, reading:

"By exception, solid ammonium nitrate based fertilizers shall be classified in accordance with the procedure as set out in the Manual of Tests and Criteria, Part III, Section 39."

In Chapter 2.9

• Insert a new paragraph in section 2.9.2, reading:

"Ammonium nitrate based fertilizers

2071 AMMONIUM NITRATE BASED FERTILIZERS

Solid ammonium nitrate based fertilizers shall be classified in accordance with the procedure as set out in the Manual of Tests and Criteria, Part III, Section 39."

• Under "Other *substances* ...", delete "2071 AMMONIUM NITRATE BASED FERTILISER".

In Chapter 3.2

- For UN No. 2067, delete 186 and 306 from column (6) Special provisions;
- For UN No. 2071, delete 186 from column (6) Special provisions.

In Chapter 3.3

- Delete Special provision 186;
- Change Special provision 193 to read:

"This entry may only be used for ammonium nitrate based compound fertilizers. They shall be classified in accordance with the procedure as set out in the Manual of Tests and Criteria, Part III, Section 39. Fertilizers meeting the criteria for this UN No. are only subject to these Regulations when transported by air or sea."

• Change Special provision 307 to read:

"This entry may only be used for ammonium nitrate based fertilizers. They shall be classified in accordance with the procedure as set out in the Manual of Tests and Criteria, Part III, Section 39."

B. Changes to the Manual of Tests and Criteria

In Section 34:

• Add the following to paragraph 34.3.1:

"By exception, solid ammonium nitrate based fertilizers are not classified as oxidizing solids on the basis of results from tests O.1 or O.3, since the hazardous properties are not sufficiently described by the outcome of tests for oxidizing properties. Instead, such fertilizers are classified on the basis of acquired experience and knowledge of their hazardous behaviour. They shall be classified in accordance with the procedure as set out in Section 39."

In Section 38:

- Throughout the Section, change 'ammonium nitrate fertilizers' into 'ammonium nitrate based fertilizers' (occurs six times in Section 38).
- In paragraph 38.2.3.3, delete the words "and provided they do not contain an excess nitrate greater than 10% by mass (calculated as potassium nitrate)"
- Insert a new paragraph 38.2.3.4, reading:

"The overall classification procedure for ammonium nitrate based fertilizers is set out in Section 39."

Annex III

Reproduction of the changes to the Dangerous Goods List and the Special Provisions (Chapters 3.2 and 3.3 of the Model Regulations)

Changes to Dangerous Goods List

UN No.	Name and description	Class or division	Subsi- diary risk	UN packing	Special provi-			Packagings and IBCs		Portable tanks and bulk containers	
				group	sions	quan	tities	Packing instruction	Special packing provisions	Instructions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	7(a)	7(b)	(8)	(9)	(10)	(11)
2067	AMMONIUM	5.1		III	186	5 kg	E1	P002	В3	T1	TP33
	NITRATE				306			IBC08		BK1	
	BASED				307			LP02		BK2	
	FERTILIZER									BK3	
2071	AMMONIUM	9		III	186	5 kg	E1	P002	В3		
	NITRATE				193			IBC08			
	BASED							LP02			
	FERTILIZER										

(Note that SP306 is retained for UN1942 with no change of wording. For UN2067 it is replaced by 39.4.2 in the new Section 39 with the same requirement.)

Changes to Special Provisions

Special Provision	Current wording	New proposed wording	Justification
	In determining the ammonium nitrate content, all nitrate ions for which a molecular equivalent of ammonium ions is present in the mixture shall be calculated as ammonium nitrate.	Deleted	Replaced by 39.3.3 in new Section 39 with the same requirement.
	nitrogen, phosphate or potash type, containing not more than 70% ammonium nitrate and not more than 0.4% total combustible/organic material calculated as carbon or with not more than 45% ammonium nitrate and unrestricted combustible material. Fertilizers within these composition limits are only subject to these Regulations when transported by air or sea and are not subject to	This entry may only be used for ammonium nitrate based compound fertilizers. They shall be classified in accordance with the procedure as set out in the Manual of Tests and Criteria, Part III, Section 39. Fertilizers meeting the criteria for this UN No. are only subject to these Regulations when transported by air or sea.	Composition limits and requirement on self-sustaining decomposition are replaced by flow chart in 39.5 of new Section 39. See also 39.3.2 and 39.4.7 of that Section.
307	containing ammonium nitrate as the main ingredient within the following composition limits: (a) [] (b) []	in accordance with the procedure	

13