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GUIDANCE FOR UN TRANSPORT CLASSIFICATION OF AMMONIUM NITRATE BASED SUBSTANCES

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Contents

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1 INTRODUCTION

A number of AMMONIUM NITRATE BASED 'SUBSTANCES' are listed as dangerous goods in the United Nations' publication, *Recommendations on the Transport of Dangerous Goods Model Regulations (Ref 1),* which is popularly known as the Orange Book. They fall in different Classes depending on their compositions and potential hazards. Most of the ammonium nitrate based products are classified based on their composition for reasons of past experience and knowledge. Those which are not covered in this way may be subject to a testing regime.

The number of fertilizer mixtures, which are produced to meet agricultural needs, is large and, consequently, considerable amount of testing would need to be carried out, if a test-based system of classification were to be applied. In order to avoid such unnecessary testing and to get a consistent approach, the classification of ammonium nitrate products is sensibly based on composition.

The composition components specified in the UN model regulations are ammonium nitrate (AN), combustible substances, total combustible/organic material, other added materials, if any, e.g. inert diluents and nutrient source materials such as phosphate and potash type (potassium salts such as KCl, K_2SO_4 and KNO_3). Clearly, such a composition-based system inevitably has to take a broad and pragmatic approach; it cannot cover all possible combinations in a precise way.

The UN transport regulations exist alongside other regulations that are designed to classify and control the use of chemicals. In the EU, chemicals are regulated by a number of different Directives and Regulations, the most recent being the "Classification, Labelling and Packaging" (CLP) Regulation (Ref 2). This Regulation is an adaption of the UN recommended Globally Harmonized System of Classification and Labelling of Chemicals (GHS).This classification system is based upon, among others, the UN transport regulations in an attempt to harmonise the classification of chemicals. This aim has largely been achieved and much of the testing and evaluation information required by the CLP Regulation is aligned with the UN GHS. Substances or mixtures which are classified as oxidizing liquids or solids in class 5.1 for transport are also classified as oxidizers under the amended CLP Regulation (Ref 2). Classification of the environmental hazards is also aligned.

In the past, separate systems of classification were in use in the EU. For labelling and packaging purposes, the Classification, Packaging and Labelling Directives, (67/548/EEC for substances and 1999/45/EC for preparations) were applied, whereas for transport purposes the UN transport classification system (Ref 1) was applied. These two were not identical and thus resulted in different classification for some substances. For example, ammonium nitrate and ammonium nitrate based fertilizers belonging to UN 2067 came under the oxidizing class 5.1 in the UN transport system but were not classified as dangerous substances under the EU system. With the implementation of the GHS such anomalies can be expected to disappear.

In order to provide a common understanding and practical approach to the classification used in the Orange Book relating to AN fertilizers, Fertilizers Europe has prepared this guidance for its members. It is based on the industry's established practices over many years, its interpretation of the intended controls, its understanding of the potential hazards and knowledge of the wide range of products produced.

2 SCOPE AND STRUCTURE OF GUIDANCE

This guidance considers only solid products containing ammonium nitrate and therefore does not include hot ammonium nitrate solution.

The guidance uses logic diagrams to cover all the relevant combinations or compositions based on AN. The official text in the Orange Book, which describes the entries for the above products and the associated Special Provisions, is included in section 4 to facilitate the process.

Notes to the diagrams are given, in section 5, to provide supplementary information to some of the boxes, where appropriate.

In some countries the competent authorities have given certain compositions derogation from classification; such exceptions are outside the scope of this guidance.

It should be noted that where trace elements such as Mn, Cu and Zn are added; products may have to be classified additionally (where appropriate) as environmentally hazardous substances in ADR (Class 9, UN 3077) or marine pollutants in IMDG depending on the concentration of the trace elements.

3 LOGIC DIAGRAM

The logic diagram is split into two figures, 1A and 1B. It uses the AN content as the main parameter. The second level parameter is based on the nature and concentration of other ingredients. The fertilizers are categorized as compounds (i.e. NP, NK or NPKs) or straight-N types (i.e. those containing only nitrogen as the nutrient). The main source of nitrogen here is AN; however, other nitrates such as potassium nitrate, sodium nitrate and calcium nitrate can also be potential sources but they are not discussed in this guidance.

Three examples of the application of this diagram for different fertilizer compositions are given in appendix 1 (Figures 2 A/B– 4 A/B).

It is important to note that the EU Detonation test is not part of the UN classification system. In the EU the Fertilizer Regulations require most high AN fertilizers to satisfy the EU detonation test.

Figure 1A

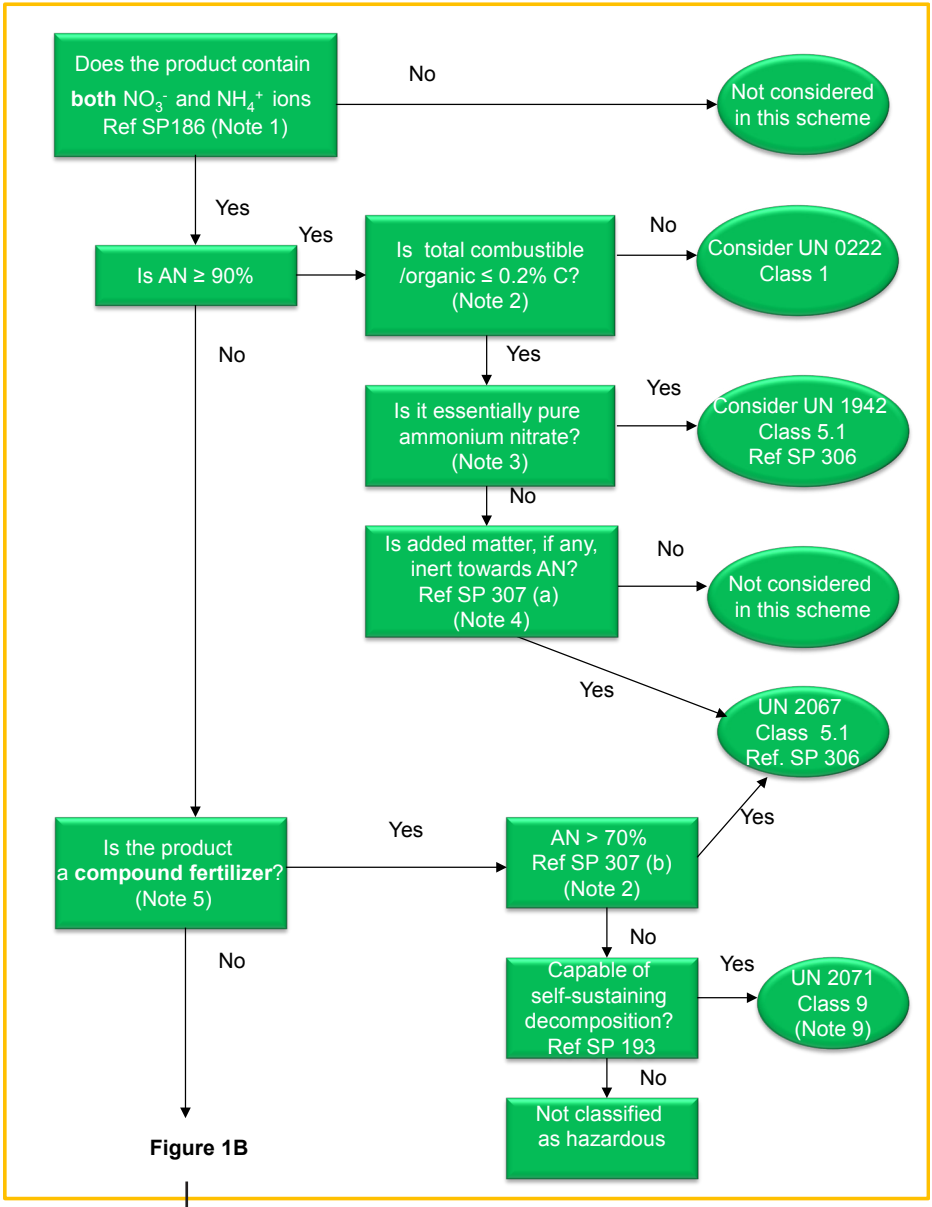
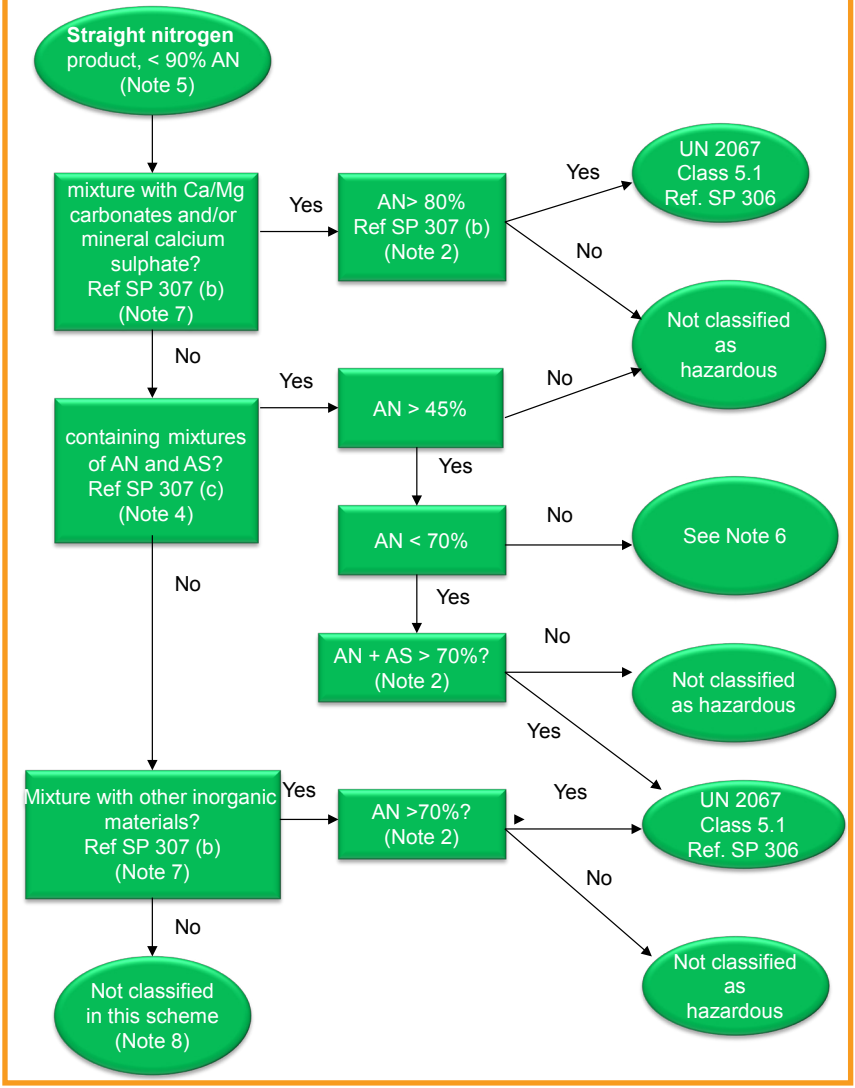


Figure 1B

Figure 1B


Straight nitrogen product, < 90% AN (Note 5)
mixture with Ca/Mg carbonates and/or mineral calcium sulphate? Ref SP 307 (b) (Note 7)
Yes
AN> 80% Ref SP 307 (b) (Note 2)
Yes
UN 2067 Class 5.1 Ref. SP 306
No
Not classified as hazardous
No
containing mixtures of AN and AS? Ref SP 307 (c) (Note 4)
Yes
AN > 45%
No
Yes
AN < 70%
No
See Note 6
Yes
AN + AS > 70%? (Note 2)
No
Not classified as hazardous
Yes
No
Mixture with other inorganic materials? Ref SP 307 (b) (Note 7)
Yes
AN >70%? (Note 2)
Yes
UN 2067 Class 5.1 Ref. SP 306
No
Not classified as hazardous
No
Not classified in this scheme (Note 8)

4 OFFICIAL TEXT FROM THE ORANGE BOOK (REF 1)

4.1 Main Substances

Ammonium nitrate based main solid products considered here are listed below with their UN numbers, shipping names, class and special provision (SP) numbers. The official text is shown in italics. Note that classified ammonium nitrate based fertilizers are covered by UN 2067 and 2071.

UN Number	Name and Description	Class or Division	Special Provision
0222	AMMONIUM NITRATE *with more than 0.2% combustible substances, including any organic substance calculated as carbon, to the exclusion of any other substance.*	1.1D	-
1942	AMMONIUM NITRATE *with not more than 0.2% total combustible material, including any organic substance, calculated as carbon to the exclusion of any other added substance*	5.1	306
2067	AMMONIUM NITRATE BASED FERTILIZER	5.1	186, 306 and 307
2071	AMMONIUM NITRATE BASED FERTILIZER	9	186 and 193

4.2 Special Provisions (SP)

SP 186

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.

SP 193

This entry may only be used for uniform ammonium nitrate based fertilizer mixtures of the 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 these Regulations if shown by a Trough Test (see Manual of Tests and Criteria, Part III, sub-section 38.2) not to be liable to self-sustaining decomposition.

NOTE: Some model regulations apply the requirements of UN 2071 even if the Trough Test does not show self-sustaining decomposition behaviour).

SP 306

This entry may only be used for substances that do not exhibit explosive properties of Class 1 when tested in accordance to Test Series 1 and 2 of Class 1 (see Manual of Tests and Criteria, Part I).

SP 307

This entry may only be used for uniform mixtures containing ammonium nitrate as the main ingredient within the following composition limits:

a) Not less than 90% ammonium nitrate with not more than 0.2% total combustible/organic material calculated as carbon and with added matter, if any, which is inorganic and inert towards ammonium nitrate; or

b) Less than 90% but more than 70% ammonium nitrate with other inorganic materials or more than 80% but less than 90% ammonium nitrate mixed with calcium carbonate and/or dolomite and/or mineral calcium sulphate and not more than 0.4% total combustible/organic material calculated as carbon; or

c) Nitrogen type ammonium nitrate based fertilizers containing mixtures of ammonium nitrate and ammonium sulphate with more than 45% but less than 70% ammonium nitrate and not more than 0.4% total combustible/organic material calculated as carbon such that the sum of the percentage compositions of ammonium nitrate and ammonium sulphate exceeds 70%.

5 NOTES TO THE LOGIC DIAGRAM (FIGURES 1A & 1B)

The following notes are intended to provide guidance and explanation; they must not be interpreted or used as strict or legal definitions/requirements. The note numbers refer to those given in the logic diagrams.

1. With reference to SP186, the nitrate ion (NO_3-) and ammonium ion (NH_4+) may originate from ammonium nitrate itself or from different materials (e.g. ammonium phosphates and potassium nitrate). The method of calculating ammonium nitrate content is illustrated by examples in appendix 2. Where the molar nitrate content is well in excess of the molar ammonium content *(e.g.>10%; this figure was specified in the eleventh/1999 and earlier editions of IMO Code, Ref 3)* consider classification due to the nitrate, as appropriate. For example, if other nitrates, such as sodium nitrate, are incorporated, reference should be made to other UN numbers under which such products may be classified e.g. UN 1477.

2. The total content of combustible and organic substances must be limited as specified in the relevant special provisions. If the limits for total combustible/ organic material calculated as carbon are exceeded, the fertilizer will not be accepted for carriage in some model regulations except under the conditions applicable to Class 1 (Ref 4).

   NOTE: Elemental sulphur (CAS No. 7704-34-9) is combustible and can react vigorously with AN; it must not be added.

3. Ammonium nitrate comes in different forms depending upon its intended use. *Ammonium nitrate* in crystalline form or as porous prills/granules (UN 1942) is mainly used for industrial applications such as base material for explosives. *Ammonium Nitrate Based Fertilizers* (UN 2067) are uniform mixtures (in prill or granular form) and contain ammonium nitrate as the main ingredient.

4. Inert towards AN (stated in SP 307a) in practice means that the added material does not significantly affect the hazardous properties of the AN. It is a common acceptable practice in the fertilizer industry to incorporate additives and/or other inorganic materials for various reasons. Typical examples of additives are magnesium nitrate, aluminium sulphate and ammonium sulphate which are added up to about 5% by weight in order to improve physical characteristics such as caking behaviour, hardness and thermal stability against temperature cycling. This improves the quality and safety of the product. Typical other inorganic materials include calcium sulphate, clay and kieselguhr, which can be used to achieve the desired chemical analysis of the product.

5. Definition of straight and compound fertilizer from CEN (EN 12944-1:1999):

   Straight fertilizer
   Qualification generally given to a nitrogenous, phosphatic or potassic fertilizer having a declarable content of only one of the primary nutrients.

   NOTE: Nitrogen type is mentioned in SP 307c to cover straight nitrogen fertilizer.

   Compound fertilizer
   Fertilizer, obtained chemically or by blending or both, having a declarable content of at least two of the primary nutrients.

6. Straight nitrogen fertilizers based on mixtures containing AN and AS are essentially binary mixtures i.e. any third component is primarily added to improve the quality and/or to achieve the desired chemical analysis of the product. AN + AS mixtures with >70% AN are not considered safe fertilizer products due to their potential dangerous properties; these are not described in the classification system in the "Orange Book".

7. It should be noted that calcium sulphate in SP 307b is described as 'mineral'. The reason for this description was to minimise contamination which may be caused by the use of by-product calcium sulphate.

8. Where this scheme fails to identify clearly the appropriate classification of any formulation e.g. where high levels of combustible/organic substances or incompatible inorganic substances are present the advice of your competent authority should be sought.

9. The Trough Test is mentioned in the UN regulations (in the UN Test Manual and BC Code) only with reference to AN based fertilizers.

    - When transporting by road or rail, the regulations concerning the Trough Test and UN 2071 do not apply.

    - Bulk cargoes of fertilizers classified as UN 2071 and showing a SSD speed >25 cm/h are not permitted in sea transport and inland waterways. This restriction can be found in the IMO (IMSBC Code) and ADNR regulations. Transport of these materials in packaged form is permitted.

    - In considering the transport of fertilizers classified as UN 2071, attention should be given to any specific requirements which may have been stipulated, e.g. speed of self-sustaining decomposition (SSD) (Ref 5).

6 REFERENCES

1. UN Recommendations on the Transport of Dangerous Goods, Model Regulations. (2009), Sixteenth edition, United Nations, ISBN` 978-92-1-139136-7.

2. Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

3. IMO, International Maritime Dangerous Goods Code (IMDG), two volumes. IMO Publications, London.

4. European Agreement Concerning the International Carriage of Dangerous Goods by Road, ADR 2009, page 147.

5. ADN 2011, European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways, ISBN 978-3-609-69337-8.

Appendix 1

Classification of three fertilizer compositions is illustrated in three sets of corresponding logic diagrams below based on the source material content. It is assumed that the organic/combustible material content is within the specified limits.

Example 1

Fertilizer composition by wt %	
Ammonium nitrate	75
Calcium carbonate or dolomite	21
Ammonium sulphate	4

Answer: The fertilizer is not classified. Clearly, the addition of ammonium sulphate is quite small and is to improve quality. The fertilizer can be regarded as a mixture of AN and limestone (or dolomite).

Example 2

Fertilizer composition by wt %	
Ammonium nitrate	75
Calcium carbonate or dolomite	10
Mineral calcium sulphate	15

Answer: The fertilizer is not classified as an oxidizer, class 5.1 as per revised SP 307.

Example 3

Fertilizer composition by wt %	
Ammonium nitrate	69
MOP (KCl)	9
Ammonium sulphate	22

Trough test shows it to be not capable of self-sustaining decomposition.

Answer: The fertilizer is not classified.

Figure 2A

Example 1: 75% AN, 21% Dolomite and 4% AS

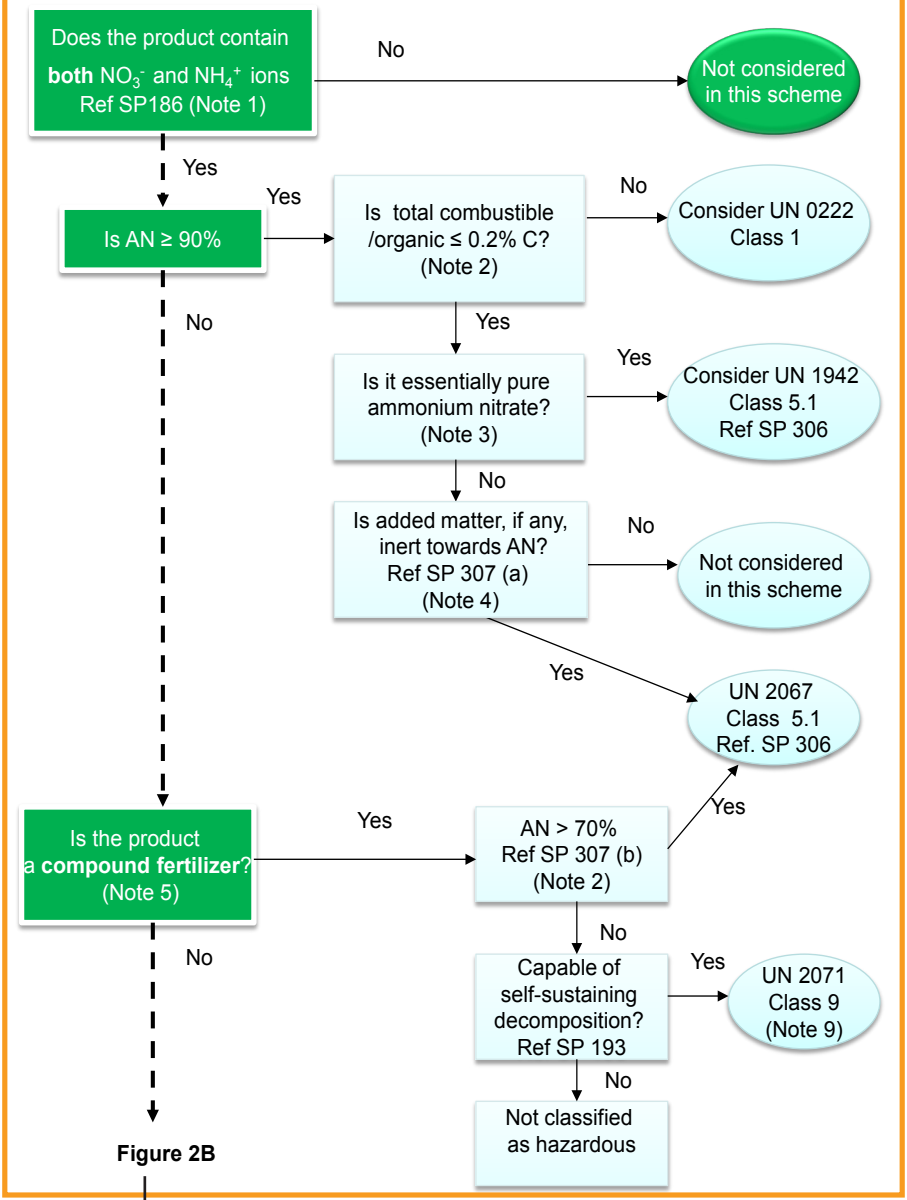
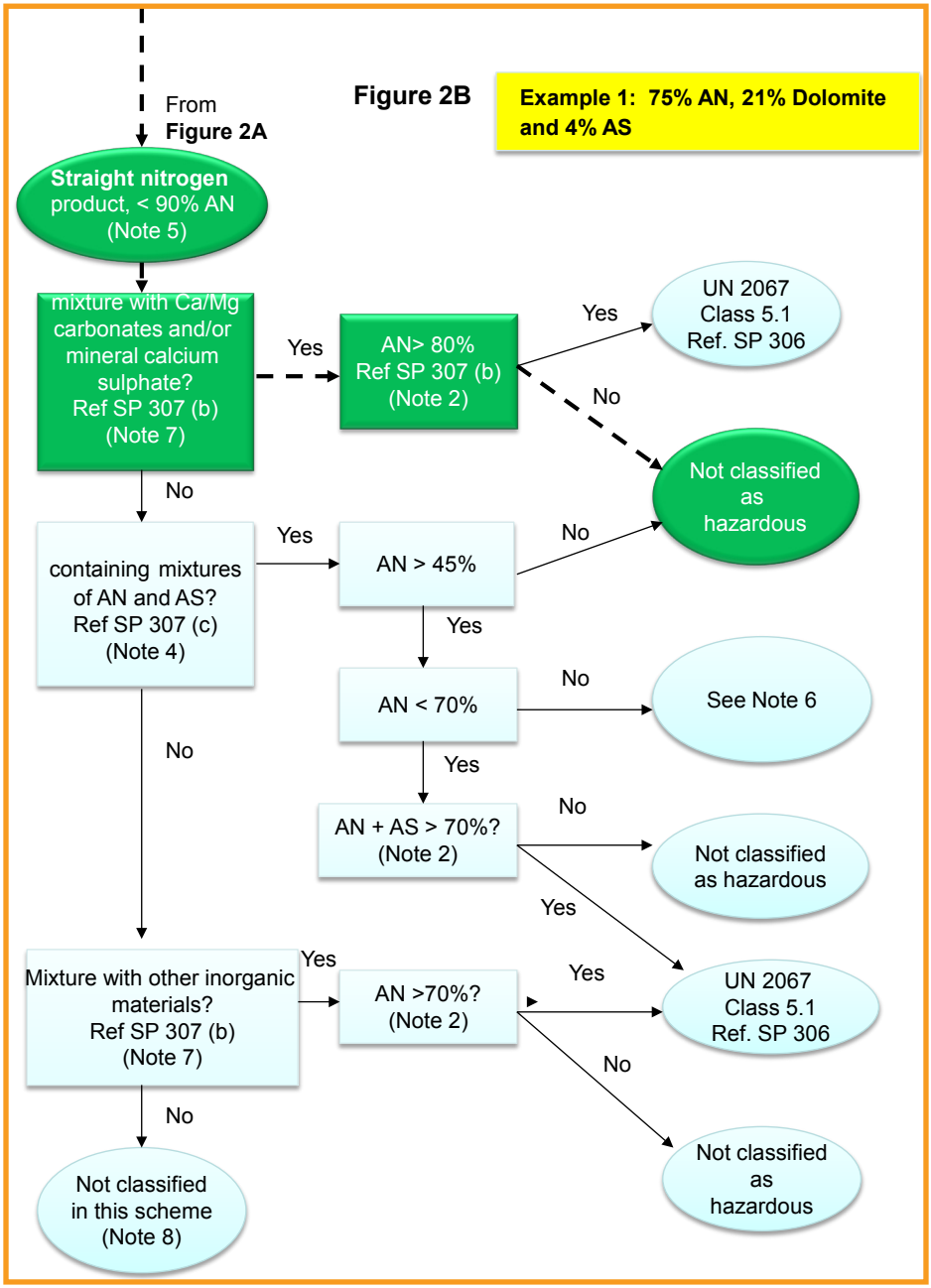


Figure 2B

Example 1: 75% AN, 21% Dolomite and 4% AS



Example 2: 75% AN, 10% Dolomite and 15% Mineral calcium sulphate

Figure 3A

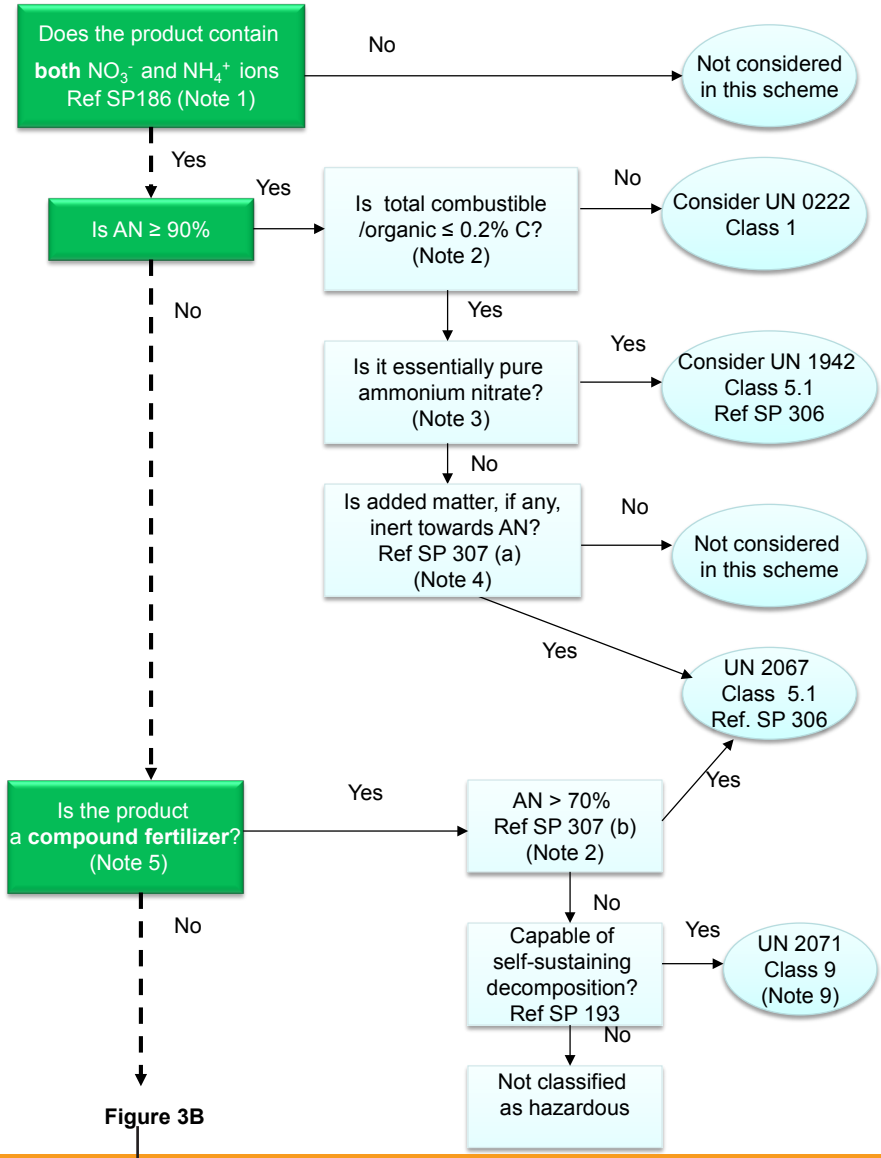
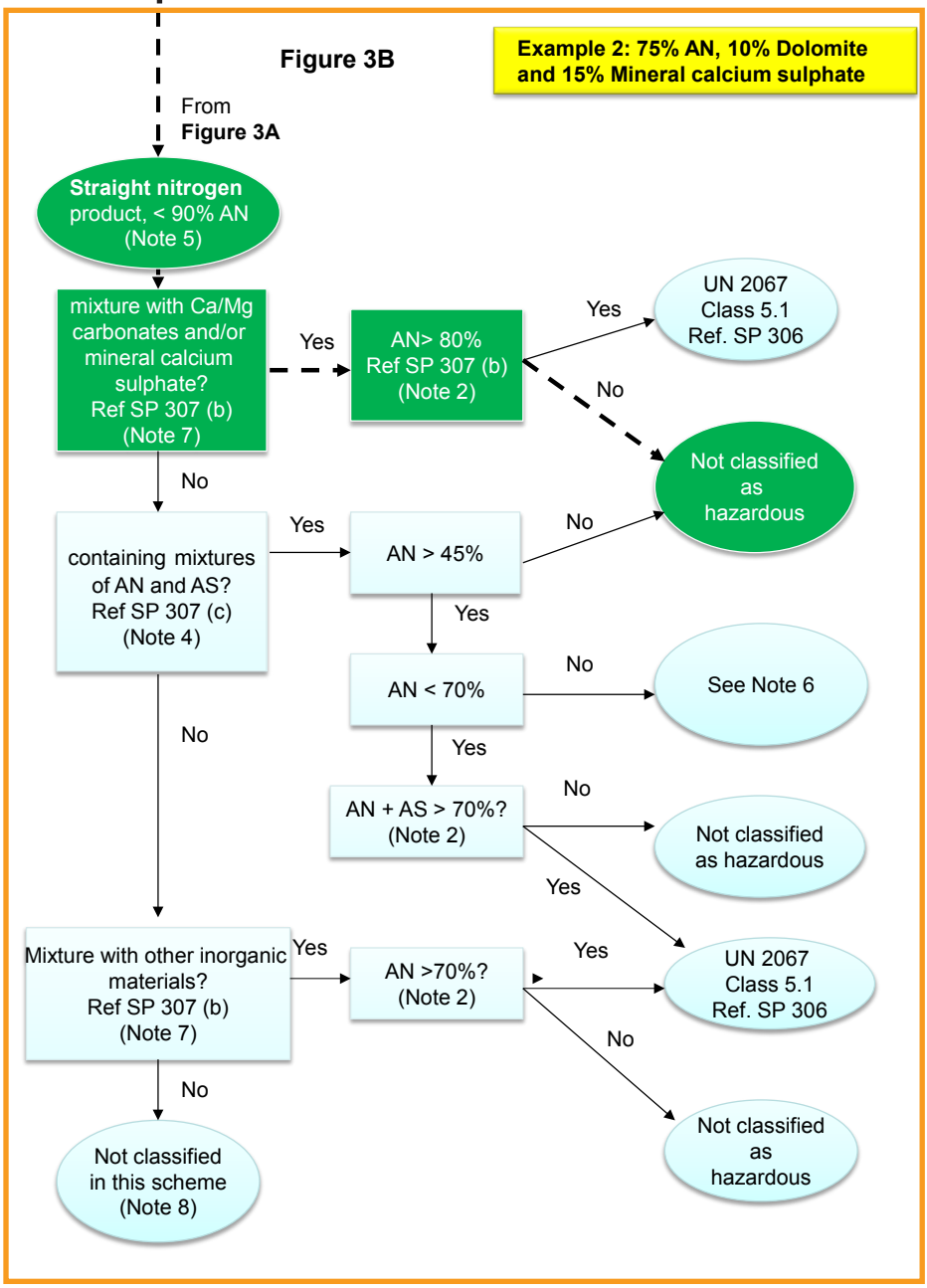


Figure 3B

Example 2: 75% AN, 10% Dolomite and 15% Mineral calcium sulphate



Example 3: 69% AN, 9% MOP and 22% AS

Figure 4A

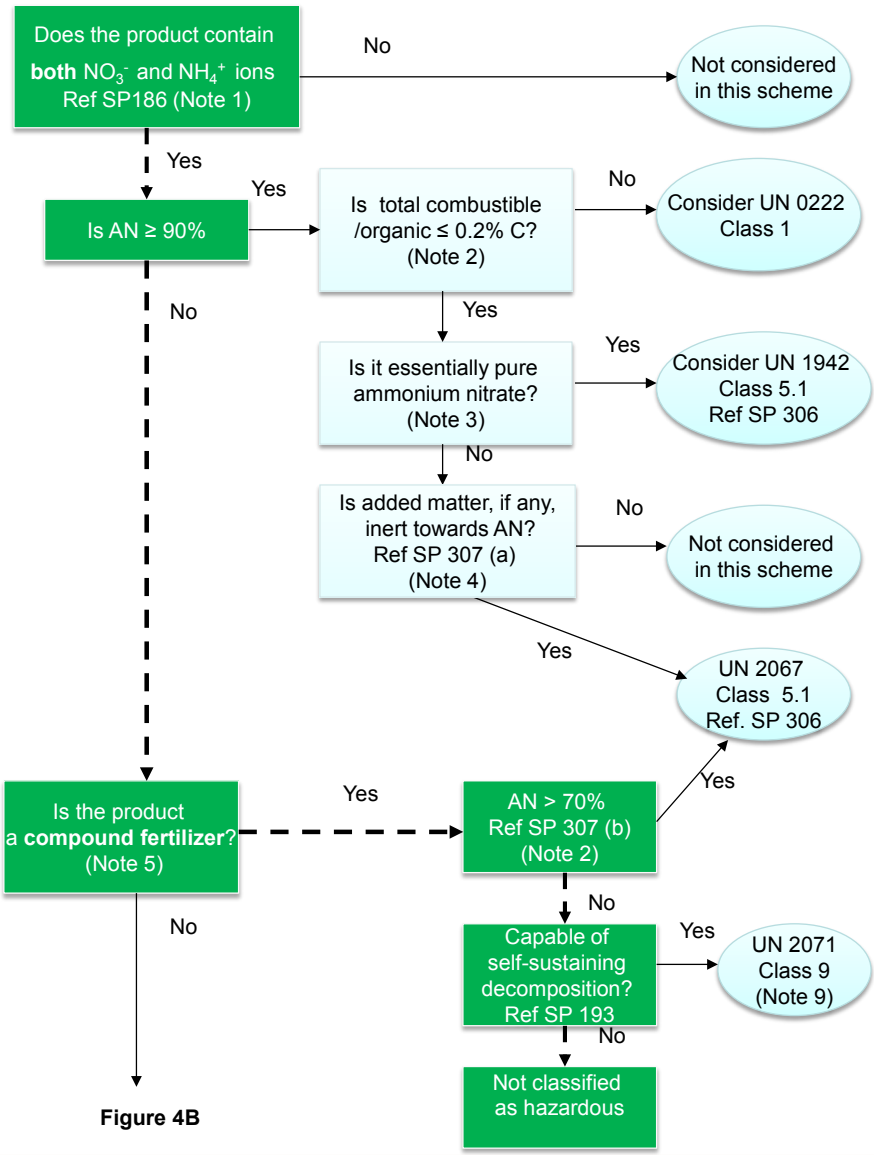
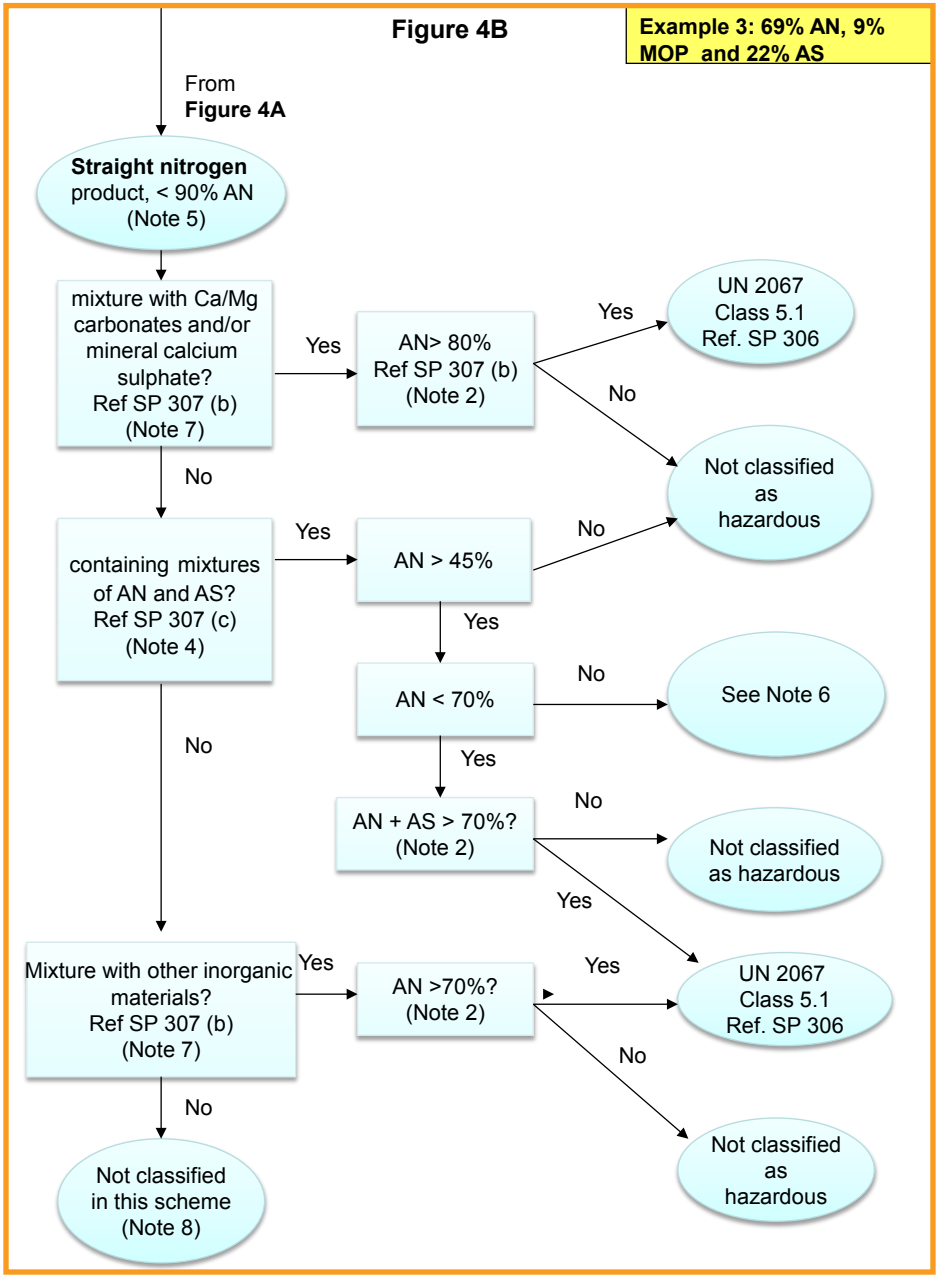


Figure 4B

Figure 4B

Example 3: 69% AN, 9% MOP and 22% AS



Appendix 2

Ammonium Nitrate (AN) Content

The content of ammonium nitrate in a fertilizer is calculated on the basis of nitrate ions for which a molecular equivalent of ammonium ions is present.

The nitrogen content of AN is 35%. The following table gives the nitrogen content in fertilizers derived from AN on a wt/wt basis.

AN %	100	90	80	70	60	45	30
N %	35	31.5	28	24.5	21	15.75	10.5

Example 1:

The ammonium nitrate (AN) content of a fertiliser which contains 7% nitrate nitrogen and 12% ammoniacal nitrogen is calculated as follows:-

Nitrogen content derived from ammonium nitrate (formula NH_4NO_3)

= 7% nitrate N + 7% ammoniacal N
= 14% N

As pure ammonium nitrate contains 35% nitrogen, the ammonium nitrate content of this fertilizer is:

$14/35 \times 100 = 40\%$

Example 2:

The ammonium nitrate (AN) content of a fertilizer which is made of 60% potassium nitrate (KNO_3) and 40% MAP ($NH_4H_2PO_4$) can be calculated as follows:

Potassium nitrate contains nil ammoniacal N and 13.86% nitrate N.
Pure MAP contains 14/115 X 100 or 12.2% ammoniacal N and nil nitrate-N. (Commercial MAP contains slightly less amounts of nutrients due to the presence of other substances.)

Therefore, the mixture contains:

nitrate-N	= 60 X 13.86/100 or 8.3% and
ammoniacal-N	= 40 X 12.2/100 or 4.9%

The ammoniacal N, being less than the nitrate-N, is the limiting number.

Total N in equivalent AN = 2 X 4.9 or 9.8%.

Therefore, the equivalent ammonium nitrate is:

9.8/35 x 100 = 28%

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