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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

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PROPOSALS OF AMENDMENTS TO THE RECOMMENDATIONS
ON THE TRANSPORT OF DANGEROUS GOODS

Model Regulations on the Transport of Dangerous Goods

Classification of ammonium nitrate-based fertilizer (UN 2067)

Submitted by the expert from European Fertilizer Manufacturers Association (EFMA)

1. Background

Ammonium nitrate (AN) based fertilizers (UN 2067) are classified on the basis of their defined compositions as oxidizers under Division 5.1, Packing Group III.

These fertilizer compositions are defined in the special provision 307, sub-sections (a), (b) and (c). One of the compositions, defined in 307 (b,) is that of AN (more than 80% but less than 90%) with calcium carbonate and/or dolomite. Where other inorganic materials such as calcium sulphate are used the minimum is set at the lower figure of 70% by virtue of the second option in SP 307 (b).

AN based fertilizers containing calcium sulphate have been used as a source of nutrient sulphur for many years. Test results obtained over a number of years, together with Industry's experience, show that these products have very similar safety characteristics to those of compositions based on calcium carbonate and/or dolomite.

2. Discussion

Existing classification and its impact on industry

Compositions containing more than 70 % but less than 80% AN with the inorganic material **calcium sulphate** are classified according to special provision 307 (b) as UN 2067, Class 5.1 oxidizing agents, whereas similar compositions containing only calcium carbonate and/or dolomite are not.

This inconsistency, which is now without scientific justification, unfairly penalizes a significant part of the fertilizer industry supplying such products and inhibits further development in this area. There are strong agronomic needs for products containing calcium sulphate as a source of nutrient sulphur. The agronomic needs are explained in annex 1, which has been prepared by the Agriculture and Environment Committee of EFMA.

Examples of commercial NS products manufactured include:

- 27% N + 2.7% S, containing approximately 77 % AN, 11.5 % calcium sulphate and the balance dolomite.
- 27% N + 3.7 % S, containing approximately 77 % AN, 15.7 % calcium sulphate and the balance dolomite.

Characteristics of calcium sulphate.

Calcium sulphate is a very common mineral found all around the world. In addition, it is also available as a by- product from some industrial processes.

Calcium sulphate ($CaSO_4$) exists in three main forms depending on the amount of crystal water present in the molecular structure: anhydrite (no crystal water), hemihydrate and dihydrate (gypsum).

$CaSO_4$ is very stable and relatively unreactive. Upon heating, it decomposes only at very high temperatures. The decomposition is highly endothermic.

Safety testing of compositions containing AN and calcium sulphate

A number of commercially available products have been tested by TNO. They contain, in addition to AN, calcium sulphate only or combinations of calcium sulphate and calcium carbonate and/or dolomite.

The tests include the UN oxidizing test (0.1: test for oxidizing solids) and the resistance to detonation test (IMO BC Code 2005; Code of Practice for Solid Bulk Cargoes, Annex 3, Test 5a). The results are given in annex 2. They show that the calcium sulphate based compositions are comparable to the calcium carbonate/dolomite based compositions and that they all passed the above tests.

As the fertilizers in question are simple nitrogen type, based on AN and inert materials, they do not possess the property of self-sustaining decomposition. Therefore, they can not belong to Class 9.

From the results it is concluded that AN-based fertilizers with AN >70% and <80% and other components (i) calcium carbonate and/or dolomite or (ii) calcium sulphate or (iii) any combination of calcium carbonate, dolomite and calcium sulphate have similar safety characteristics.

3. Proposal

EFMA proposes that the following existing text in UN 2067, SP 307 (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 not more than 0.4% total combustible/organic material calculated as carbon*

be replaced as follows:

> *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 calcium sulphate*** *and not more than 0.4% total combustible/organic material calculated as carbon.*

Annex 1 (English only)

Importance of ammonium nitrate based fertilizers with less than 80 % ammonium nitrate mixed with calcium sulphate

Nitrogen (N) and Sulphur (S) are essential plant nutrients which play a vital role in protein formation. In plant nutrition N and S are complementary and synergic to each other. Even though S-deficiency is recognized in farming, the most important N-fertilizers in Europe are AN (>90%) and AN-based fertilizers (< 80 % AN) mixed with calcium carbonate and/or dolomite (CAN), and contain no sulphur. The continuous reductions of S-anthropogenic emissions to the atmosphere, which have been achieved during last decades to the benefit of air quality, result nowadays in a negative balance of S inputs versus outputs (export from crop harvest and sulphate leaching) in many parts of Europe. This imbalance can be rectified by the production and use of AN based fertilizers containing calcium sulphate. As a consequence the continuous development of adapted N-S fertilizers or any other form of S-fertilizers is critical for the well being of agriculture.

The physiologic plant requirement of N and S is for most crops in the N:S ratio of 7:1 to 10:1. In view of the higher leaching rate of sulphate (SO_4), N-S fertilizer products better address crop needs with formulations having N:S ratios between 5:1 and 7:1, depending on soil and climatic conditions. Mismatching this ratio between N and S in plant nutrition may result in plant growth reduction and imbalanced plant nutrient uptake of either N or S.

In the present regulatory situation, the maximum AN content of fertilizers based on AN and calcium sulphate is kept below 70% in order to avoid their classification under 5.1 as oxidizers. Consequently, in order that crops receive the required amount of nitrogen (N), farmers need to apply fertilizer in bigger quantity than they would, if they use mixtures of AN and/or calcium carbonate and/or dolomite, which contain > 70%, (but not more than 80 %) AN (e.g. CAN). This legal constraint limits the possibilities and, in certain conditions, induces additional field applications to the detriment of the environment.

Beneficial characteristics of mixtures of AN and calcium sulphate with more than 70 % and less than 80 % AN in modern farming systems:

- By using $CaSO_4$ instead of calcium carbonate as a fertilizer component, the required amount of S is made available without reducing the N concentration. As a result extra applications of lower concentration fertilizers will not be required, thus reducing application costs and the risk of additional soil compaction.
- The N:S ratio in mixtures of AN and calcium sulphate with more than 70 % and less than 80 % AN better fit the average plant requirements (e.g. 27% N + 4.8% S corresponds to an N:S ratio of 5.6:1).

During the growth period, the continuous availability of both nutrients according to plant needs is important because:

a. Any deficiency of S inhibits plant growth, reduces the N uptake and thus increases the potential of N leaching with its undesirable environmental impact. Consequently this S deficiency has an important impact on the economics of modern farming.

b. Any overdosing of S leads to S-losses to ground water (the leaching rate for SO_4 is higher than for NO_3), resulting in economic losses.

- The combination of N+S with Calcium (Ca)
  Sulphur can produce acidifying effects. The use of calcium sulphate reduces this effect. In addition, applying a calcium based fertilizer adds an important additional plant nutrient; Ca being one of the essential secondary elements for plant growth.

In conclusion, fertilizers containing AN (>70% and <80%) and calcium sulphate make an essential contribution to the development of sustainable farming systems across the world.

Annex 2 (English only)

TNO report

Summary of properties of fertilisers based on ammonium nitrate (<80%) and calcium sulphate.

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TNO report

Summary of properties of fertilisers based on ammonium nitrate (<80%) and calcium sulfate

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Introduction

This report provides a summary of typical properties of fertilisers based on ammonium nitrate (less than 80 mass-%) and dolomite and/or calcium carbonate and/or calcium sulfate. The data was collected in the time period 2000 – 2006 with production samples from various manufacturers.

The data can be considered as a representative summary of hazardous properties of these fertiliser formulations.

Both the explosive properties and the oxidising properties of production samples were determined by TNO.

A summary of results is given in this report.

Explosive properties

Test Series 1 was used to determine the explosive properties of ammonium nitrate (< 80%) / calcium sulfate fertilisers.
The results listed for Test Series 1 were obtained with a formulation containing 27% nitrogen (corresponding to 77% ammonium nitrate), 3% sulphur (corresponding to 12.7 % calcium sulfate) and filler (dolomite / calcium carbonate).

Test name	Test code	Observations	Result
UN Gap test	1(a)	average fragmentation length: 193 mm	Not able to propagate a detonation
Koenen test	1 (b)	limiting diameter < 1 mm	Not sensitive to heat under high confinement
Time/pressure test	1 (c) (i)	maximum pressure 720 – 1220 kPa	Not sensitive to ignition under confinement

The results also apply to formulations containing different percentages of calcium sulfate. It is concluded that these mixtures do not have explosive properties.

In the time period of 2000 – 2006 more than 30 production samples containing less than 80% ammonium nitrate; sulphur content ranging from 2.7% to 5.2% (corresponding to 11.5% to 22.1% calcium sulfate) with and without dolomite and/or calcium carbonate filler from various manufacturers have been tested using the Resistance to Detonation Test (Reference: IMO BC Code 2005; Code of Practice for Solid Bulk Cargoes, Annex 3, Test 5a) which is similar to the EEC Resistance to Detonation Test. Basically, it consists of a steel tube of 1000 mm length, wall thickness 5 – 6.5 mm, external diameter 114 mm. A booster consisting of 500 g PETN based plastic explosive is use to apply an intense shock to the sample. Six lead cylinders are used to measure the degree of expansion (caused by the reacting sample) of the test tube. A sample is considered positive (i.e. capable of propagating a detonation) when each lead cylinder is indented at least 5%
Each sample was submitted to five thermal cycles (25° C → 50° C → 25° C) to include the influence of ageing.

None of the tested samples detonated in this test, the decomposition reaction initiated by the booster typically died out after approximately 350 – 400 mm. Only two or three of the six cylinders were indented more than 5%.

It was concluded that these formulations are not capable of propagating a detonative reaction.

Oxidising properties

Various samples have been subjected to Test O.1: test for oxidizing solids, as described in the UN Manual of Test and Criteria. Samples containing 27% nitrogen (or 77% ammonium nitrate) and 2.7% or 3.7% sulphur (corresponding to 11.5% to 15.7% calcium sulfate) and dolomite and/or calcium carbonate filler were tested with the conical pile test in the physical form as received.

Tests were conducted on the samples mixed with dry fibrous cellulose in mixing ratios of 1:1 and 4:1, by mass, of sample to cellulose. The burning characteristics of the mixture are compared with the standard 3:7 mixture, by mass, of potassium bromate to cellulose. If the burning time is equal to or less than this standard mixture, the burning times are compared with those from the Packing Group I or II reference standards, 3:2 and 2:3 ratios, by mass, of potassium bromate and cellulose. Both the cellulose and the potassium bromate are sieved and dried to constant mass, and kept in a desiccator.
The ignition source comprises of an inert metal wire (NiCr), connected to an electrical power source.

The results are summarised in the following table.

27% N / 2.7% S		27% N / 3.7% S	
Mixing ratio	Burning time (s)	Mixing ratio	Burning time (s)
1 : 1	175	1 : 1	192
4 : 1	136	4 : 1	147
Reference substances			
3 : 7	116	3 : 7	116
2 : 3	39	2 : 3	39
3 : 2	8	3 : 2	8

Based on the provisions included in the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, fourth revised edition, paragraph 34.4.1, the materials are not oxidizing substances.

Recommendation

Based on the properties as listed in this summary report it is recommended that fertiliser formulations with less than 80% ammonium nitrate and containing dolomite and/or calcium carbonate and/or calcium sulfate should not be subjected to the provisions of the Model Regulations.
