

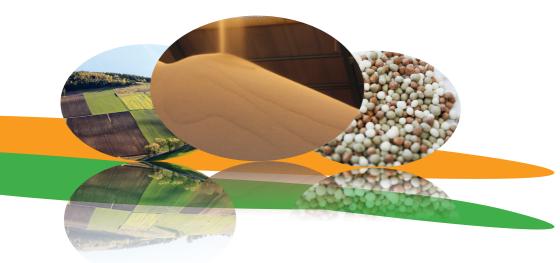
GUIDANCE FOR COMPATIBILITY OF FERTILIZER BLENDING MATERIALS



product stewardship fertilizers

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1. INTRODUCTION

A large number of blended fertilizers are produced from basic primary fertilizer products (e.g. ammonium nitrate, urea, and mono-ammonium phosphate) and natural materials (e.g. rock phosphate, potassium chloride). All such materials are not necessarily compatible with each other and some may produce undesirable effects when mixed with others. These undesirable effects can include, for example, chemical reaction(s) and physical effects (e.g. stickiness which can cause handling difficulties, moisture migration giving rise to caking tendency).

The Handbook of Solid Fertiliser Blending: Code of Good Practice for Quality produced by The European Blenders Association (Ref. 1), gives some information about these potential compatibility problems. Fertilizers Europe has reviewed this information and has produced this guidance with wider scope by including most commonly used blending materials.

2. SCOPE

Only *solid* blending components which are sources of primary (N, P and K) and/or secondary (e.g. Ca, Mg) nutrients are considered here. These blending components also include complex granular NPK/NP/NK fertilizers but fluid materials and micronutrients such as zinc and copper are not considered.

The assessment concerning compatibility is based on considerations of safety (e.g. chemical reaction causing release of toxic gases), production problems (e.g. liquid formation, state of stickiness, corrosive mix due to free acidity) and/or quality aspects (e.g. high tendency for caking). It is important to note that legislative controls e.g. limits imposed by classification schemes, impurity levels etc. are not taken into account in the assessment. For example, regulations concerning safety and classification would have a bearing on the limits of total combustible/organic matter and total ammonium nitrate level.

It is important to bear in mind that most regulations define Ammonium Nitrate as mixtures containing NH_4^+ and NO_3^- ions irrespective of their source materials, which for example, could be ammonium phosphate and sodium nitrate. Manufacturers are advised to consider the legislative controls and identify 'no-go' areas up-front prior to going into the compatibility aspects.



3. BLENDING MATERIALS & GENERAL CONSIDERATIONS

3.1 General

A range of blending components is available and the common ones are listed in the Compatibility Table (page 12). Some blending materials such as calcium cyanamide and basic slag are not included in the table as they are not widely used. Some relevant information about them is given in another guidance document from Fertilizers Europe, dealing with storage and handling and transportation of solid ammonium nitrate based and other fertilizers. If in doubt, seek expert advice when using an unlisted/uncommon component.

3.2 Nitrate-Containing Substances

Nitrates are important sources of nitrogen, particularly in the European climatic conditions and the main ones are ammonium nitrate, potassium nitrate, sodium nitrate and calcium nitrate. Most of them possess oxidising properties and thus can support combustion but differ in their thermal behaviour and reactivity. Their main properties related to the potential hazards are summarised below (Ref. 2).

3.2.1 Ammonium Nitrate

Solid ammonium nitrate (AN) can exist in a number of different crystalline forms. Transitions from one form to another are accompanied by changes in the bulk density. This can lead to product break-down due to thermal cycling, unless it is stabilised against this effect by suitable conditioners. AN melts at 169°C and, when heated further, decomposes releasing gases containing mainly water vapour, NO_x and ammonia. The exothermic decomposition, which is a complex set of exothermic reactions, is accompanied by reversible endothermic dissociation and is catalysed by a number of substances. AN has oxidising properties and will, if involved in a fire, intensify the fire even in the absence of air. AN, particularly the fertilizer grade, is difficult to detonate. The sensitivity to detonation depends on a number of factors such as bulk density, porosity and temperature.

For fertilizer application, EU regulations require the use of the dense grade, which has low porosity and a high resistance to detonation. It must be able to pass the EU Resistance to Detonation Test.

It is important to note that AN content can be derived from different sources of nitrate ions and ammonium ions, as described in section 2 above. Also, the classification of the blend may be affected if there is an excess of nitrate ions above those derived from actual or calculated AN.



3.2.2 Potassium Nitrate

Potassium nitrate has a melting point around 334°C. Commercially it is available in both granular and crystalline forms. It is not combustible, however it has oxidising properties and will, if involved in a fire, intensify the fire even in the absence of air. Above 400°C it decomposes and liberates oxides of nitrogen. Potassium nitrate is not sensitive to detonation.

3.2.3 Sodium Nitrate

Sodium nitrate has a melting point close to 308°C. It is not combustible, however, it has oxidising properties and will, if involved in a fire, intensify the fire even in the absence of air. When heated to decomposition, it gives off toxic gases, which include oxides of nitrogen. Sodium nitrate is not sensitive to detonation.

3.2.4 Calcium Nitrate

Pure calcium nitrate (chemical formula $Ca(NO_3)_2$) is not normally traded as a fertilizer. Fertilizer grade calcium nitrate (chemical formula $5Ca(NO_3)_2.NH_4NO_3.10H_2O$) is essentially the hydrated ammonium calcium nitrate double salt. It is not classified as an oxidising material, but as with other nitrates, it should not be mixed with combustible materials, alkalis and acids. Its ammonium nitrate component decomposes above 190°C, whereas the calcium nitrate component decomposes above 500°C and the thermal decomposition products are mainly nitrogen oxides.

3.3 Other Materials and General Notes

The following points should be noted:

- The compatibility data are based on the assumption that the components have typical and acceptable moisture content and thermal stability.
- In general the presence of anti-caking agents and additives in fertilizers may affect their compatibility.
- The type of manufacturing process used can also affect the product properties, e.g. materials made by the nitrophosphate process may behave differently from those made by the mixed acid phosphate route.
- Calcium sulphate as listed does not cover impure by-product gypsum.
- Limestone and dolomite generally refer to mined material.
- Calcium nitrate refers to the fertilizer grade material which contains 12% water, is a double salt and is not classified as Class 5.1 oxidiser.
- Rock phosphate is listed in two forms: normal mineral and acidulated rock which, although this is not normally the case, can contain some free acid.
- Elemental sulphur can give rise to formation of dust, particularly in the mixing

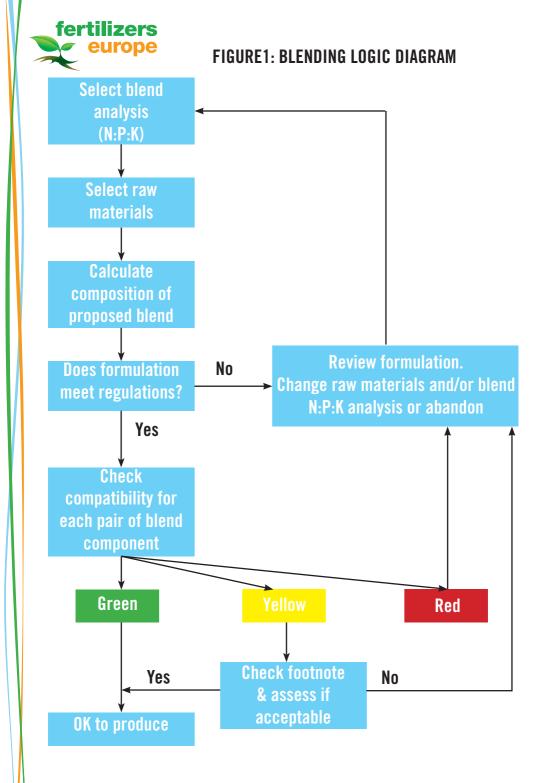
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process and this dust can present a potential 'dust explosion' hazard.

- Where AN forms a part of the blend, care should be taken to ensure that the specified limits of total combustible/organic substances, including any coating oil, are not exceeded in the blend.
- In some countries there may be restrictions regarding the use of coating oil or the type of oil. This point should be taken into consideration.
- The addition of certain micronutrients such as copper or manganese to chloride containing AN-based blends can enhance the thermal decomposition potential. This may convert a non-classified type to a self-sustaining decomposition type. An appropriate assessment should be made.

The overall approach to the evaluation and selection of blend composition is outlined in Figure 1.





4. **RELATIVE HUMIDITY**

Some fertilizer materials are hygroscopic which means they can pick up moisture from humid air. The Critical Relative Humidity (CRH) is the property which is used as an indicator of the degree of likely interaction with the atmospheric moisture. It is the value of the relative humidity of the surrounding air, above which the material absorbs moisture and below which it does not. Thus, the lower the CRH the greater the tendency to pick up moisture from the atmosphere. It is, therefore, desirable to have high values of the CRH for the raw materials and the finished fertilizers. CRH values are measured or calculated at 30°C and the values tend to decrease slightly with increase in temperature.

In most cases, the CRH for blended or compound fertilizers is below the average derived from their components. This drop in the CRH can be significantly high in some cases. A blend consisting of ammonium nitrate and urea is an extreme example of this effect. Such a blend picks up moisture very quickly and it is difficult to handle in a dry state. This can be a significant factor to consider in the selection of the blend components. CRH values of pure components and blends based on them are summarised in Table 1 (Ref. 3). It should be borne in mind that these values are for pure salts and the corresponding commercial materials may have slightly different values depending on any impurities present.

TABLE I: CRITICAL RELATIVE HUMIDITIES OF PURE SALTS AND Mixtures at 30°C (86°F)					PHATE	DIAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE	POTASSIUM NITRATE	90.5 MONDAMMONIUM PHOSPHATE	59.8 91.6 MONOCALCIUM PHOSPHATE	87.8 88.8 93.6 POTASSIUM SULPHATE	87.8 79.0 -** 96.3
E I: CRIT Jres at				LORIDE	AMMONIUM SULPHATE	DIAMN	\backslash	84.0	78.6	72.8**	* *	81
TABLE MIXTU				UM CH	MMONI	\backslash	82.5	70*	-	78*	78*	77*
		ATE	A	AMMONIUM CHLORIDE	A	79.2	72*	71.3**	69.2	75.8	87.7	81.4
	IRATE	A NITR	UREA	\backslash	77.2	71.3	•	73.5	6'.9	•	73.9	71.3
ш	lin mui	SODIUM NITRATE		72.5	57.9	56.4	62*	60.3	65.2	65.2	65.1	71.5
IUM NITRATE	AMMONIUM NITRATE		72.4	45.6	51.9**	**	,	**6.99	64.5	63.8	68.1	73.3**
CALCIUN		59.4	46.3	18.1	51.4	62.3	59*	67.9**	59.9	58.0	52.8	69.2**
10	46.7	23.5	37.7	•	ı	•	·	<22.0	31.4	52.8**	46.2	76.1**

* Approximate values obtained by TVA (Tennessee Valley Authority) (Ref.3). Other data are from literature ** Unstable salt pair; the value given is for the stable pair

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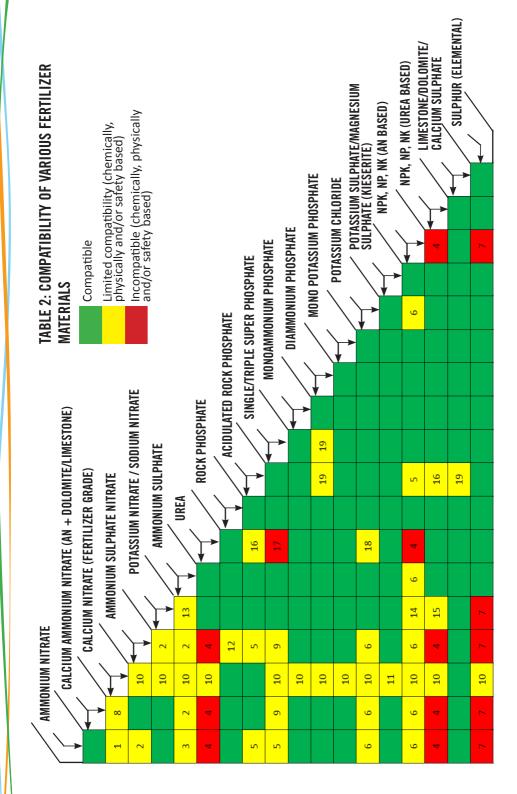


5. COMPATIBILITY DATA

The compatibility data are presented in three categories as follows:

- 1. Compatible (indicated in green): No undesirable effect is predicted.
- 2. Limited compatibility (indicated in yellow): Blends are permitted but there may be a risk of the blend being incompatible in some cases or situations e.g. if one or more of the components is out of specification or contains abnormal levels of an objectionable substance such as free acid. An appropriate risk assessment should be carried out, as necessary.
- 3. Incompatible (indicated in red): Considered as not being compatible and, therefore, should not be mixed.

For categories 2 and 3 the explanation/reason for the categorisation is given by way of a serial number in the box and footnote for each allocated number. No explanation is deemed necessary for compatible mixes.





FOOTNOTES FOR THE NUMBERS IN THE BOXES IN TABLE 2

- 1. Due to the hygroscopic behaviour of both products, the type of stabilisation of the ammonium nitrate grade could influence storage properties.
- 2. Consider the safety implications regarding detonability of the blend (AN/AS mixtures) and legislative implications.
- 3. Consider the safety implications regarding detonability of the blend (AN/AS mixtures), impact of free acid and organic impurities, if present, and legislative implications.
- 4. Mixture will quickly become wet and absorb moisture resulting in formation of liquid or slurry. There could also be safety implications.
- 5. If free acid is present it could cause very slow decomposition of AN, affecting, for example, packaging.
- 6. Consider the possibility of self-sustaining decomposition and the overall level of oil coating.
- 7. Sulphur is combustible and can react with nitrates e.g. AN, KNO₃ and NaNO₃.
- 8. Due to the hygroscopic behaviour of both products, the type of stabilisation of the ammonium nitrate based fertilizer could influence the storage properties.
- 9. Consider the moisture content of the SSP/TSP.
- 10. Consider the relative humidity during blending.
- 11. Risk of formation of gypsum.
- 12. No experience but this can be expected to be compatible. Confirm by test and/or analysis.
- 13. Consider impurities in AS and the drop in the critical relative humidity of the blend.
- 14. Consider the likely impact of additional nitrate.
- 15. Consider the possibility of ammonium phosphate/potassium nitrate reaction with urea and relative humidity during blending to avoid caking.
- 16. If free acid present, there is a possibility of hydrolysis of urea giving ammonia and carbon dioxide.
- 17. Formation of very sticky urea phosphate.
- 18. Potential caking problem due to moisture.
- 19. If free acid is present, consider the risk of a reaction e.g. neutralisation with ammonia and acid attack with carbonates.



6. **REFERENCES**

- 1. European Fertiliser Blenders Association, 2005, 'Handbook of Solid Fertiliser Blending Code of Good Practice for Quality', second edition. European Fertiliser Blenders Association, Avenue Gaston Phoebus, 64231 Lescar Cedex, France.
- 2. Fertilizers Europe, '*Guidance for the Storage, Handling and Transportation of Solid Mineral Fertilizers*' (2007).
- 3. Clayton W E, 1984, '*Humidity Factors Affecting Storage and Handling of Fertilizers*'. International Fertilizer Development Center, Muscle Shoals, AL 35662, USA.





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Product Stewardship defined "the is ลร management of the safety, health and environmental aspects of a product throughout its lifecycle in an ethically responsible way". It is Responsible Care as applied to products. In our application of Product Stewardship we cover the total value chain, but also address additional issues such as Best Practices that are not necessarily just dealing with the product characteristics.

The Product Stewardship Program covers mineral fertilizers, their raw materials and intermediate products.

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