Chapter 11 – Fertilisers

Fertilisers are synthetic or natural, organic or inorganic materials used to supply nutrients vital for plant growth. Plants uptake nutrients dissolved in water through their roots, with nitrogen (N), potassium (K) and phosphorus (P) being the primary elements required for plant growth. Therefore, fertilisers are mainly useful to agriculture. The estimated global fertiliser market is expected to increase to 188.18 billion USD by 2024, which is likely to be accompanied by an increase in fertiliser distribution across the globe.

Commercial fertilisers can be composed of varying elements: standard nomenclature for combined NPK fertilisers states the composition in the order of N, P and K followed by the percentage of each constituent. For example, NPK 15-15-15 consists of 15% N, 15% P and 15% K. Commonly shipped fertilisers include urea, ammonium nitrate and potassium nitrate.

Although common types of NPK fertiliser have known compositions, the numerical values do not necessarily determine what the chemical entities in the mix are. Therefore, knowing that a fertiliser is a given NPK does not mean hazardous properties can be determined. The most likely hazardous ingredient of an NPK fertiliser is ammonium nitrate, and many NPK mixes do contain this. There are schedules in the IMSBC and IMDG Codes for fertilisers containing ammonium nitrate. Potential hazards include being an oxidising agent, self-heating, emitting toxic fumes, and undergoing self-sustaining decomposition.

A wide range of fertilisers are shipped globally and while not all of them have specific associated hazards, care must be taken when handling Group B cargoes such as ammonium nitrate and potassium nitrate. Using the relevant Code and appropriate cargo declaration is key to safe transportation by sea. Whereas other fertilisers may not be associated with special hazards, they can nonetheless be involved in incidents such as caking, water damage and contamination.

11.1 Fertiliser Shape

Fertilisers are most commonly in prill or granule form. Importantly, their spherical shape and free-flowing nature allow them to be utilised in typical gravity fed field distribution equipment. Prills and granules exhibit differences in properties, some of which are relevant to transport and storage claims.

Prilling forms reasonably uniform spherical particles by forcing liquid through either a nozzle or a rotating bucket to form a small jet. This jet breaks up into individual liquid melt droplets that are cooled and solidified by freefalling in a 'prill tower' (Figure 11.1), forming 0.5–4 mm spherical prills. Often, fans are added to the bottom of the tower to provide an upward steam of cool air.

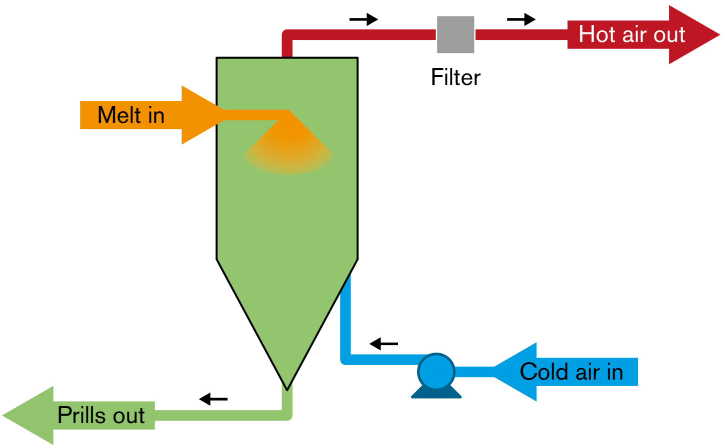

Figure 11.1: Granulation process.

There are two types of granulation: wet or dry. Wet granulation is more common, with rotary drum granulators being the most frequently used method. Here, a mist of melt and binding agent droplets are fed into a high-speed rotating drum; small particles absorb the mist, growing to form larger granules of the desired size. The high temperature within the drum dries the granules.

Prills and granules have differing physical and mechanical properties: the key differences are their resistance to crushing, ie hardness, and their size. Figure 11.2 shows the difference in hardness between prills and granules, depending on particle size. Granules are shown to be harder and therefore more resistant to crushing than prills, regardless of size.

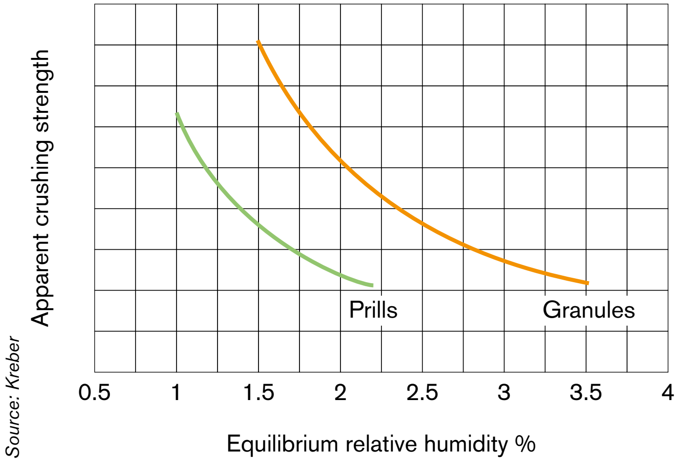

Figure 11.2: Granulation properties.

Regardless of whether the fertilisers are prills or granules, the end product should meet these criteria:

- Consistent size
- free from crushed granules and dust
- easily spread
- quickly dissolved
- contaminant free.

11.2 Caking in Fertilisers

Between production and use in soil, fertilisers may need to be stored for long periods, and it is essential that they remain free-flowing during this time. Under certain conditions, lumps or agglomerates (caking) can form in fertilisers, and as fertiliser usage relies on its free-flowing nature, it is important to prevent caking. The contacts formed between fertiliser particles can provide an indication of the cause of caking. Furthermore 'free-flowing' is different for fertilisers than, for example, grain, in that it is inevitable that some fertiliser compaction (adhesion contacts) will occur within the stow. These cliffs are easily collapsed by normal handling during discharge operations of the cargo, for example, using a grab.

The types of contacts that can form between fertiliser particles are detailed as follows. It is noteworthy that adhesion contacts, ie reversible compaction, is distinct from hard caking, the latter being irreversible.

Adhesion contacts, or capillary adhesion, is a relatively weak attraction between the in-contact molecule surfaces. Pressure exerted on the fertiliser particles in bulk can result in adhesion bound particles (ie compaction). Typically, adhesion contacts are easily reverted to a free-flowing state with minimal handling.

Liquid contacts are caused by fertiliser wetting or moisture vapour absorption. The saturated solutions formed between the wetted particles stick them together. As this liquid is mobile, the 'sticking' of the fertiliser particles is relatively easily broken. However, when the wetting is severe, phase contacts will be achieved.

Phase contacts, or salt bridges, are crystal bridges that form between fertiliser particles. These crystal bridges form due to dissolution/recrystallisation and/or thermal effects. The salt bridges are often the most troublesome form of caking, resulting in hard caking that cannot be broken apart easily.

A wide range of factors, both external and inherent to the fertiliser, can affect the propensity for a cargo to cake, as discussed in detail below.

Moisture content at production influences the extent of caking, and fertilisers with higher moisture content, even if they are within contractual specifications, are more prone to caking. The extent of drying required to limit the chances of caking depends on properties such as composition, morphology, size and hardness.

The **uniformity, size and crushing strength** of fertilisers also impacts their likelihood to cake. Fertilisers with a small range in particle size, high crushing strength and larger overall size are less prone to caking due to reduced specific surface area for contact between particles, and decreased likelihood of breaking into smaller particles. Impurities within the fertiliser can also affect caking tendency, for example, iron and aluminium impurities decrease the propensity of caking in diammonium phosphate fertilisers.

Moisture uptake during storage and handling prior to and during loading is another point of consideration. Moisture uptake is a particular risk during loading when all the cargo becomes exposed for at least some time on the conveyor. All fertilisers are hygroscopic, meaning they absorb moisture from the air. This occurs above the critical relative humidity (RH), which differs for individual fertilisers. RH is the amount of moisture in the air relative to the maximum the air can contain at any one temperature. For example, with urea, it is common practice to suspend loading at times of high atmospheric humidity, usually above 75–80% RH. It is also critical that fertilisers are not exposed to moisture during transportation.

Anti-caking agents are often added to fertilisers to minimise caking. These anti-caking agents are usually liquid or powder coatings that act as a barrier to prevent caking and can control the absorption of moisture by creating a hydrophobic barrier. They can also act as a physical barrier between particles or weaken bonds that may have formed between particles. Powder coatings can cause dust issues. Anti-caking agents can also be so-called 'conditioning agents', which improve the crushing strength and decrease dust formation. In the past, there have been issues related to incorrectly or incompletely treated fertilisers.

Inappropriate ventilation can enhance caking, resulting in surface crusting from moisture uptake from humid ventilating air and/or caking in the top layer from excessive cooling. The respective IMSBC Code schedules for all bulk fertilisers specify that they shall not be ventilated during the voyage.

Temperature gradients can enhance caking if there are large temperature differences between the load port and discharge port, resulting in caking along the periphery when cargo cools down. Similarly, if different production batches of fertilisers with different temperatures are loaded, this can also produce temperature gradients within the stow.

11.3 Fertiliser Cargo Issues

The two main issues of fertiliser carriage relate to caking. The first issue arises when the Master observes caking during loading, the second issue being caking from any cause at outturn.

Most often, these issues concern bulk fertilisers rather than bagged, and shippers frequently bring bagged cargo to the vessel and open bags into the holds. If there are any signs of firm caking before loading, caution is advised. For example, fertiliser cargoes have been encountered that were still caked after being loaded from a warehouse onto a truck, followed by a sling and onto a pontoon over the hatch. The caked fertiliser was rendered free-flowing by passing it through a mesh over the hold but re-caked into firm lumps at disport, resulting in a large claim.

Therefore, it is advised that if caked lumps of cargo are observed at any point during the loading process, a protest is made and the Master considers clausing the bills of lading accordingly. Often, lumps or caking seen at outturn are attributed to a condition suspected or observed during loading, and if the Master has not complained or claused documents, then the ship may well be criticised. Therefore, it is recommended that the duty officers take photos of the cargo during normal routine inspection. This can be highly valuable evidence when dealing with such complaints.

Caking might later be blamed on rain during loading, so it is crucial that accurate logs are kept stating whether there were any periods of rain during the loading, and if the hatches were closed in a timely fashion. Ensuring that hatch covers are watertight and that hatch cover surveys are up to date prior to loading can also assist in defending claims.

In the event of wetting during loading, the wetted areas of cargo must be removed as much as possible. However, as the water will be spread quickly and absorbed by the surrounding fertiliser, it will be difficult to remove all of the wetted fertiliser.

11.4 Ammonium Nitrate

Ammonium nitrate is a hazardous compound that has the potential to explode upon contact with ignition sources. The risk of explosion is higher when ammonium nitrate is contaminated by organic material such as fuel oil and/or externally heated, for example by hot work or buried cargo lamps. Some of the most serious cargo-related disasters have been caused by ammonium nitrate, for example in Texas City, Tianjin and Beirut.

There are four entries in the IMSBC Code for ammonium nitrate and ammonium nitrate based fertilisers. There are numerous other entries of ammonium nitrate cargoes within the IMDG Code. The criteria stated in the IMSBC Code for determining which entry a cargo belongs to depends on:

- Percentage of ammonium nitrate
- percentage of total combustible organic material calculated as carbon
- the chemical nature of the components besides the ammonium nitrate
- the outcome of UN standard tests such as the self-sustaining decomposition trough test.

Amendment 05-19 of the IMSBC Code entered into force on 1st January 2021 and reclassified ammonium nitrate based fertiliser as an IMSBC Code Group B cargo (cargoes that possess a chemical hazard which could give rise to a dangerous situation on a ship). This is because the cargo is liable to decomposition leading to flammable and toxic concentrations of ammonia and nitrogen.

Further to this, in May 2021, IMO MSC considered an additional revision of ammonium nitrate cargoes within the IMSBC Code and adopted Amendment 06-21 to the Code. These amendments are due to enter into force on 1st December 2023. The amendments introduced new individual schedules for different ammonium nitrate based cargoes, differentiating these cargoes as follows:

- Ammonium nitrate based fertiliser defined as

"Straight nitrogen fertilisers containing less than 2% chloride, and

.1 not more than 70% ammonium nitrate with other inorganic materials; or

.2 not more than 80% 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

.3 mixtures of ammonium nitrate and ammonium sulphate with not more than 45% ammonium nitrate and not more than 0.4% total combustible organic material calculated as carbon.

Compound NPK/NK/NP fertilizers:

.1 mixtures of nitrogen with phosphate and/or potash containing not more than 70% ammonium nitrate and not more than 0.4% total combustible organic material calculated as carbon or not more than 45% ammonium nitrate and unrestricted combustible material; and

.2 either less than 20% of ammonium nitrate content or less than 2% of chloride …"

For these straight cargoes, the IMSBC Code Group is now Group C (neither A nor B).

- Ammonium nitrate based fertiliser MHB defined as

"Ammonium nitrate-based fertilizers transported under conditions mentioned in this schedule are uniform mixtures of nitrogen with or without potash and/or phosphate within the following composition limits:

.1 not more than 70% ammonium nitrate and not more than 0.4% total combustible organic material calculated as carbon or not more than 45% ammonium nitrate and unrestricted combustible material; and

.2 both the ammonium nitrate content is equal to or greater than 20% and the chloride content is equal to or greater than 2% …"

These ammonium nitrate cargoes are still categorised as Group B (possesses a chemical hazard which could give rise to a dangerous situation on a ship). The cargo should be kept as dry as possible and kept away from external sources of heating that may cause its decomposition.

For both cargoes, the shipper should declare the ammonium nitrate content and the chloride content in accordance with Section 4.2 of the Code.

11.4.1 Safety Principles

Before 2021, all ammonium nitrate based fertiliser was categorised as a non-hazardous IMSBC Group C cargo, however the cargo was linked to several serious ship fires, including the *'MV Cheshire'* in 2017. Following this incident, the IMO published a guidance circular on the carriage of ammonium nitrate based fertilisers (CCC.1/Circ.4). Based on guidance from the Fertilizers Europe Organisation, the safety principles for this cargo are as follows:

"• *Avoidance of storage of combustible substances near fertilisers*
- *avoidance of storage of incompatible substances near fertilisers*
- *avoidance of cross contamination with remains of previous cargoes*
- *avoidance of cross contamination of next cargo with fertiliser*
- *avoidance of sources of heat likely to affect the fertiliser*
- *avoidance of application of heat (eg, welding) to any section which may have trapped/confined fertiliser."*

The circular also notes that:

"The best protection for seafarers is awareness of the decomposition process to allow it to be identified at an early stage. Regular monitoring of the cargo throughout the voyage is crucial to detect beginning of decomposition.

When heated strongly, this cargo may decompose and release toxic gases. Timely opening of cargo hatches can prevent the build-up of pressure and help cool the cargo, impeding the development of cargo decomposition.

In case of decomposition or fire involving this cargo:

- *Provide maximum ventilation to remove the gases resulting from decomposition. These gases may include toxic fumes of ammonia and oxides of nitrogen and sulphur*
- *wear, as necessary, protective clothing and self-contained breathing apparatus*
- *application of water is most effective where injection pipes are used to deliver water to hot spots. Water spraying may not be sufficient to control the decomposition*
- *flooding of the cargo space may be considered, giving due consideration to the ship's stability and structural strength*
- *the ship's gas firefighting installation will be ineffective."*

Ammonium nitrate based fertiliser comes in different forms depending on its composition, and the cargo has several UN numbers (UN 1942, 2067, 2071). Ammonium nitrate as a crystal is UN 1438. It is important that the Master is aware of the composition of the cargo being loaded.

Further information on hazards, stowage and segregation is available in the individual schedules of solid bulk cargoes (Appendix 1) of the IMSBC Code (Reference 17).

11.4.2 Self-Sustaining Decomposition (SSD)

The decomposition of ammonium nitrate based fertilisers can be highly exothermic (heat-producing) and violent. Toxic fumes and nitrous oxides (NOx) are produced during this decomposition. The decomposition of ammonium nitrate is referred to as self-sustaining as, whilst a considerable amount of energy is required to initiate the reaction, once the decomposition begins, the energy released (as heat) is enough to support further decomposition, ie the reaction is self-sustaining.

As the decomposition reaction does not involve external reagents, such as oxygen, the decomposition cannot be controlled using inert gases, or by restricting oxygen. Instead, cooling the cargo is necessary to stop further decomposition. SSD can be controlled by quenching the reaction with water, whilst opening the hatch covers prevents over-pressurisation. The IMSBC Code states that in the event of a fire, copious amounts of water should be used and the heat source should be isolated.

Decomposing ammonium nitrate in one hold can act as a heat source for adjacent holds, therefore care needs to be taken to prevent SSD from spreading. The IMSBC Code states that hatch covers of adjacent holds should be opened to allow for maximum ventilation and dividing bulkheads should be cooled.

The decomposition of ammonium nitrate is complex but thought to initially involve an unfavourable, energy absorbing proton (H^+) transfer, which is why heat is required to begin the decomposition. Without a sufficient heat source, there would not be enough energy in the system to begin SSD. Temperatures of around 160–170°C are thought to be necessary before decomposition can initiate. Examples of ship-related sources of heat found to have caused SSD in the past include energised lights in the cargo hold and thermal oil heating pipes.

The propensity of ammonium nitrate based fertilisers to undergo SSD can also be influenced by the presence of trace levels of transition metals, chlorides or contamination by chemicals or fuel oil. The IMSBC Code relies on the trough test (UN Manual of Tests Methods Part III, Section 38.2.4) to determine whether nitrates containing fertiliser are capable of undergoing SSD. In this test, the trough (see Figure 11.3) is filled with fertiliser and decomposition is initiated at one end of the trough. Around 20 minutes after the removal of the initial heating source, the propagation of decomposition is measured. If the decomposition has continued after removal of the source, then the fertiliser is considered capable of showing SSD behaviour. One major limitation of this test is that in bulk, fertilisers are excellent insulators. This means that, in case of exposure to external heat sources, such as a light in the hold, the heat is unable to dissipate, causing the temperature of the fertiliser surrounding the heat source to rise. Over an extended period of exposure to the heat source, the temperatures could feasibly reach the point where the fertiliser begins to undergo decomposition.

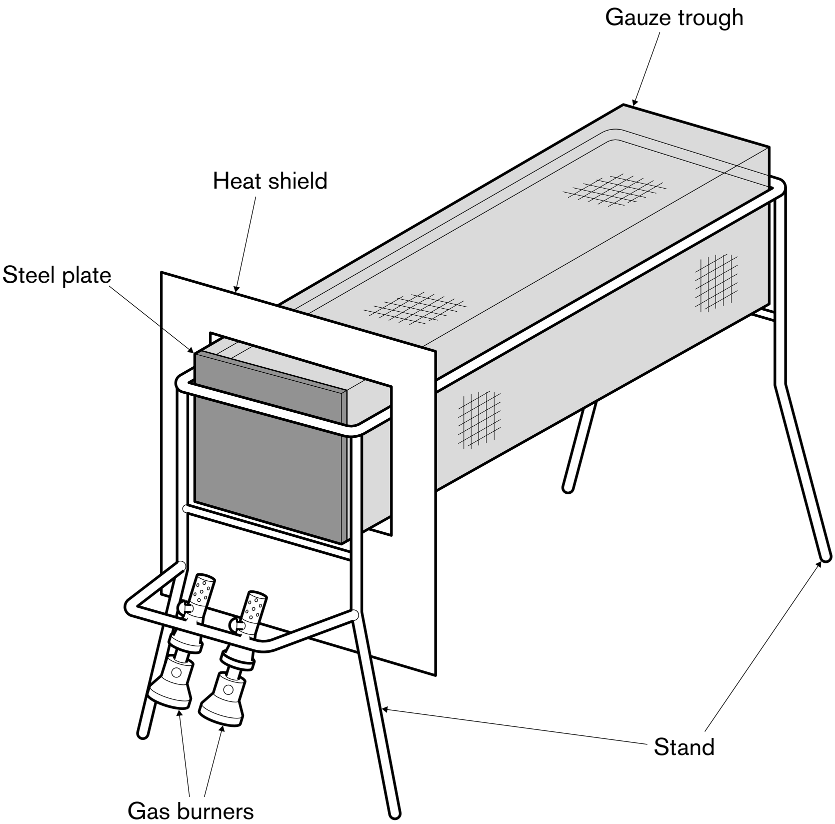

Figure 11.3: Granulation test equipment.

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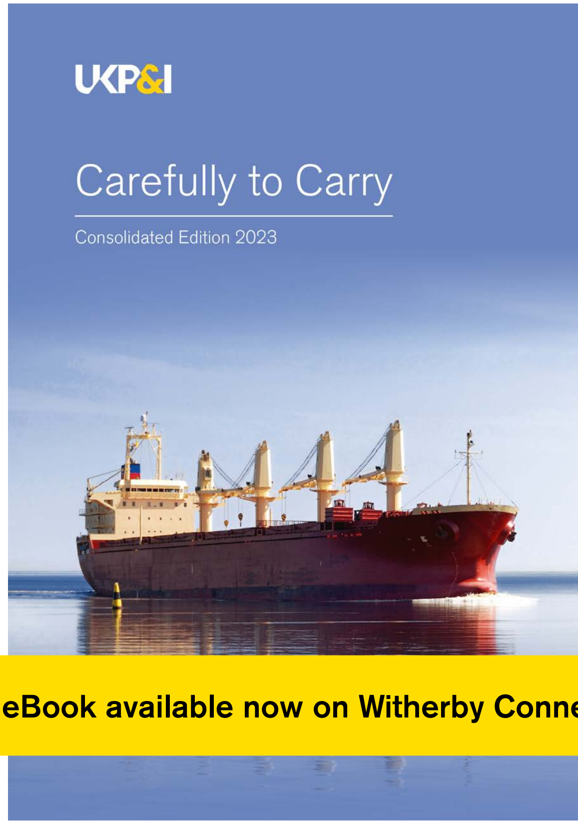

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