Chapter 45
The Characterization of Ammonium Nitrate Mini-Prills

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Abstract Ammonium nitrate (AN) is commonly used as a fertilizer and is the fundamental ingredient of industrial explosives [1]. It has been observed that one of the most important factors that affect explosive performance of ammonium nitrate and fuel oil is the prills volume of porosity. The large amount of porosity identified in explosive grade AN prills allows for an absorption rate between 12 and 16%. While, the agriculture grade ammonium nitrate prills are manufactured with an increased density and thus, have an absorption rate between 7 and 8%. In this study, we explore an agriculture grade ammonium nitrate mini-prill, as this type of AN prill has not been characterized before. In order to determine how effective this agriculture grade prill is as an explosive, this mini-prill is compared to an explosive grade AN prill. This study observes and records its morphology and blasting performance as related to an explosive grade ammonium nitrate prill. Based upon instrumentation analysis, preliminary results indicate, as expected, that the mini-prill does have a more dense structure. Although, the decrease in fuel oil content that comes with a decrease in porosity has been observed, it demonstrates to be almost negligible as compared to the increase in velocity of detonation from the increase in charge density.

Keywords Ammonium nitrate • ANFO • Porosity • Explosive properties • Detonation velocity • Scanned electron microscopy

45.1 Introduction

Ammonium nitrate is readily used for commercial purposes (e.g. mining, military, and industrial) due to its low cost, ease of accessibility, and simplicity of manufacture process. The intent of this study is to grasp a better understanding about mini ammonium nitrate prill’s structure and ultimately, to determine if the blasting performance changes over the shelf life of pre-mixed ammonium nitrate plus fuel oil (ANFO). Once the identifying characteristics of ammonium nitrate prills, revealed from their physical properties, has been confirmed, it becomes significantly important to discover and document that these findings can impact the velocity of detonation of miniature ammonium nitrate prills.

Ammonium nitrate prills are generally in the form of odorless, transparent, hygroscopic, deliquescent crystals or white granules and are available in three grades. The two key chemicals utilized in the manufacture of AN include ammonia and nitric acid. Coating agents and modifying agents are incorporated into the manufacture in order to improve the properties of the prills. The three grades of AN prills include fertilizer, explosive, and chemical grade. Agriculture grade AN exist as high-density prills which are utilized as a fertilizer in the agricultural industry. The more dense ammonium nitrate crystals are formed by spraying droplets of molten ammonium nitrate solution (>99.6%) down a short tower. The spray produces spherical particles known as prills. These crystals are non-absorbent and are commonly used in conjunction with NG, for their explosive effect. Explosive grade AN exists as low-density porous prills which are commonly mixed with a fuel oil, known as ammonium nitrate fuel oil (ANFO). An absorbent form of ammonium nitrate can be obtained by spraying a hot,
95 % solution of ammonium nitrate down a high tower. The resultant spheres are carefully dried and cooled to prevent breakage during handling. Ammonium nitrate is used by itself and in conjunction with fuels, or with other explosives such as NG and TNT, [1]. AN prills may be coated in an amine based coating agent to minimize caking, thereby, effecting its explosive properties. Caking occurs due to Van der Waals, which are electrostatic and moisture bonding forces when particles come into contact. The deviation of particle shape from round or spherical increases the area of particle contact and thereby increases caking. [6]. Other additives (e.g. aluminum sulfate) can also be added in trace quantities to improve properties such as stability, [4].

45.2 Materials

Two samples of ammonium nitrate prills were utilized in the study. Two companies donated the samples. Lubrizol donated the agriculture grade mini ammonium nitrate prills and Dyno Nobel donated the explosive grade ammonium nitrate prills. For the velocity of detonation studies, mixing the explosive grade AN prill and agriculture grade AN mini-prill with fuel oil were carried out separately and all mixing equipment was cleaned between the two mixing operations. The ANFO mixes consisted of a nominal 93-7 % ammonium nitrate and fuel oil mix.

The charge assemblies consisted of steel cylinders with an inner diameter of 8.89 cm (3.5 in.) and wall thickness of 0.25 in., the steel cylinders at the 3.5 in. diameter were utilized due to successful full detonation discovered from previous studies of the role of confinement on detonation. VOD probes, measuring 1 m long, are inserted in the tubes. The length of all charges is 91.44 cm and the ANFO mixture was a 93/7 % of AN/FO by weight. PETN boosters with a mass of 450 g were used to initiate detonation from one end of the cylindrical charge.

45.3 Morphology

45.3.1 Scanned Electron Microscopy (SEM)

The Quant 600 SEM was used to visualize any unique physical characteristics of the ammonium nitrate prills (the mini ammonium nitrate prills and the explosive grade prills). The SEM is an extremely versatile instrument that provides a wide range of magnification (approximately 50×−100,000×), a remarkable depth of field, and elemental information with minimal sample preparations [5]. In this study, two prills were arranged onto a sample medium. The prills were viewed under low vacuum as to prevent any potential interference from the gold coating utilized in previous studies.

Microscopic images illustrate the differences between the surfaces of the agriculture grade (AG) AN mini-prill and explosive grade (EG) AN prill. Note that the mini-prill has a much smaller diameter and much smoother surface as compared to the explosive grade AN prill, Fig. 45.1. Additionally, the surface of the explosive grade AN prill has a ridged surface that does not exist with the mini-prill. The differences in the surfaces are due to their manufacture processes. At times, coatings and modifying agents are added to the process to improve porosity and characteristics of the AN prills.

While pores are present within the AG-AN prills, most do not extend to the surface of the prill, which is not ideal for sufficient diffusion of diesel fuel throughout the prill. The more dense ammonium nitrate crystals are commonly formed by spraying droplets of molten ammonium nitrate solution (>99.6 %) down a short tower. These crystals are basically non-absorbent and thus, may reduce efficacy of mini-prills as an explosive material.

The prills were then cross-sectioned to visualize the internal physical structure of the AN prills, Fig. 45.2. It’s interesting to observe how the structures of the pores differ between the two grades of AN, but, as stated above, two different manufacturing processes and modifying agents may produce this effect. The structure of the explosive grade AN prill reveals many stream-like pathways that meander throughout the body of the prill. The explosive grade prills are heated for longer time periods while progressing down a longer tower. The longer heating times cause more porosity/absorbency effects. While, the agriculture grade mini-prills demonstrate more dense pathways. Air-pockets are also observed, which do not extend to the surface of the prills.
The size of the crystals, grains, granules, prills, etc has a great influence on the properties of the explosives, especially on the oxidizer–fuel mixture. The sensitivity to external stimuli and the parameters of detonation increase when the size of the particle decreases [2, 7]. This is demonstrated through this test, where, the mini-prill had a slight increase of velocity of detonation (VOD) as compared to explosive grade, Fig. 45.3. It was observed that the mini prill AN had an increased VOD when the cylinder diameter was increased. The 6 in. diameter steel cylinder produced a VOD close to 5,000 m/s. Where, the
explosive grade AN produced a VOD close to 3,750 m/s. The explosive grade AN velocity detonations this same procedure was completed began to decrease after the 4 in. steel cylinder diameter. Demonstrating that the larger prill sized explosive grade AN has a critical diameter between 3.5 and 4 in. steel cylinder. This must be achieved in order to result in a full detonation.

45.5 Influence of ANFO Shelf Life on VOD

It has been reported that the shelf life of ANFO is at a maximum six (6) months, but is dependent on temperature and humidity conditions [3]. Storage in a high humidity and high temperature environment will accelerate product breakdown and should be avoided. Signs of ANFO degradation are hardening or caking, which are due to electrostatic and moisture bonding forces when particles come into contact. This may lead to difficulty in loading and as a result, may lead to poor blasting performance [3].

The intent of this section is to explore the effect of shelf life of pre-mixed agriculture grade ANFO-miniprills versus explosive grade ANFO on the velocity of detonation. As seen in previous studies, steel cylinders were determined to be most effective for optimal blasting performance, delivering full detonation, due to confinement. The 3.5 in. cylinder diameter cylinders were used in the study due to its effectiveness with both grades of ANFO (Fig. 45.4).

On day 0, the fuel oil content of the miniprill ANFO was roughly 6 % which is expected because sampling was completed, immediately after mixing occurred, Fig. 45.5. As the shelf-life study progressed, the fuel oil content decreased to approximately 3 %. These fuel oil studies were completed via Windex tests utilized by the Lubrizol Corporation guidelines. The Windex test results also demonstrate that the miniprill are not absorbing the diesel fuel into the pores. FO content ranged between 2.0 and 3.5 %, indicating that the diesel fuel was not being retained on the miniprill. This information provides evidence that the diesel fuel is not retained on the mini-prill ANFO. Even so, the VOD of the miniprill still ranged between 3,000 and 4,500 m/s. Although, the fuel oil content is important pertaining to the required oxygen balance, it may not be necessary because of confinement and smaller prill diameter, which allows for steady propagation resulting in a full detonation. Over an almost 2 month period of time, Fig. 45.5, the fuel oil content of the explosive grade ANFO did not change significantly, remained 6–7 %, which indicates that the porous structure of the prills are beneficial for adequate absorption. The VOD did not vary much over time. Demonstrating that the ANFO could be stored for long periods of time (2 months), if necessary.

45.6 Conclusion

Critical diameter is the diameter below which detonation will not propagate and is influenced by stiffness of the encasing material and also on bulk density of prill and porosity of prill. In the critical diameter study, the agriculture grade mini prill ANFO samples demonstrated their efficacy as compared to the more commonly used explosive grade ANFO, by producing a faster velocity of detonation (VOD) with larger diameters of the steel cylinder. This phenomena can also be seen when
explosive grade ANFO is crushed into smaller mesh sizes, which improves the propagation of detonation due to the close proximity of the fuel and oxidizer. The mini-prill detonated in steel tubes of a diameter 3.5 in., which is comparable to the explosive grade AN prills. The shelf-life explorations demonstrated that both grades of ANFO prills successfully produced full order detonations after almost 60 days of storage. The shelf-life experiments produced VODs around 3,600 m/s for the mini-prills when the ANFO is placed within steel encasing tubes with an inside diameter of 3.5 in. This value is very similar to the VOD found for explosive grade prill in similar size charges of the same encasing material. It is important to have an oxygen balance in energetic materials because it is necessary to supply oxygen to oxidizing atoms, like fuel oil as to prevent noxious fumes (e.g. carbon monoxide and nitric oxide). It was observed that the percent of fuel oil content of agriculture grade mini-prills drastically decreased over the 60 day period, which causes a deficient oxygen balance and thus when detonated can release these types of noxious fumes. Even though the percent of fuel oil was 2–3 %, the mini-prill still produced a full detonation; therefore, one can infer that the smaller diameter of the mini-prills allow for increased confinement which leads to increased continuity of detonation.
References